GASEOUS STATE

Introduction :

Matter as we know broadly exists in three states.

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

- Inter molecular attractive forces.
- The molecular motion / random motion.

Matter

Properties	Solid state	Liquid state	Gaseous state
Attractive force	• large	• Smaller	• Almost zero
Thermal motion	• Almost zero	• Greater	• Random motion
Volume	• Fixed volume	• Fixed volume	• varies with container
Geometry	• Definite	• Not definite	• Not definite

In this chapter the properties and behaviours of the gases will be analysed and discussed in detail. These properties are measured with the help of the gas laws as proposed Boyle,Charles,Gay lussac etc

Section (A) : Gas Laws

Boyle's law and measurement of pressure :

Statement :

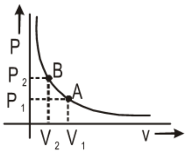
For a fixed amount of gas at constant temperature, the volume occupied by the gas is inversely proportional to the pressure applied on the gas or pressure of the gas.

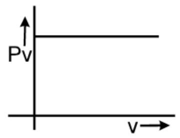
$$V \propto \frac{1}{P}$$

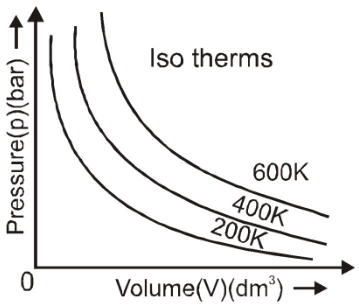
hence PV = const

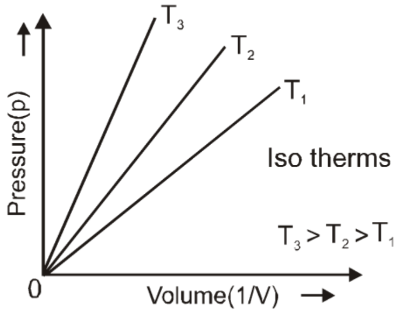
this constant will be dependent on the amount of the gas and temperature of the gas.

$P_1V_1 = P_2V_2$









Applications of Boyles Law. For the two points 'A' and 'B' $P_1V_1 = K$ & $P_2V_2 = K$

hence it follows that $P_1V_1 = P_2V_2$.

Units

Volume	Pressure	Temperature
Volume of the gas is the Volume of the container S.I. unit → m^3 C.G.S. unit → cm^3 $1\ \ell = 10^{-3}\ m^3$ $1\ \ell = 10^3\ cm^9$ $1\ dm^3 = 1\ \ell = 10^{-3}\ m^3$ $1\ ml = 10^{-3}\ \ell = 1\ cm^3 = 1cc$	Pressure = N/m^2 = Pa → S.I. unit C.G.S unit = dyne-cm^2 Convert $1N/m^2$ into dyne/cm^2 $\frac{1N}{1m^2} = \frac{10^5\ dyne}{10^4\ cm^2}$ $1\ N/m^2 = 10\ dyne/cm^2$ $1\ atm = 1.013 \times 10^5\ N/m^2$ $1\ bar = 1 \times 10^5\ N/m^2$ 1 atm = 760 mm of Hg = 760 torr.	Kelvin scale → Boiling point = 373 K ice point = 273 K Farenheit scale → B.P. = 212ºF ice point = 32ºF Celcius scale → B.P. = 100ºC ice point = 0ºC $\frac{C-0}{100-0} = \frac{K-273}{373-273} = \frac{F-32}{212-32} = \frac{R-R(0)}{R(100)-R(0)}$ where R = Temp. on unknown scale.

Atmospheric pressure :

The pressure exerted by atomosphere on earth's surface at sea level is called 1 atm.

1 atm = 1.013 bar

$1\ atm = 1.013 \times 10^5\ N/m^2 = 1.013\ bar = 760\ torr$

Solved Examples

Ex.1 103 mL of carbon dioxide were collected at 27°C and 763 mm pressure. What will be its volume if the pressure is changed to 721 mm at the same temperature ?

Sol.

Given Conditions	Final Conditions
$V_1 = 103$ mL	$V_2 = ?$ mL
$P_1 = 763$ mm	$P_2 = 721$ mm

By applying Boyle's Law since temperature is constant,

$$P_2 \times V_2 = P_1 \times V_1$$

Substituting the corresponding values, we have

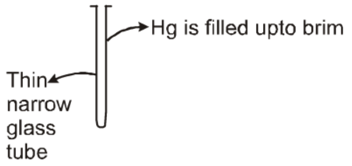
$$721 \times V_2 = 763 \times 103 \Rightarrow V_2 = \frac{763 \times 103}{721} = 109\ mL$$

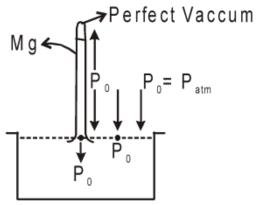
∴ Volume of carbon dioxide = 109 mL

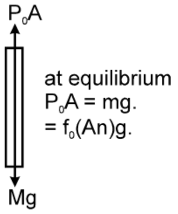
Measurement of Pressure

Barometer :

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

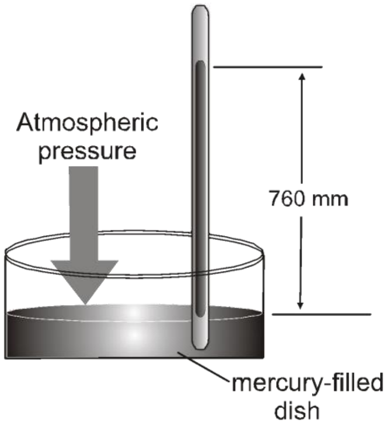






Cross sectional view of the capillary column.

A mercury barometer is used to measure atmospheric pressure by determining the height of a mercury column supported in a sealed glass tube. The downward pressure of the mercury in the column is exactly balanced by the outside atmospheric pressure that presses down on the mercury in the dish and pushes it up the column.



A thin narrow callibrated capillary tube is filled 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.

Applying force balance, we get,

$P_{atm} \times A = m \times g$ (‘A’ is the cross-sectional area of the capillary tube)

If ‘ρ’ is the density of the fluid, then $m = \rho \times v$

Hence, $P_{atm} \times A = (\rho \times g \times h) \times A$ $(v = A \times h)$

(‘h’ is the height to which mercury has risen in the capillary)

or, $P_{atm} = \rho g h$

☞ Normal atmospheric pressure which we call 1 atmosphere (1 atm), is defined as the pressure exerted by the atmosphere at mean sea level. It comes out to be 760 mm of Hg = 76 cm of Hg. (at mean sea level the reading shown by the barometer is 76 cm of Hg)

$1 \text{ atm} = (13.6 \times 10^3)\ 9.8 \times 0.76 = 1.013 \times 10^5$ Pas.

1 torr = 1 mm of Hg. ; $1 \text{ bar} = 10^5 \text{ N/m}^2$ (Pa)

Charle's law :

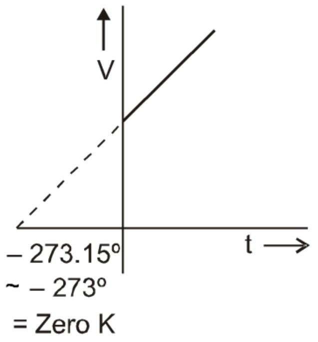
For a fixed amount of gas at constant pressure volume occupied by the gas is directly proportional to temperature of the gas on absolute scale of temperature.

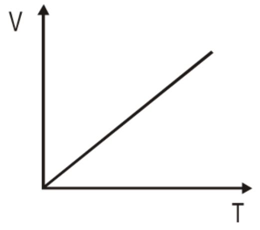
$V \propto T$ or $V = kT$

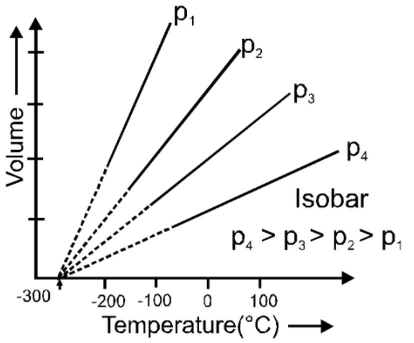
$\frac{V}{T}$ = constant where ‘k’ is a proportionality constant and is dependent on amount of gas and pressure.

$\frac{V_1}{T_1} = \frac{V_2}{T_2}$ Temperature on absolute scale, kelvin scale or ideal gas scale.

$V = a + bt$ Temperature on centigrade scale.







Relation : T = t + 273

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

Solved Examples

Ex.2 If the temp. of a particular amount of gas is increased from 27ºC to 57ºC, find final volume of the gas, if initial volume = 1 lt and assume pressure is constant.

Sol. $\frac{V_1}{T_1} = \frac{V_2}{T_2}$ $\Rightarrow$ $\frac{1}{(273+27)} = \frac{V_2}{(273+57)}$ So $V_2 = 1.1$ lt.

Ex.3 An open container of volume 3 litre contains air at 1 atmospheric pressure. The container is heated from initial temperature 27ºC or 300 K to tºC or (t + 273) K the amount of the gas expelled from the container measured 1.45 litre at 17ºC and 1 atm.Find temperature t.

Sol. $T_1 = 300$ K

It can be assumed that the gas in the container was first heated to (t + 273), at which a volume 'ΔV' escaped from the container.

Hence applying charles law :

$$\frac{3}{300} = \frac{3+\Delta V}{t+273}$$

Now, this volume 'ΔV' which escapes trans the container get cooled

$$\therefore \quad \frac{\Delta V}{t+273} = \frac{1.45}{290}$$

Solve the two equations and get the value of ΔV an a t.

Determine Δ v & calculate t that will be the answer.

Gay-lussac's law :

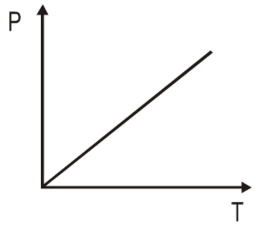
For a fixed amount of gas at constant volume, pressure of the gas is directly proportional to temperature of the gas on absolute scale of temperature.

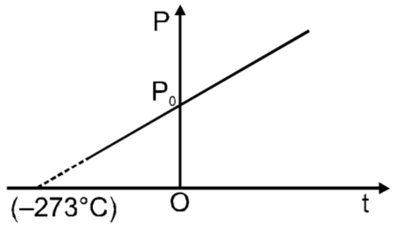
$P \propto T$

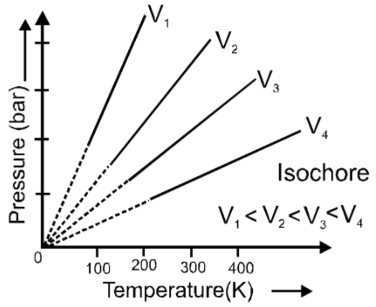
$\frac{P}{T}$ = constant → dependent on amount and volume of gas

$\frac{P_1}{T_1} = \frac{P_2}{T_2}$ → temp on absolute scale

originally, the law was developed on the centigrade scale, where it was found that pressure is a linear function of temperature $P = P_0 + bt$ where 'b' is a constant and P_0 is pressure at zero degree centigrade.







Solved Examples

Ex.4 The temperature of a certain mass of a gas is doubled. If the initially the gas is at 1 atm pressure. Find the % increase in pressure ?

Sol. $\frac{P_1}{T_1} = \frac{P_2}{T_2}$; $\frac{1}{T} = \frac{P_2}{2T}$

% increase = $\frac{1}{1} \times 100 = 100\%$

Ex.5 The temperature of a certain mass of a gas was increased from 27°C to 37°C at constant volume. What will be the pressure of the gas.

Sol. $\frac{P_1}{T_1} = \frac{P_2}{T_2}$; $\frac{P}{300} = \frac{P_2}{310}$; $P_2 = \frac{31}{30} P$

Avogadro's Hypothesis :

For similar values of pressure & temperature equal number of molecules of different gases will occupy equal volume.

$N_1 \longrightarrow V$ (volume of N_1 molecules at P & T of one gas)

$N_1 \longrightarrow V$ (volume of N_1 molecules at P & T of second gas)

Molar volume or volume occupied by one mole of each and every gas under similar conditions will be equal.

One mole of any gas or a combination of gases occupies 22.413996 L of volume at STP.

The previous standarad is still often used, and applies to all chemistry data more than decade old, in this definition Standard Temperature and Pressure STP denotes the same temperature of 0°C (273.15K), but a slightly higher pressure of 1 atm (101.325 kPa) .

Standard Ambient Temperature and Pressure (SATP), conditions are also used in some scientific works. SATP conditions means 298.15 k and 1 bar (i.e. exactly 10^5 Pa) At SATP (1 bar and 298.15 K), the molar volume of an ideal gas is 24.789 L mol^{-1}

Equation of State :

Combining all the gas relations in a single expression which discribes relationship between pressure, volume and temperature, of a given mass of gas we get an expression known as equation of state.

$\frac{PV}{T}$ = constant (dependent on moles of the gas n).

$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$$

Ideal gas Equation : $\frac{PV}{nT}$ = constant [universal constant]

= R (ideal gas constant or universal gas constant)

Experimentally

R = 8.314 J/Kmole ≈ 25/3

= 1.987 cal/mole ≈ 2

= 0.08 Latm/mole ≈ 1/12

Solved Examples

Ex.6 At 27°C and one atmosphere pressure, a gas volume V. What will be its volume at 177°C and a pressure of 1.5 atmosphere ?

Sol.

Given conditions	Final conditions
$V_1 = V$	$V_2 = ?$
$P_1 = 1$ atm	$P_2 = 1.5$ atm
$T_1 = 273 + 27 = 300$ K	$T_2 = 273 + 177 = 450$ K

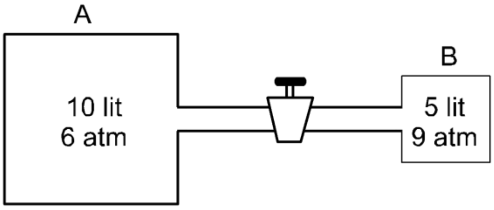
Applying gas equation, we have

$$\frac{1 \times V}{300} = \frac{1.5 \times V_2}{450}$$

∴ $V_2 = \frac{1 \times V \times 450}{300 \times 1.5} = V$ ∴ Volume of the gas = V

Ex.7 The stop cock connecting the two bulbs of volume 5 litre and 10 litre containing as ideal gas at 9 atm and 6 atm respectively, is opened. What is the final pressure if the temperature remains same.

Sol. After the opening of the stop cock the pressure of the each bulb will remain same.



At the beginning, the no. of moles of gas in A = $\frac{10 \times 6}{RT}$

At the beginning, the no. of moles of gas in B = $\frac{5 \times 9}{RT}$

∴ Total no. of mole at the beginning = $\frac{105}{RT}$

Total no. of mole of gas before opening the stop cock

Total no. of moles of gas after opening stop cock = $\frac{105}{RT}$

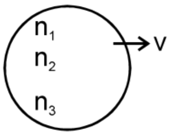
∴ Pressure after the opening of the stop cock

$$P = \frac{105}{RT} \times \frac{RT}{V_{total}} = \frac{105}{10+5} = 7 \text{ atm}$$

Section (B) : Daltons law of partial pressure

Partial pressure :

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



Partial pressure of first component gas :

$$P_1 = \frac{n_1RT}{v} \; ; \qquad P_2 = \frac{n_2RT}{v} \; ; \qquad P_3 = \frac{n_3RT}{v}$$

Total pressure = $P_1 + P_2 + P_3$.

Daltons law :

For a *non reacting* gaseous mixture total pressure of the mixture is the summation of partial pressure of the different components gases.

$$P_{Total} = P_1 + P_2 + P_3 = \frac{(n_1 + n_2 + n_3)RT}{v}$$

$\frac{P_1}{P_T} = \frac{n_1}{n_T}$ = x_1 (mole fraction of first component gas)

$\frac{P_2}{P_T} = \frac{n_2}{n_T}$ = x_2 (mole fraction of second component gas)

$\frac{P_3}{P_T} = \frac{n_3}{n_T}$ = x_3 (mole fraction of third component gas)

Solved Examples

Ex.8 A mixture of gases at 760 torr contains 55.0% nitrogen, 25.0% oxyegn and 20.0% carbon dioxide by mole. What is the partial pressure of each gas in torr ?

Ans. P_{N_2} = 418 torr, P_{O_2} = 190 torr, P_{CO_2} = 0.152 torr, total pressure = 760.

Sol. Let total moles of gas mixture be 100.

$$P_{N_2} = \left(\frac{n_{N_2}}{n_T}\right) \times P_T = \frac{55}{100} \times 760 = 418 \text{ torr.}$$

$$P_{O_2} = \left(\frac{n_{O_2}}{n_T}\right) \times P_T = \frac{25}{100} \times 760 = 190 \text{ torr.}$$

$$P_{CO_2} = (760 - 418 - 190) = 152 \text{ torr.}$$

Analysis of gaseous mixture :

Vapour density :

Vapour density of any gas is defined as the density of any gas with respect to density of the H_2 gas under identical conditions of temperature T and pressure P.

Vapour density = $\frac{\text{density of gas at T \& P}}{\text{density of } H_2 \text{ under same P \& T}}$

$P = \frac{m}{V}.\frac{RT}{M} \Rightarrow P = \rho \frac{RT}{M} \qquad \rho = \frac{PM}{RT}$

Vapour density = $\frac{PM_{gas}RT}{RT\ PM_{H_2}} = \frac{M_{gas}}{M_{H_2}} = \frac{M_{gas}}{2}$

M_{gas} = 2 × vapour density

Average molecular mass of gaseous mixture :

total mass of the mixture divided by total no. of moles in the mixture

$M_{mix} = \frac{\text{Total mass of mixture}}{\text{Total no. of moles in mixture}}$

If we have 'n_1', 'n_2' and 'n_3' are moles of three different gases having molar mass 'M_1', 'M_2' and 'M_3' respectively.

$M_{min} = \frac{n_1M_1 + n_2M_2 + n_3M_3}{n_1 + n_2 + n_3}$

Solved Examples

Ex.9 Calculate the mean molar mass of a mixture of gases having 7 g of Nitrogen, 22 g of CO_2 and 5.6 litres of CO at STP.

Sol. Moles of N_2 = 7/28 = 1/4

Moles of CO_2 = 22/44 = 1/2

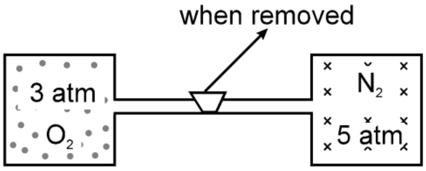
Moles of CO = 5.6 / 22.4 = 1/4

mean molar mass = $M_{min} = \frac{n_1M_1 + n_2M_2 + n_3M_3}{n_1 + n_2 + n_3}$ = (7 + 7 + 22) / 1 = 36

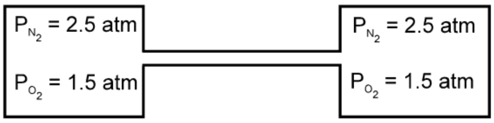
Section (C) : Grahams Law of diffusion

Diffusion :

Net spontaneous flow of gaseous molecule from region of high concentration (higher partial pressure) to region of lower concentration (lower partial pressure)



$\rightleftharpoons$ flow will be from both sides, N_2 will try to equalise its partial pressure in both the vessels, and so will O_2.



Graham's Law :

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

- rate of diffusion $r \propto \frac{1}{\sqrt{d}}$ d = density of gas

$$\frac{r_1}{r_2} = \frac{\sqrt{d_2}}{\sqrt{d_1}} = \frac{\sqrt{M_2}}{\sqrt{M_1}} = \sqrt{\frac{V.D_2}{V.D_1}}$$ V.D is vapour density

r = volume flow rate = $\frac{dV_{out}}{dt}$

r = mole flow rate = $\frac{dn_{out}}{dt}$

r = distance travelled by gaseous molecule per unit time = $\frac{dx}{dt}$

- The general form of the grahams law of diffusion can be stated as follows, when one or all of the parameters can be varied.

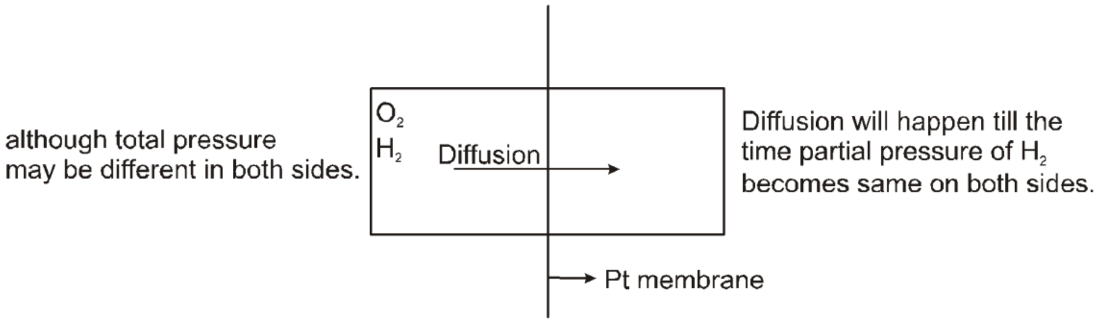
  rate $\propto \frac{P}{\sqrt{TM}} A$; P – Pressure, A – area of hole, T – Temp. , M – mol. wt.
- If partial pressure of gases are not equal.
  Then rate of diffusion is found to be proportional to partial pressure & inversely proportional to square root of molecular mass.

  $r \propto P$

  $r \propto \frac{1}{\sqrt{M}}$; $\frac{r_1}{r_2} = \frac{P_1}{P_2}\sqrt{\frac{M_2}{M_1}}$

Selective diffusion :

If one or more than one components of a mixture are allowed to diffuse and others are not allowed then it is selective diffusion of those components.

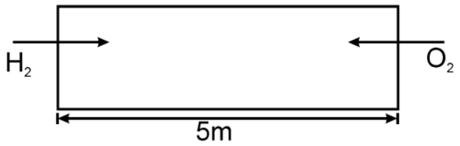


☞ **Platinum allows only H_2 gas to pass through**

Effusion : (forced diffusion) a gas is made to diffuse through a hole by application of external pressure.

Solved Examples

Ex.10 In a tube of length 5 m having 2 identical holes at the opposite ends. H_2 & O_2 are made to effuses into the tube from opposite ends under identical conditions. Find the point where gases will meet for the first time.



Sol. $\frac{r_1}{r_2} = \frac{ax}{dt} \times \frac{dt}{dx} = \sqrt{\frac{m_2}{m_1}} = \frac{dx_1}{dx_2} = \sqrt{\frac{32}{2}}$

$\frac{dx_1}{dx_2} = 4 \quad \Rightarrow \quad \frac{\text{distance travelled by } H_2}{\text{distance travelled by } O_2} = 4$

$\frac{x}{(5-x)} = 4 \quad \Rightarrow \quad x = (5 - x)\,4 \quad \Rightarrow \quad x = 20 - 4x$

$5x = 20 \quad \Rightarrow \quad x = 4$ from H_2 side

Ex.11 The pressure in a vessel that contained pure oxygen dropped from 2000 torr to 1500 torr in 40 min as the oxygen leaked through a small hole into a vacuum. When the same vessel was filled with another gas, the pressure dropped from 2000 torr to 1500 torr in 80 min. What is the molecular weight of the second gas ?

Ans. M = 128 g/mol

Sol. Change in pessure = 2000-1500 = 500 torr; time-taken = 40 min

$\text{rate}_1 = \frac{500}{40}$ torr/min; similarly $\text{rate}_2 = \frac{500}{80}$ torr/min

$\frac{\text{rate}_1}{\text{rate}_2} = \sqrt{\frac{M}{32}}$

Section (D) : Kinetic theory of gases

Postulates / assumptions of KTG :

1. A gas consists of tiny spherical particles called molecules of the gas which are identical in shape & size (mass)
2. The volume occupied by the molecules is negligible in comparision to total volume of the gas.
For an ideal gas, volume of the ideal gas molecule $\simeq$ 0.
3. Gaseous molecules are always in random motion and collide with other gaseous molecule & with walls of the container.
4. Pressure of the gas is due to these molecular collisions with walls of the container
5. These collisions are elastic in nature
6. Molecular attraction forces are negligible. Infact, for an ideal gas attraction or repulsion forces are equal to zero.
7. Newton's laws of motion are applicable on the motion of the gaseous molecule.
8. Effect of gravity is negligible on molecular motion.
9. The average K.E. of gaseous molecules is proportional to absolute temp of the gas.

$\frac{1}{2} M \overline{(u^2)} \propto T$ (bar is for average)

Kinetic equation of gaseous state (expression for pressure of gas)

Derivation :

m = mass of one molecule

$\vec{U} = U_x \hat{i} + U_y \hat{j} + U_z \hat{k}$

Consider collision with ABCD

initial $\vec{P}_i = mU_x\hat{i}$; final $\vec{P}_f = -mU_x\hat{i}$

change in momentum due to collision = 2 U_x m

time taken between two successive collision with face ABCD = t = $\frac{2\ell}{U_x}$

frequency of collision = $\frac{1}{t} = \frac{U_x}{2\ell}$

change in momentum in one sec. = force = 2m $\frac{U_x \times U_x}{2\ell} = \frac{mU_x^2}{\ell}$

force due to all the molecules = $\frac{m}{\ell}\{U_{x_1}^2 + U_{x_2}^2 + ... + U_{x_N}^2\}$

average value of $U_N^2 = \overline{U_N^2} = \frac{Ux_1^2 + U_{x_2}^2 + ...U_{x_N}^2}{N}$

$F_x = \frac{m}{\ell}\{N\overline{U_x^2}\}$

all the three direction are equal as the motion is totally random in all directions, hence

$\overline{U_x^2} = \overline{U_y^2} = \overline{U_z^2}$

$\overline{U^2} = \overline{U_x^2} + \overline{U_y^2} + \overline{U_z^2} = 3\overline{U_x^2}$

$F = \frac{m}{\ell} N \frac{1}{3}\overline{U^2}$

Pressure = $\frac{F}{\ell^2} = \frac{1}{3}\frac{mN}{\ell^3}\overline{U^2}$ The volume of the container 'v' = ℓ^3

∴ $PV = \frac{1}{3}mN\overline{U^2}$ Kinetic equation of gases

where $\overline{U^2}$ is mean square speed

root mean square speed = $U_{rms} = \sqrt{\overline{U^2}} = \sqrt{\left(\frac{U_1^2 + U_2^2 + U_3^2 + ...\ U_N^2}{N}\right)}$

Verification of Gaseous Laws Using Kinetic Equation :

- From postulates ; $PV = \frac{1}{3}mN\overline{U^2}$

  $\frac{1}{2}m\overline{U^2} \propto T = \lambda T$ Where 'λ' is a proportionality constant

  $PV = \frac{2}{3}\left(\frac{1}{2}m\overline{U^2}\right)N$; $PV = \frac{2}{3}\lambda NT$

- Boyle's Law : N : constant
  T : constant
  PV = constant
- Charles law : N : constant
  P : constant
  v ∝ T

- Kinetic energy of gaseous molecule (translation K.E.)

  To calculate λ we have to use ideal gas equation (experimental equation)

  $PV = nRT$

  kinetic equation $PV = nRT = \frac{2}{3}\lambda NT = \frac{2}{3}\lambda (nN_A)T$

On comparing $\lambda = \frac{3}{2} \times \frac{R}{N_A}$

$\lambda = \frac{3}{2}K$ where $K = \frac{R}{N_A}$ = Boltzmann constant

Average K.E. of molecules = $\frac{1}{2}m\overline{U^2} = \lambda T$

Average K.E. = $\frac{3}{2}KT$ (only dependent on temperature not on nature of the gas.)

Average K.E. for one mole = $N_A\left(\frac{1}{2}m\overline{U^2}\right) = \frac{3}{2}KN_AT = \frac{3}{2}RT$

- **Root mean square speed (U_{rms})**

  $U_{rms} = \sqrt{\overline{U^2}} = \sqrt{\frac{3kT}{m}} = \sqrt{\frac{3RT}{mN_A}}$ Where m-mass of one molecule

○ Dependent on nature of gas i.e mass of the gas

  $U_{rms} = \sqrt{\frac{3RT}{M}}$ M = molar mass

- **Average speed (U_{av})**

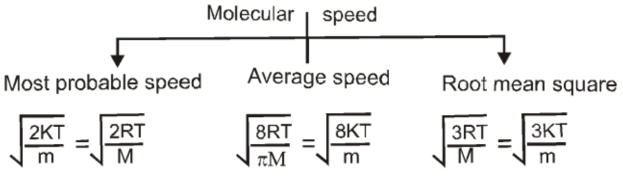
  $U_{av} = \frac{U_1 + U_2 + U_3 + \dots\dots\dots U_N}{N}$

  $U_{av} = \sqrt{\frac{8RT}{\pi M}} = \sqrt{\frac{8KT}{\pi m}}$ K is Boltzmann constant

- **Most probable speed (U_{mp})** :

  The speed possessed by maximum number of molecules at the given temperature.

  $U_{mp} = \sqrt{\frac{2RT}{M}} = \sqrt{\frac{2KT}{m}}$



$$U_{mp} : U_{av} : U_{rms} = \sqrt{2} : \sqrt{\frac{8}{\pi}} : \sqrt{3}$$

Solved Examples

Ex.12 In a container of capacity 1 litre there are 10^{23} molecules each of mass 10^{-22} g. If root mean square speed is 10^5 cm/sec then calculate pressure of the gas.

Sol. $PV = \frac{1}{3}mNU_{rms}^2$

$P = ?$; $V = 10^{-3}\ m^3$

$m = 10^{-25}$ kg ; $N = 10^{23}$

$\sqrt{\overline{U^2}}$ = 10^5 cm/sec = 10^3 m/sec

$\overline{U^2}$ = $10^6\ m^2/sec^2$

$$P \times 10^{-3} = \frac{1}{3} \times 10^{-25} \times 10^{23} \times 10^{6}$$

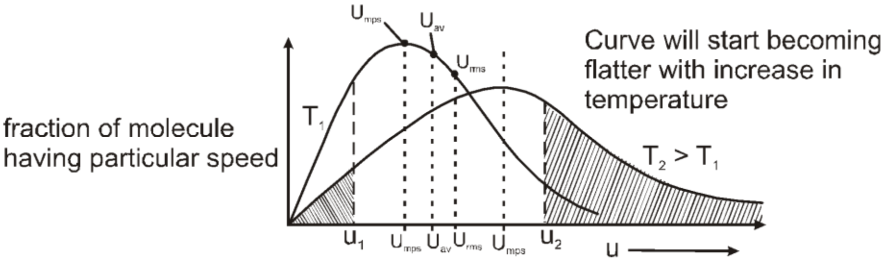
$$P = \frac{1}{3} \times 10^{-2} \times 10^{6} \times 10^{3} \quad ; \quad P = \frac{1}{3} \times 10^{7} \text{ pascals}$$

Maxwell's distributions of molecular speeds :

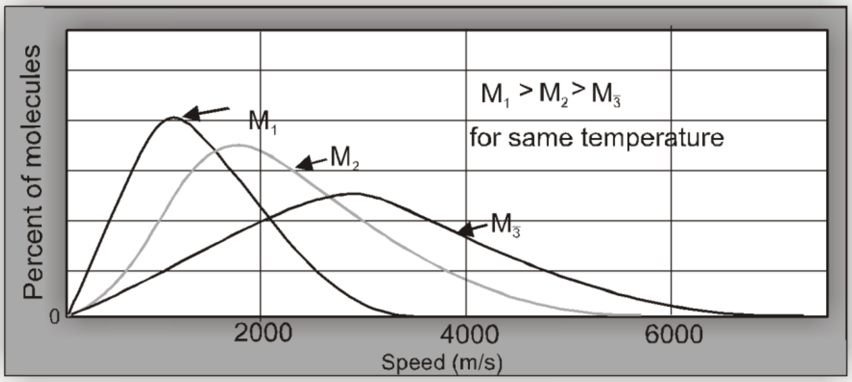
Postulates/Assumptions of speed distributions

- It is based upon theory of probability.
- It gives the statistical averages of the speed of the whole collection of gas molecules.
- Speed of gaseous molecules of may vary from 0 to ∞.

The maxwell distribution of speed can be plotted against fraction of molecules as follows.



- ○ The area under the curve will denote fraction of molecules having speeds between zero and infinity
- ○ Total area under the curve will be constant and will be unity at all temperatures.
- ○ Area under the curve between zero and u_1 will give fraction of molecules racing speed between 0 to u_1. This fraction is more at T_1 and is less at T_2.
- ○ The peak corresponds to most probable speed.
- ○ At higher temperature, fraction of molecules having speed less than a particular value decreases.
- ○ For Gases with different molar masses will have following graph at a given temperature.

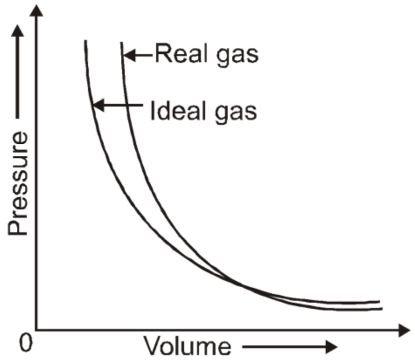


Section (E) : Real gases

- Real gases do not obey the ideal gas laws exactly under all conditions of temperature and pressure.
- Real gases deviates from ideal behaviour because
  - ○ Real gaseous molecules have a finite volume.

{since on liquefication real gases occupies a finite volume}

- Inter molecular attraction forces between real gas molecules is not zero.
  {Real gases can be converted into liquid where as ideal gases can't be}



- Deviation of real gases from ideal behaviour can be measured by using compressibility factor : (Z)

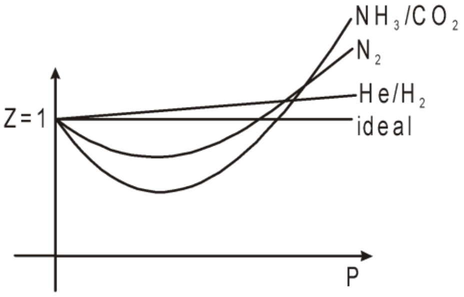
$Z = \frac{(PV)_{real}}{(PV)_{ideal}}$ $(PV)_{ideal} = nRT$

$\Rightarrow Z = \frac{PV}{nRT} = \frac{PV_m}{RT}$

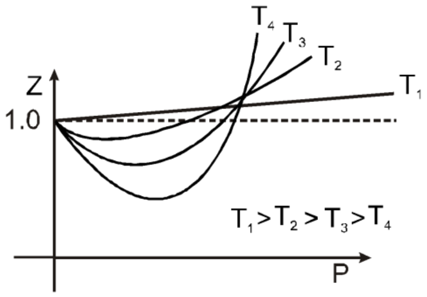
V_m is volume of one mole or molar volume.

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

Variation of Z with pressure at constant temperature :



Variation of Z with pressure at different temperature (for same gas) :



Conclusions :

Z = 1 for ideal gas

Z > 1 at all pressures for He/H_2

Z < 1 at low pressure (for alll other gases)

Z > 1 at high pressure (for alll other gases)

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 the ideal gas equation by taking the effect of
(a) Molecular volume **(b)** Molecular attraction

- **Volume correction :**

Ideal gas equation :

$P_i V_i = nRT$; In the equation 'V_i' stands for the volume which is available for free movement of the molecules.

V_{ideal} = volume available for free movement of gasesous molecule

hence, $V_i = V$ – {volume not available for free movement} For an ideal gas

$V_i = V$ {V = volume of container}

but for a real gas

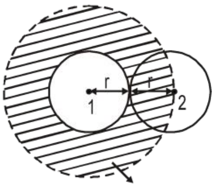
$V_i \neq V$, as all the volume is not available for free movement

Molecules have finite volume :

Excluded volume per molecule = $\frac{1}{2}\left\{\frac{4}{3}\pi(2r)^3\right\}$ = Co-volume per molecule.

The volume that is not available for free movement is called excluded volume.

let us see, how this excluded volume is calculated.



Excluded volume
(not available for free momement)

For above example, the entire shaded region is excluded, as its centre of mass cannot enter this region. If both molecules were ideal, then they would not have experienced any excluded volume but not in the case, of real gas as the centre of mass of '2' cannot go further.

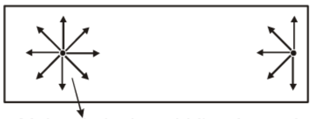
Hence for this pair of real gas molecules, excluded volume per molecule = $\frac{1}{2}\left\{\frac{4}{3}\pi(2r)^3\right\} = 4\left\{\frac{4}{3}\pi r^3\right\}$

Excluded volume per mole of gas (b) = $N_A \times 4 \times \left\{\frac{4}{3}\pi r^3\right\}$ = 4 x N_A × Volume of individual molecule

for n moles, excluded volume = nb

$V_i = V - nb$ volume correction

- **Pressure correction or effect of molecular attraction forces :**



Molecule in the middle of container

Due to these attraction, speed during collision will be reduced
Momentum will be less
Force applied will be less
Pressure will be less.

$P_{ideal} = P$ + {correction term}

Correction term α no. of molecules attracting the colliding molecule (n/v).

Correction term α density of molecules (n/v).

no. of collision α density of molecules $\left(\frac{n}{v}\right)$

net correction term ∝ $\left(\frac{n}{v}\right)\left(\frac{n}{v}\right) = \frac{an^2}{v^2}$

'a' is constant of proportionality and this is dependent on force of attraction

Stronger the force of attraction greater will be 'a' (Constant)

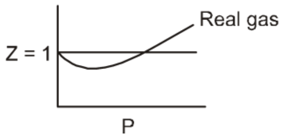
$$P_i = P + \frac{an^2}{v^2}$$

Vander waal's equation is

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

Verification of Vander Waal's Equations

Variation of Z with P for vander waals' equation at any temperature.



Vander waal equation for 1mole

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

V_m = volume of 1 mole of gas

- **AT LOW PRESSURE** (at separate temp.)

At low pressure V_m will be high.

Hence b can be neglected in comparision to V_m. but $\frac{a}{V_m^2}$ can't be neglected as pressure is low

Thus equation would be

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

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

$$\frac{PV_m}{RT} + \frac{a}{V_mRT} = 1 \qquad Z = 1 - \frac{a}{V_mRT} \qquad Z < 1$$

Real gas is easily compressible in comparision to an ideal gas.

- **AT HIGH PRESSURE** (moderate temp.)

V_m will be low

so b can't be neglected in comparision to V_m

but $\frac{a}{V_m^2}$ can be neglected in comparision to much high values of P.

Then vander Waals' equation will be

$P(V_m - b) = RT$

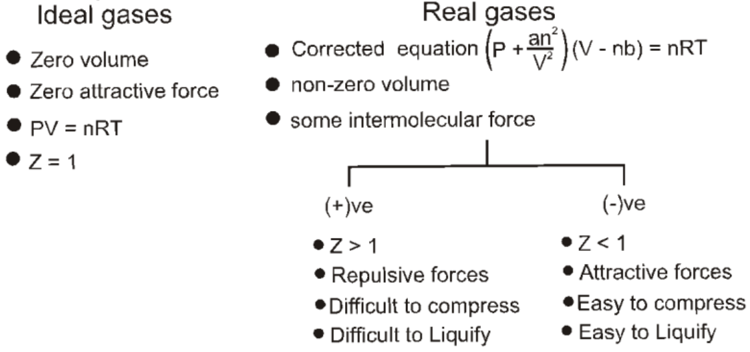
$PV_m - Pb = RT$

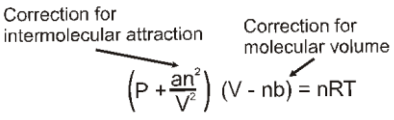
$$\frac{PV_m}{RT} = \frac{Pb}{RT} + 1$$

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

If Z > 1, then gas is more difficult to compress in comparision to an ideal gas.

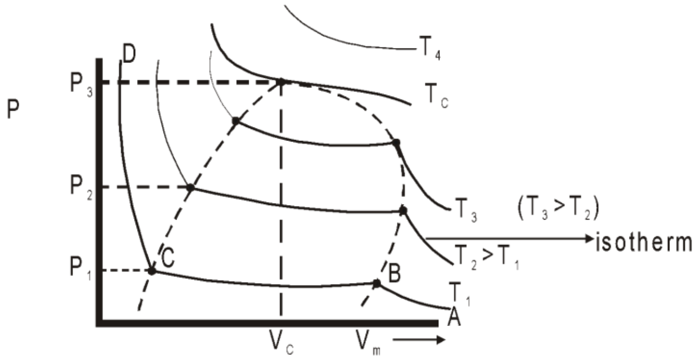
- At low pressure and very high temperature.
  V_m will be very large
  hence 'b' can be neglected and $\frac{a}{V_m^2}$ can also be neglected as V_m is very large
  $PV_m = RT$ (ideal gas condition)
- For H_2 or He $a \simeq 0$ because molecules are smaller in size or vander wall forces will be very weak, these are non polar so no dipole-dipole interactions are present in the actions.
  $P(V_m - b) = RT$
  so $Z = 1 + \frac{Pb}{RT}$
- 'a' factor depends on inter molecular attraction forces.
  - ○ 'a' factor for polar molecule > 'a' factor for non polar molecule.





Critical constant of a gas :

When pressure increases at constant temp volume of gas decreases



$T_4 > T_c > T_3 > T_2 > T_1$

AB → gas BC → vapour + liquid CD → liquid

Critical point : At this point, all the physical properties of liquid phase will be equal to physical properties in vapour such that

density of liquid = density of vapour

T_C or critical temp : Temperature above which a gas can not be liquified

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

P_C or critical pressure : Minimum pressure which must be applied at critical temp to convert the gas into liquid. $P_C = \frac{a}{27b^2}$

V_C or critical volume : Volume occupied by one mole of gas at T_C & P_C

$$V_C = 3b$$

Solved Examples

Ex.13 Arrange following in decreasing 'a' factor (H_2O, CO_2, Ar)

H_2O > CO_2 > Ar

polar

○ **For non polar molecules :**

Greater the size or surface area, greater will be vander waals' forces, so greater will be 'a' constant.

Solved Examples

Ex.14 Arrange following gases according to 'a'

He , Ar, Ne, Kr.

$a_{Kr} > a_{Ar} > a_{Ne} > a_{He}$

○ More 'a' factor means high boiling point.

○ **liquification pressure (LP) :** Is the pressure required to convert gas into liquid.

for easy liquefaction a↑ and LP↓

When $Z < 1$, $V_m < V_{m,\ ideal}$ easily liquifiable

$Z > 1$, $V_m > V_{m,\ ideal}$ more difficult to compress.

Solved Examples

Ex.15 Arrange the following according to liquification pressure (n-pentane ; iso-pentane , neo pentane).

Sol. $a_{n\text{-pentene}} > a_{iso\text{-pentane}} > a_{neo\text{-pentane}}$

liquification pressure = LP

$LP_{n\text{-pentene}} < LP_{iso\text{-pentane}} < LP_{neo\text{-pentane}}$

- **b** is roughly related with size of the molecule. (Thumb rule)

$$b = N_A\, 4 \left\{\frac{4}{3}\pi r^3\right\}$$

Ex.16 Two vander waals gases have same value of b but different a values. Which of these would occupy greater volume under identical conditions ?

Sol. If two gases have same value of b but different values of a, then the gas having a larger value of a will occupy lesser volume. This is because the gas with a larger value of a will have larger force of attraction and hence lesser distance between its molecules.

MISCELLANEOUS SOLVED PROBLEMS (MSPs)

1. The diameter of a bubble at the surface of a lake is 4 mm and at the bottom of the lake is 1 mm. If atmospheric pressure is 1 atm and the temperature of the lake water and the atmosphere are equal. what is the depth of the lake ?

(The density of the lake water and mercury are 1 g/ml and 13.6 g/ml respectively. Also neglect the contribution of the pressure due to surface tension)

Sol. $P_1V_1 = P_2V_2$

$$\therefore\ (760\text{ mm} \times 13.6 \times g)\ \frac{4}{3}\pi\,(4\text{ mm}/2)^3 = (760\text{ mm} \times 13.6 \times g + h \times 1 \times g)\ \frac{4}{3}\pi\,(1\text{ mm}/2)^3$$

$760 \times 13.6 \times 64 = (760 \times 13.6 + h)$

$h = 64 \times 760 \times 13.6 - 760 \times 13.6$

$h = 63 \times 760 \times 13.6$ mm

$h = \dfrac{63 \times 760 \times 13.6}{1000 \times 1000}$ km = 0.6511 km = **651.1 m Ans.**

2. A gas is initially at 1 atm pressure. To compress it to 1/4 th of initial volume, what will be the pressure required ?

Sol. $P_1 = 1$ atm $\quad V_1 = V$

$P_2 = ?$ $\quad V_2 = \dfrac{V}{4}$

$P_1V_1 = P_1V_2$ at const. T & n ; $P_2 = \dfrac{P_1V_1}{V_2} = \dfrac{1\text{ atm} \times V}{\frac{V}{4}}$ = **4 atm Ans.**

3. A vessel contains H_2 & O_2 in the molar ratio of 8 : 1 respectively. This mixture of gases is allowed to diffuse through a hole, find composition of the mixture coming out of the hole.

Sol. Here, $n_{H_2} : n_{O_2} = 8 : 1$ & $\dfrac{r_{H_2}}{r_{O_2}} = \dfrac{n_{H_2}}{n_{O_2}}\sqrt{\dfrac{M_{O_2}}{M_{H_2}}}$

$\Rightarrow \dfrac{r_{H_2}}{r_{O_2}} = \dfrac{8}{1} \times \sqrt{\dfrac{32}{2}} = \dfrac{32}{1}$

$\Rightarrow \dfrac{(\text{no. of moles of } H_2 \text{ coming out})/\Delta t}{(\text{no. of moles of } O_2 \text{ coming out})/\Delta t} = \dfrac{32}{1}$

Required composition of $H_2 : O_2$ coming out = **32 : 1 Ans.**

4. The rate of diffusion of a sample of a ozonized oxygen is 0.98 times than that of oxygen. Find the % by volume of ozone in the ozonized sample.

Sol. Let, rate of diffusion of ozonized oxygen be r_g

& Let, reat of diffusion of oxygen be r_{O_2}

$\therefore \quad \dfrac{r_g}{r_{O_2}} = 0.98$ (given) .... (1)

but $\dfrac{r_g}{r_{O_2}} = \left(\dfrac{M_{O_2}}{M_g}\right)^{1/2}$ (mean molar mass of ozonized oxygen = M_g)

Form **(1)** ⇒ $0.98 = \sqrt{\frac{32}{M_g}}$

⇒ $(0.98)^2 = \frac{32}{M_g}$ ∴ $M_g = \frac{32}{(0.98)^2} = 33.32$

Let % of O_3 be x % O_2 = (100 – x) in ozonized oxygen.

∴ $\frac{48x + (100 - x) \times 32}{100} = 33.32$ ⇒ $3200 + 16x = 33.32$ ∴ $x = \frac{132}{16} = 8.25$ %

i.e. % of O_3 = **8.25 % Ans.**

5. Under critical states of a gas for one mole of a gas, compressibility factor is

(1) $\frac{3}{8}$ (2) $\frac{8}{3}$ (3) 1 (4) $\frac{1}{4}$

Sol. For 1 mole of gas $Z = \frac{P_C V_C}{RT_C}$ (Under critical condition)

But, $P_C = \frac{a}{27b^2}$, $V_C = 3b$, $T_C = \frac{8a}{27Rb}$

$Z = \left(\frac{a}{27b^2}\right) \times \frac{3b}{R} \times \frac{27Rb}{8a} = \frac{3}{8}$ **Ans. (1)**

6. A weather balloon filled with hydrogen at 1 atm and 300 K has volume equal to 12000 litres. On ascending it reaches a place where temperature is 250 K and pressure is 0.5 atm. The volume of the balloon is :

(1) 24000 litres (2) 20000 litres (3) 10000 litres (4) 12000 litres

Sol. Using $\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$; $\frac{1\text{ atm} \times 12000\text{ L}}{300\text{ K}} = \frac{0.5\text{ atm} \times V_2}{250\text{ K}}$

∴ V_2 = 20,000 L

Hence **Ans. (2)**

7. If for two gases of molecular weights M_A and M_B at temperature T_A and T_B ; $T_AM_B = T_BM_A$, then which property has the same magnitude for both the gases.

(1) Density (2) Pressure (3) KE per mol (4) RMS speed

Sol. Given that $T_A M_A = T_B M_A$ ⇒ $\frac{T_A}{M_A} = \frac{T_B}{M_B}$

But, r.m.s. = $\sqrt{\frac{3RT}{M}}$

r.m.s$_A$ = $\sqrt{\frac{3RT_A}{M_A}}$ & r.m.s$_B$ = $\sqrt{\frac{3RT_B}{M_B}}$

r.m.s$_A$ = r.m.s$_B$ **Ans. (4)**