Gas Law

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Introduction

- V = f(T,P,n)
- Pressure is force per unit area.
- Force = mass x acceleration

= density of Hg x height x area x acceleration
= 13.59gm/cc x 76cm x 1cm^2 x 980.7cm/sec^2
= 1.013 x 10^{6}gm.cm/sec^2 = 10.13 kg m/sec^2
= 1.013 x10^6 dynes = 10.13 Newton

- This is force exerted by column of Hg of 76.0cm and 1-cm^2 cross – sectional area. This corresponds to 1-atm. pressure.

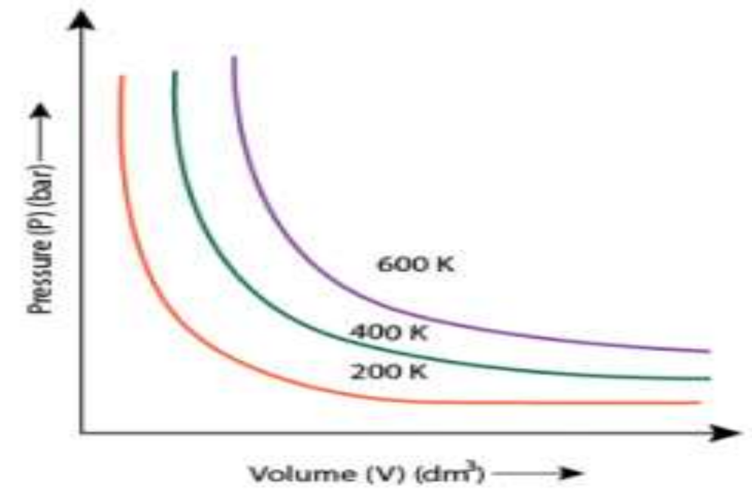
1atm. = 76.0 cm of Hg.
= 1.013 x 10^{6}dyne/cm^2
= 1.013 x 10^{5}newton/m^2

- “mm Hg” is replaced by equivalent torr.
- In SI unit , the unit of pressure is the Newton per square meter and one Newton per square meter is called Pascal(Pa)

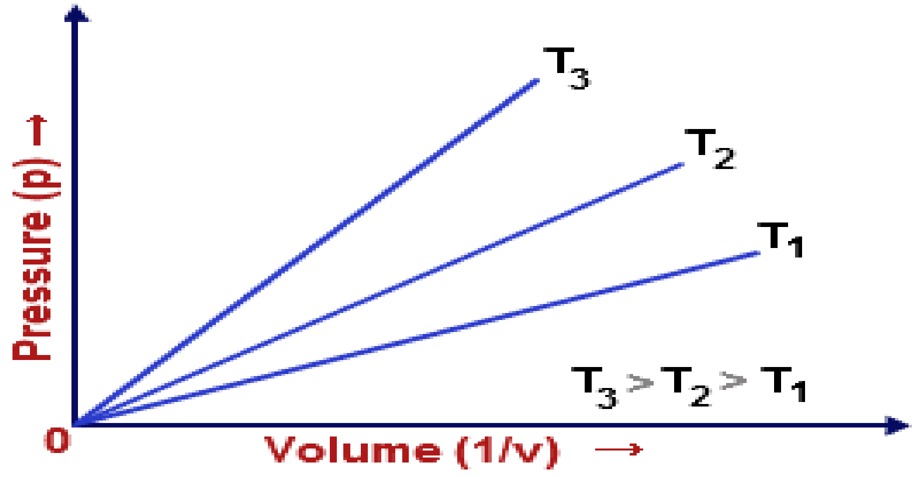
Boyle’s law

- Pressure is inversely proportional to volume at constant no. of moles and temp
- $P = \frac{K_{m,t}}{V}$ or $\frac{dP}{dV} = \frac{-C}{V^2}$

or $\log P = \log C - \log V$



P Vs V graph of a gas at different temperatures



Gay-Lussac's law or Charles law:

- These both laws state that volume is directly proportional to temperature at constant pressure and no. of moles.
- $V_t = V_0(1+t/273)$; V_0 = vol. of given mass of a gas at 0^0c & V_t = vol. of given mass of a gas at t^0c.
- It has been observed that :
- $\frac{V_2}{V_1} = 1.366$ **(V_2 at 100^0c & V_1 at 0^0c) ;**

$$V_2 = 1.366V_1 \qquad = V_1(1+0.366V_1)$$

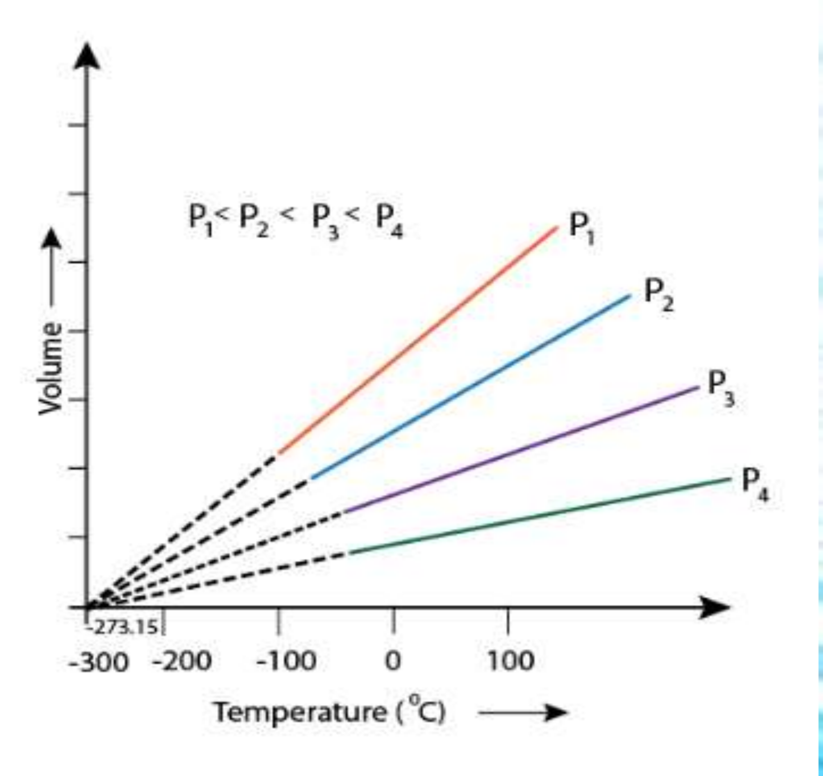
- i.e. vol. at 100^0c is greater than its vol. at 0^0c by o.366 times its vol. at 0^0c
- So, expansion per unit degree = $\frac{0.366V_1}{100} = \frac{V_1}{273}$

i.e. for every 1^0c change in temp. the volume of the gas changes by 1/273 of its vol. at 0^0c.

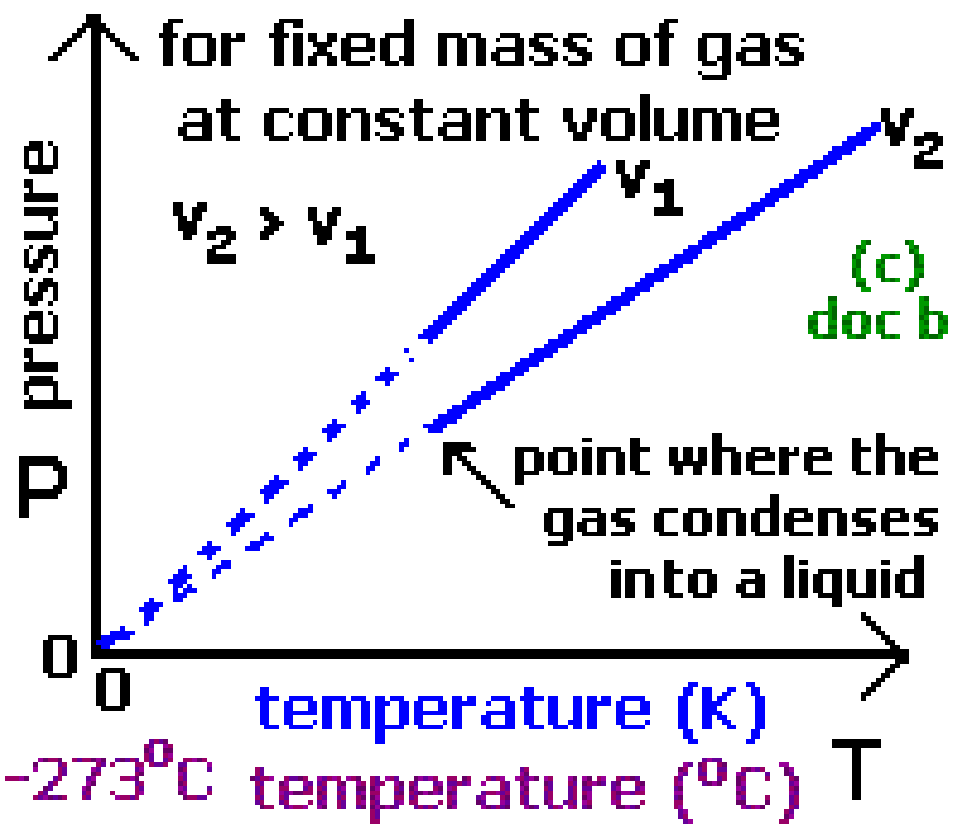
- If V_1 & V_2 are the volumes at temp. t_1 & t_2 :
- $V_1 = V_0(1+t_1/273)$ & $V_2 = V_0(1+t_2/273)$
- or $V_1/V_2 = \frac{273+t_1}{273+t_2}$; $T = 273 + t$

$V_1/V_2 = T_1/T_2$ or $V/T = \text{const.}$

Graphs for Isobar and Isochor



Volume Vs Temperature graph (°C)



Avogadro’s law:

Under similar condition of pressure & temp. the same volume of different gases will have the same no. of molecules. From this law it can also be derived that at const. temp. & pressure , the vol. of any gas is directly proportional to the no. of mole i.e. $V \alpha n$

Ideal gas equation or equation of state for an ideal gas:

Combination of all the above laws give: **$PV = nRT$**

- This equation is applicable to ideal gases.
- Ideal or perfect gas is hypothetical & imaginary. Real gases show ideal behavior at low P & moderately high temp.
- The deviation from ideal behavior becomes greater as we go nearer to the temp. & pressure at which gas can be condensed to liquid. It is due to increase in intermolecular force of attraction.

Numerical value of the universal gas constant (R)

(i) In lit.atm.deg^{-1}.mol^{-1}

$$R = \frac{(1\text{atm})(22.4\text{lit})}{(1\text{mole})(273.15\text{deg})} = \mathbf{0.08206\text{lit-atm-mol}^{-1}\text{-deg}^{-1}}$$

(ii) In erg-deg^{-1}-mole^{-1}

$$R = \frac{76\text{cm} \times 13.595\text{g/c} \times 981\text{dyne/sq cm} \times 22400\text{cc}}{1\text{mole} \times 273\text{K}}$$

$$\mathbf{= 8.314 \times 10^{7}\ \text{erg} - \text{deg}^{-1} - \text{mole}^{-1}}$$

(iii) In Joule-deg^{-1}-mole^{-1} **= 8.314 Joules– deg^{-1} – mole^{-1}**

(10^{7}ergs =1joule) or N m^{-2} or Pa or kPa

(iv) In calories-deg^{-1}-mole^{-1} **= 1.987 calories-deg^{-1}-mole^{-1}**

(4.187x107ergs =1calorie)

Gas Constant (R)

- R= PV/nT;

  = Force X Area X Length/ Area x Temp

  = Force x Length

  = Work

So, R is defined as the work done by one mole of a gas for one-degree change in temperature. Since this value comes to be constant irrespective of the nature of the gas, so it is called universal gas constant

Ideal gas equation in terms of wt . & density

- $PV = \frac{w}{M}RT$; $PM = \frac{w}{V}RT$; $PM = dRT$
- **Pressure of a moist gas:** $P_{moist} = P_{dry}$ + Pressure of water vap.
- Pressure of water vap.is also termed as aq. tension.

DALTON’ LAW OF PARTIAL PRESSURE

when two or more non-reacting gases are mixed , the total pressure of the mixture is the sum of the partial pressures of the individual gases.

$P_{\text{total}} = P_a + P_b + \ldots\ldots\ldots\ldots\ldots P_n$;

are pressure of gases a,b & n respectively.

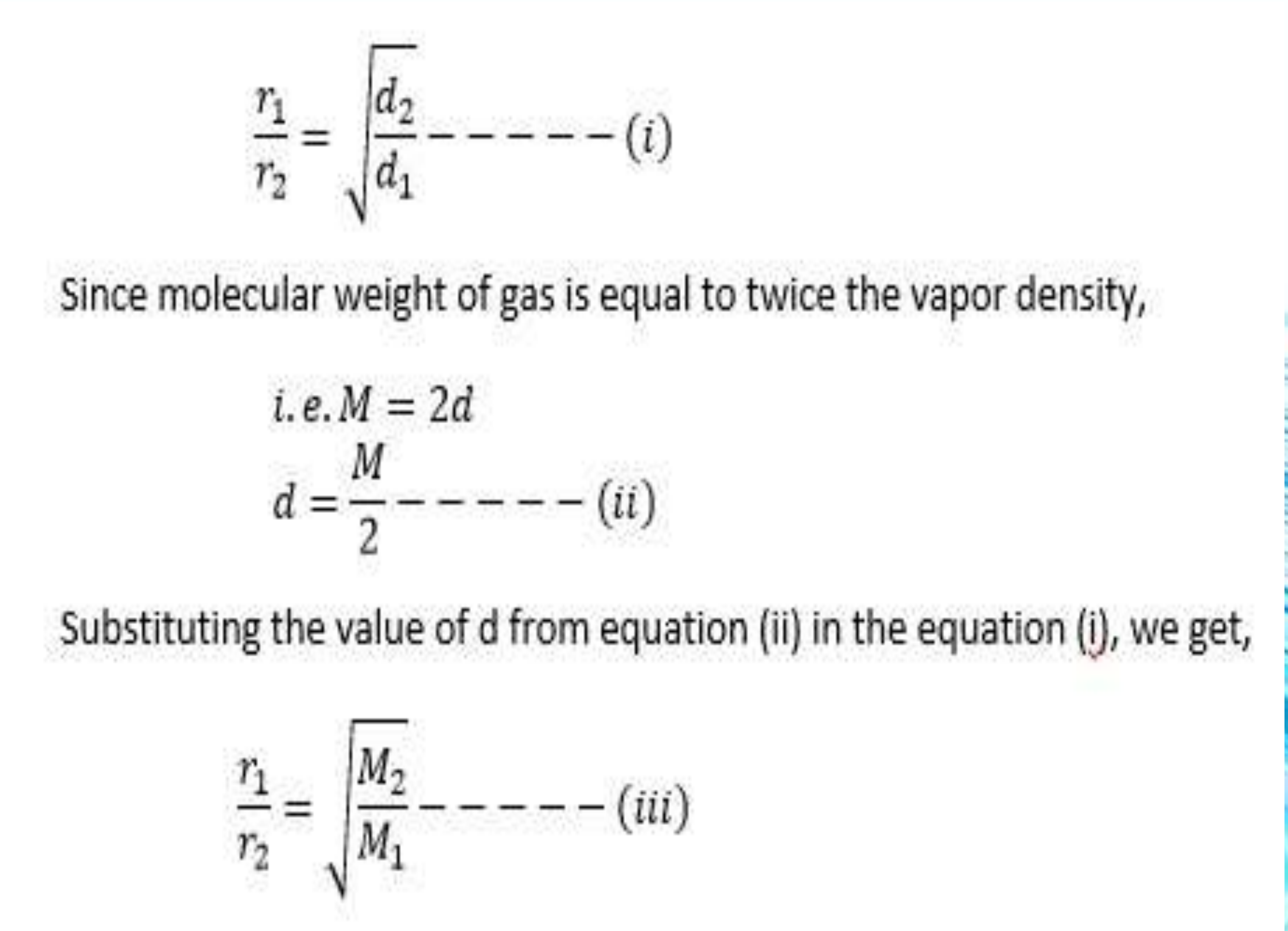
$$= \frac{n_aRT}{V} + \frac{n_bRT}{V} + \frac{n_cRT}{V} + \ldots\ldots\ldots \frac{n_nRT}{V}$$

$$= \frac{RT}{V} (n_a + n_b + n_c + \ldots\ldots n_n$$

$$P_a/\mathbf{Ptotal} = \mathbf{n_a/\sum n}$$

- P_a = P_{total} x mole fraction
- Similarly, P_a = P_{total} x volume fraction

- **Diffusion & Effusion :**
- **Diffusion :** The tendency for any substance to spread uniformly throughout the space available to it. Diffusion relates to the movement of the two gases in and out of the container.
- Diffusion is exhibited by gases ,liquids and even solids, but it is more rapid with gases
- **Effusion :** It is defined as the tendency for any gas to spread through fine pores uniformly throughout the space available to it.
- **Rate of diffusion(r) :**
- r = Vol. diffused/ time taken **or** no. of mole diffused/time taken **or** length (distance) covered/ time taken
- **Grahm's law of diffusion :**The rate of diffusion(effusion) of a gas is inversely proportional to the square root of its density.



$$\frac{r_1}{r_2} = \sqrt{\frac{d_2}{d_1}} ------(i)$$

Since molecular weight of gas is equal to twice the vapor density,

$$i.e. M = 2d$$

$$d = \frac{M}{2} ------(ii)$$

Substituting the value of d from equation (ii) in the equation (i), we get,

$$\frac{r_1}{r_2} = \sqrt{\frac{M_2}{M_1}} ------(iii)$$

$$Rate\ (r) = \frac{Volume\ of\ gas\ diffused}{time\ taken}$$

$$i.e. r = \frac{V}{t}$$

If t_1 and t_2 are the time taken for diffusion of V ml of two gases, then

$$r_1 = \frac{V}{t_1} - - - - - - - (iv)$$

$$r_2 = \frac{V}{t_2} - - - - - - (v)$$

Using equation (iv) and (v), in equation (iii), we get,

$$\frac{t_2}{t_1} = \sqrt{\frac{M_2}{M_1}}$$

Numericals

Q.1. A manometer is connected to a gas containing the bulb. The open arm reads 43.7cm whereas the arm connected to the bulb reads 15.6cm. If the barometric pressure is 743mm of Hg, find the pressure of gas in bar? (Ans: 1.347bar)

Q.2. A gas occupy one liter under atmospheric pressure. what will be the volume of the same amount of gas under750mm of Hg at the same temperature? (ans : 1013.3mL)

Q.3. A gas cylinder containing cooking gas withstand a pressure of 14.9atm. The pressure gauge of cylinder indicates 12 atm at 27^0c.Due to sudden fire in the building, the temp. rises. At what temp., cylinder will explode? (Ans: 372.56K)

Q.4. 5g of ethane is confined in a bulb of one-liter capacity. The bulb is so weak that it will burst if the pressure exceeds 10atm. At what temperature will the pressure of the gas reach the bursting value? (T=731.7K)

Q.5. The density of a gas is 1.43g/lit at STP. Determine the density of the gas at 17^0c& 700torr? (ans: 1.24g/lit)

Q.6. A gas at 0^0c and 1atm pressure occupies 2.5litres. What change in temp. would be necessary if the pressure is to be adjusted to 1.5atm and the gas has been transferred to a 20 liter container? (ans: 327.6K)

Q.7.The pressure exerted by 12g of an ideal gas at t^0c in a vessel of V lit, is 1atm. When the temp. is increased by 10^0 at the same vol, the press. increase by 10%. Calculate the temp. t & volume V. (mol. wt of the gas is 120) ans: 0.82lit

Q.8.A bottle is heated with its mouth open from 15^0c to 100^0c. What percentage of air originally contained in the vessel is expelled? (Ans: 22.8%)

Q.9. A sample of nitrogen gas is bubbled through liquid water at 25^0c and then collected in a volume of 750cc. The total pressure of the gas which is saturated with water vapor ,is found to be 740mm at 25^0c. The vapor pressure of water at this temperature is 24mm. How many moles of nitrogen are in the sample ?(ans: 0.028)

Q.10 At constant temp. 200mL of hydrogen at 700mm pressure and 300mL of nitrogen at 600mm pressure were put in a flask of 1.0 liter capacity. What will be the final pressure of the mixture? (ans: 320mm)

Q.11. Atmospheric air cotains 20% O_2 and 80% N_2 by volume and exerts a pressure of 760mm. Calculate the partial pressure of each gas (P_{O2} = 152mm ; P_{N2} = 608mm)

Q.12. One mole of nitrogen gas at 0.8atm. takes 38sec. to diffuse through a pinhole, whereas one mole of an unknown compound of xenon with fluorine at 1.6 atm. takes 57 sec. to diffuse through the same hole. calculate the molecular formula of the compound?

Q.13. A mixture consisting of 80mole percent of H_2 and 20mole percent deuterium at 25^0c and a total pressure of 1 atm. is permitted to effuse through a small orfice area 0.20mm2. Calculate the composition of the initial gas that pass through (ans: 5.65:1)

Q.14. A mixture consisting of 80mole percent of H_2 and 20mole percent deuterium at 25^0c and a total pressure of 1 atm. is permitted to effuse through a small orfice area 0.20mm^2. Calculate the composition of the initial gas that pass through (ans: 5.65:1)

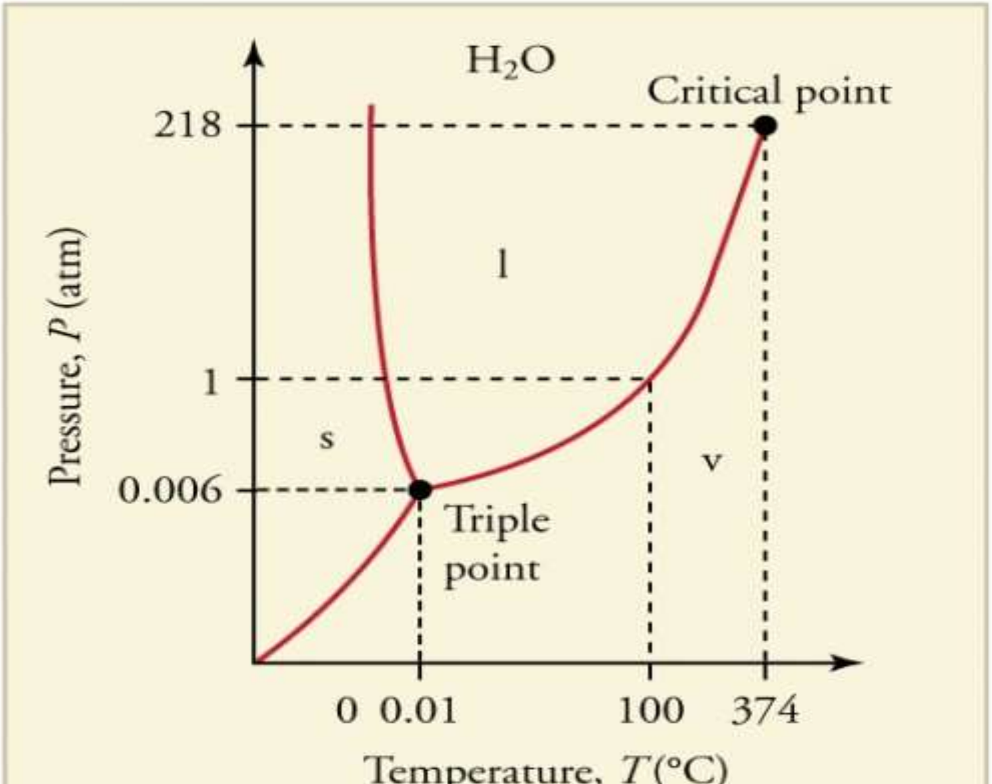
Q.15. At 27^0c, H_2 is leaked through a tiny hole into a vessel for 20min. Another unknown gas at the same temp. & pressure as that of H_2 is leaked through the same hole for 20 minutes. After the effusion of the gases the mixture exerts a pressure of 6atm.The hydrogen content of the mixture is 0.7 mole. If the vol. of the container is 3L ,what is the mol. wt. of the unknown gas ?(ans:1033)

Vapor pressure and Liquefaction of gas

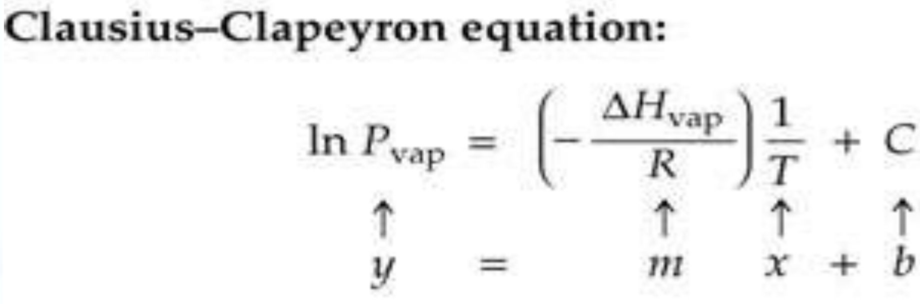
- The pressure under which liquid and vapor can coexist at equilibrium is the saturation vapor pressure or the vapor pressure of the liquid.
- The variation of coexistence of vapor and liquid with change in temp. can be shown as :

i. Above temp. 374 deg. Celsius liquid can not exist. This temp. is called critical temp.

ii. Triple point: The freezing point of the liquid under its own V.P.



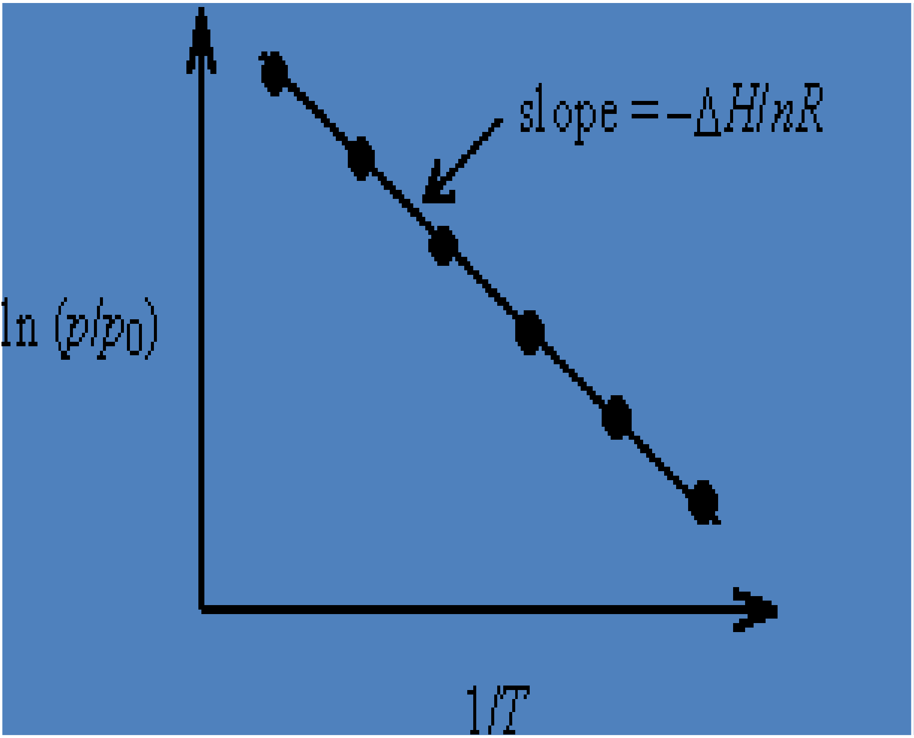
Clapeyron-Clausius equation



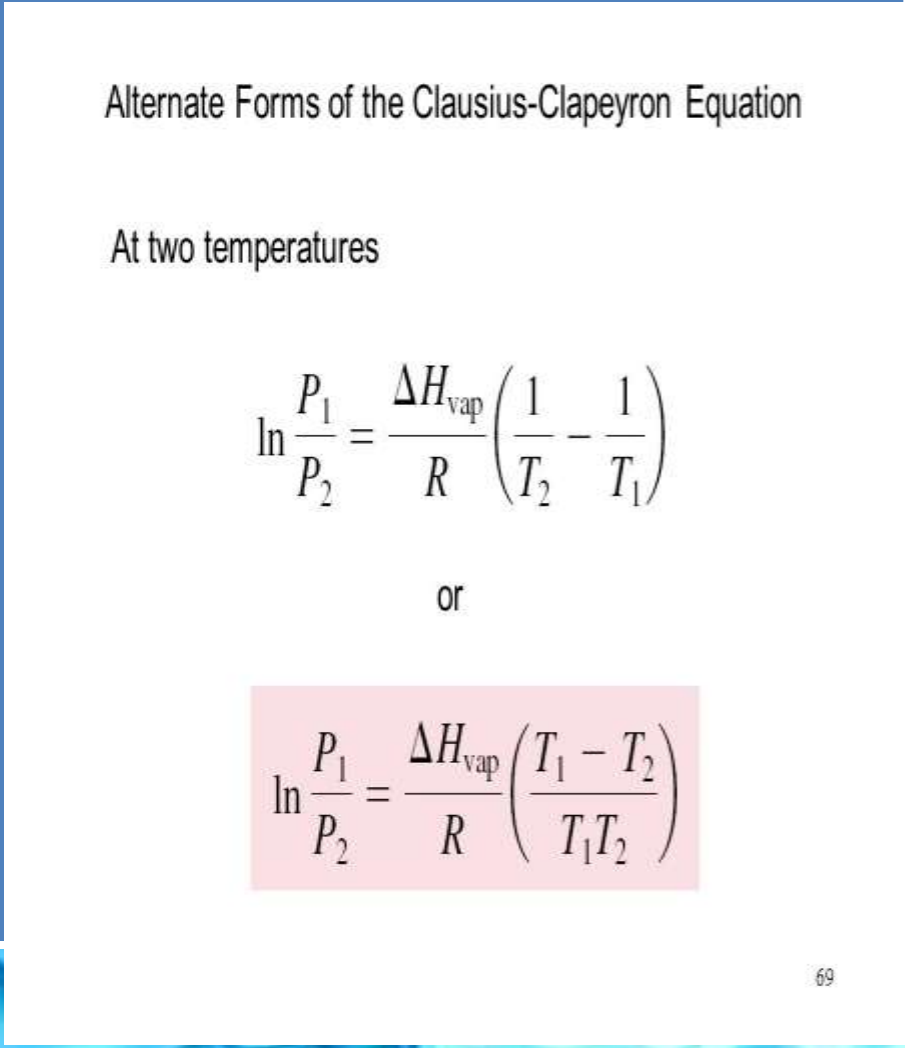
Clausius–Clapeyron equation:

$$\ln P_{\text{vap}} = \left(-\frac{\Delta H_{\text{vap}}}{R}\right)\frac{1}{T} + C$$

$$\underset{y}{\uparrow} = \underset{m}{\uparrow}\ \underset{x}{\uparrow} + \underset{b}{\uparrow}$$



Or $P = A.e^{(-Hv/RT)}$



Alternate Forms of the Clausius-Clapeyron Equation

At two temperatures

$$\ln\frac{P_1}{P_2} = \frac{\Delta H_{\text{vap}}}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

or

$$\ln\frac{P_1}{P_2} = \frac{\Delta H_{\text{vap}}}{R}\left(\frac{T_1 - T_2}{T_1 T_2}\right)$$

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Features of Critical temperature

- It is the maximum temperature at which a gas can be liquefied i.e the temp. above which liquid can not exist.
- The term vap. is used to describe a gaseous substance when its temp. is below the critical value.
- A vapor can therefore be condensed to liquid by pressure alone.
- At critical point the densities are identical i.e. there is no difference between liquid and gas and the surface of separation between the two phase disappear.
- The b.p of a liquid , at 1atm, is approx. two third of the critical temp. $T_b/T_c = 0.66$
- Relation among critical constants is :

$V_c=3b$; $P_c= a/27b^2$; $T_c= 8a/27b^2$

- For a given gas ,the deviation from ideal behavior is maximum at or near the critical temp
- **Trouton's rule :** The molar heat of vaporization ,in cals, divided by the normal b.p. on absolute scale , is approx. 21.
- i.e. $L_v/T_b =21$

Liquefaction of gas

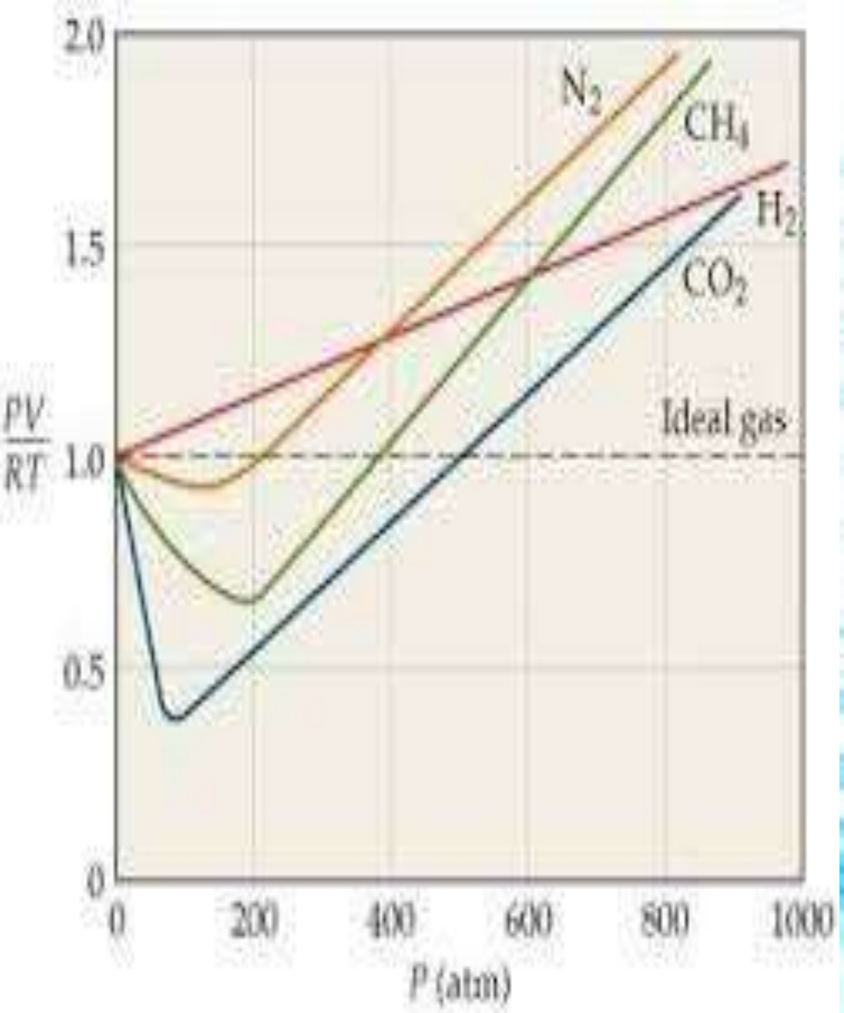
Two methods are used as :

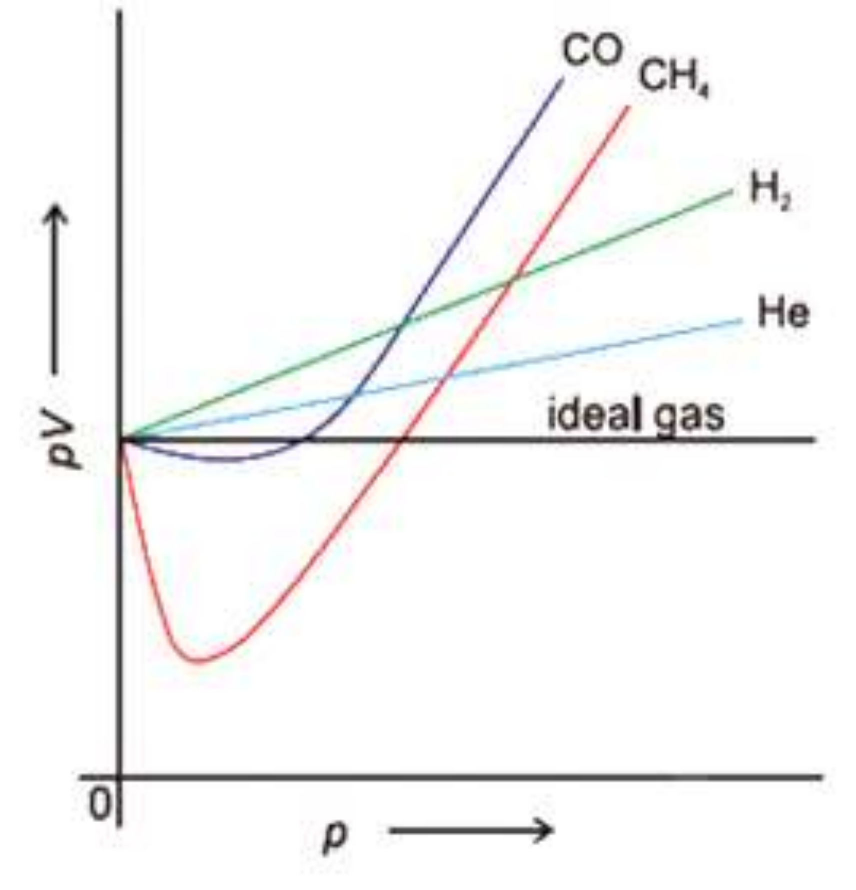
(i) Joule – Thomson effect : The gas ,at an initial pressure , is allowed to stream through a throttle . This causes lowering in temperature of the gas and ultimately liquefaction of the gas.

- But this is again possible when J.T. expansion is done at certain temperature, known as **INVERSION TEMP.** Above inversion temperature, warming effect is observed in stead of cooling in J.T. expansion

(ii) Adiabatic expansion. The gas is compressed first and then allowed to do some mechanical work. As a result ,kinetic energy is removed from the gas molecule and temperature falls.

Deviation from ideal behaviour





- Considerable deviation from ideal behavior is observed at high pressure. At 1atm or less, the deviation from Boyl's law is usually small.
- PV for H_2 increases with increase in pressure. For other gases , there is at first decrease followed by an increase.
- If the temp. is lowered ,the shape of the curve changes and in each case it becomes like that for CH_4 & CO. On the other hand ,at sufficiently high temp. P-V curve of these other gases become like those for H_2.
- Near critical temp. the PV curve is like that of CO but when far away ,the curves are like that of H_2.

- The temp. at which a gas behaves ideally over a wide range of pressure is called **Boyle's temperature**.
- Graph(I) suggests that Z=PV/RT known as compressibility factor is less than one for CH_4 & CO.
- But it is greater than one for H_2. The dip in the beginning of the curve is more pronounced for the gases which are easily liquefiable.
- The extent of deviation depend upon

(a) the nature of the gas (b) temp. (c) pressure

Cause of deviation from ideal behavior

Ideal gas eqn. is derived from kinetic theory of gas. This theory is based on the following assumptions :

(i) Volume of the gaseous molecule is negligibly small in comparison to the total vol. of the gas.

(ii) Gaseous molecules exert no attraction or repulsion upon one another.

(iii) When the molecules approach each other , both attractive and repulsive force operate.

- At very close distance ,repulsive force dominates. As the distance increases repulsion force falls off extremely rapidly than force of attraction. So there is certain intermolecular distance at which the force of attraction is maximum.
- At very high pressure ,repulsive force dominates so $Z>1$. At low pressure attractive force dominates and $Z<1$.
- The intermolecular-distance at which the potential energy is zero i.e. force of attraction balances the force of repulsion ,is called **collision diameter.**

Deviation from ideal gas and Vanderwaal's gas equation:

- **Pressure correction** : a/V^2 is added to match with ideal pressure P.
- **Volume correction :** Space available for movement is less than the actual measured vol. of the gas. In order to obtain ideal vol. it is necessary to subtract an appropriate correction term. This correction term is equal to **four times** the actual volume of the molecule.
- Now the vanderwaal's gas equation is : **$(P+n^2a/V^2)\ (V-nb) = nRT$**
- 'a' & ' b' are vanderwaal's gas constant. a measures intermolecular force of attraction.
- Larger the 'a' stronger the intermolecular force of attraction and easier to liquefy the gas.
- 'b' is the vol. of the molecule and it indicates the repulsive force. The effective vol. is four times greater than the actual vol.

- **Unit of 'a' : p= n^2a/V^2 or, a = pV^2/n^2 ; so unit is atm. $lit^2.mol^{-2}$. Unit of 'b' : unit of vol**

Application of Vanderwaal's gas equation:

- At extremely low pressure : V is very large ,a/V^2 & b can be neglected. The equation becomes: PV=RT
- At moderate pressure: The difference between PV & RT increases as V decreases with increase in pressure.
- a/V^2 measures the force of attraction. At moderate pressure, the attractive force dominates and dip in the curve is observed. Z<1. The eqation is $PV=RT-a/V$.
- At high pressure : The equation becomes $PV=RT + Pb$. Repulsive force dominates and Z>1.

Limitation of Vanderwaal’s gas equation

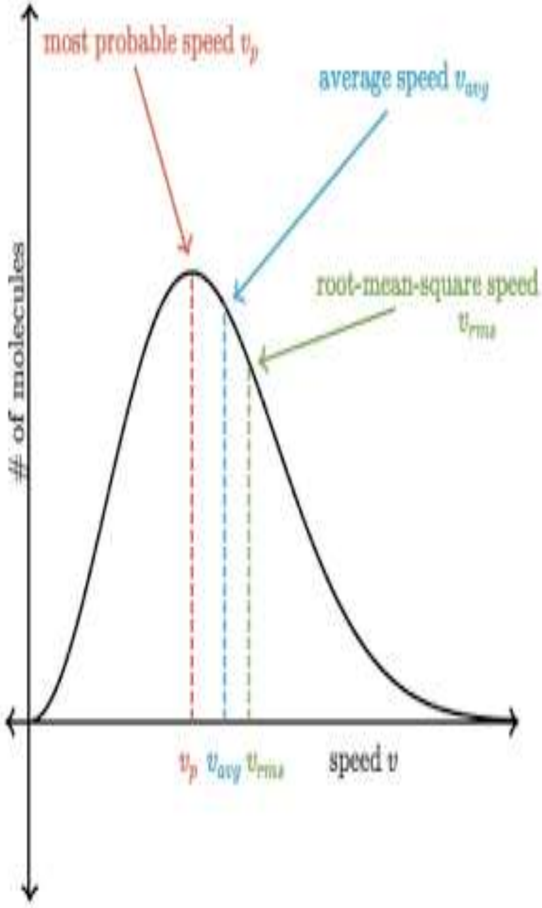
The so-called constants a & b vary to some extent with temp. and this shows that the Vanderwaal’s gas equation is not a complete solution.

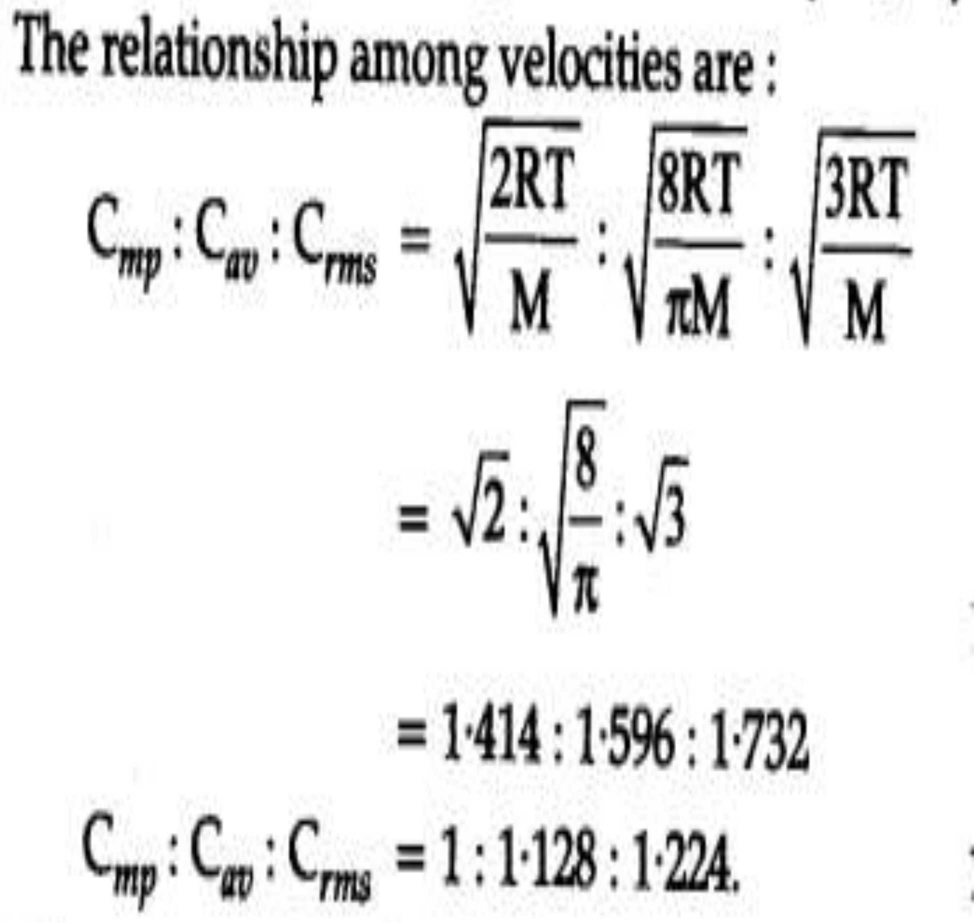
Kinetic theory of gas

Main postulates :

- Gaseous particles are assumed to be solid, spherical and perfectly elastic.
- Volume occupied by the molecule is negligible small as compared to the total volume of the gas.
- Gaseous molecules are in random motion. During the motion ,they collide with each other and with the wall of the container.
- All collisions are perfectly elastic i.e none of the transnational energy is lost as a result f collision.
- The pressure exerted by a gas is due to the collision of the particle and is equal to the average force per unit area which the molecules exert on the wall of the container. Newtonian mechanics is applied i.e f=ma.

The distribution of molecular speeds remain unchanged at any particular temp. The distribution of molecular speed is known as Maxwell-Boltzman distribution. It can be shown graphically as :




The relationship among velocities are :

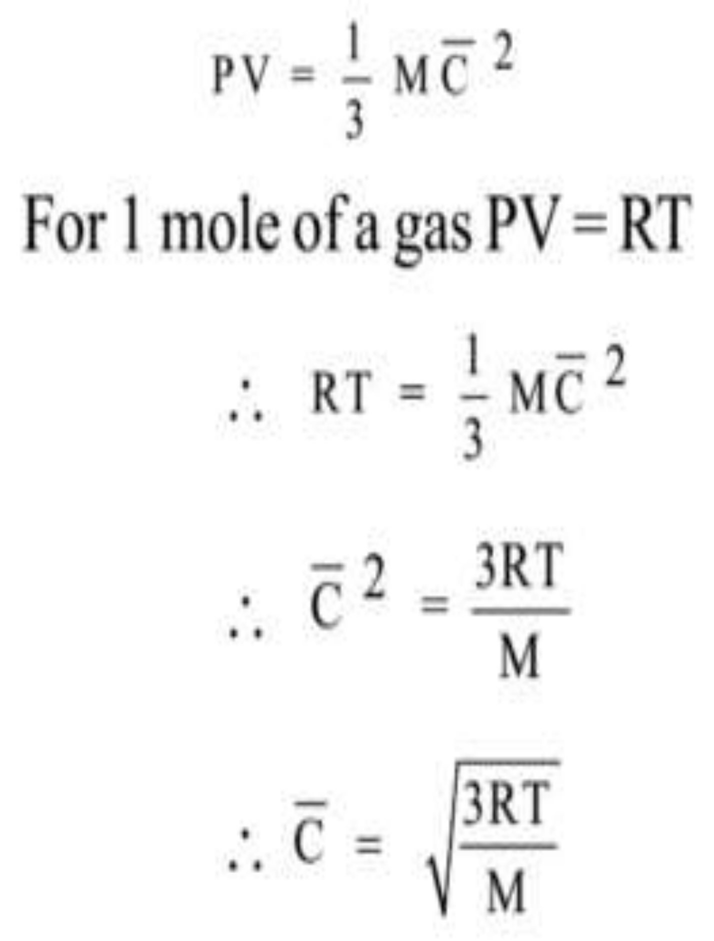
$$C_{mp} : C_{av} : C_{rms} = \sqrt{\frac{2RT}{M}} : \sqrt{\frac{8RT}{\pi M}} : \sqrt{\frac{3RT}{M}}$$

$$= \sqrt{2} : \sqrt{\frac{8}{\pi}} : \sqrt{3}$$

$$= 1{\cdot}414 : 1{\cdot}596 : 1{\cdot}732$$

$$C_{mp} : C_{av} : C_{rms} = 1 : 1{\cdot}128 : 1{\cdot}224.$$

- Fraction of molecules having very low and very high velocity is very small.
- With increase in temp. the whole curve shifts toward r.h.s. i.e toward higher velocity.
- Reaction i.e bond breaking takes place due to effective collision of gaseous molecules.
- For effective collision, molecules must possess certain required velocity known as **Threshold velocity.**
- It has been observed that by 10^0 rise in temp, molecules having threshold velocity become double in number. So rate of reaction increases 2-3 times by 10^0 rise in temp. taking 25^0 as a base temp.



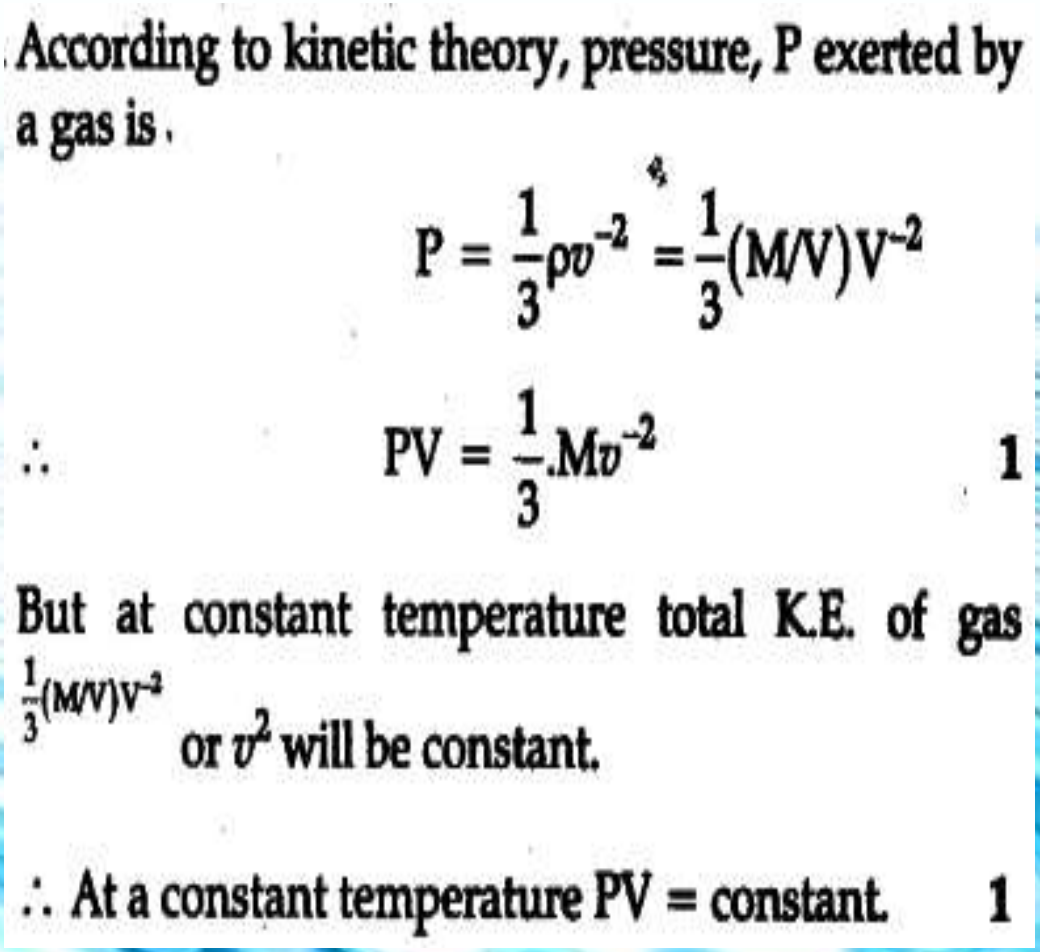
$$PV = \frac{1}{3} M\bar{C}^2$$

For 1 mole of a gas PV = RT

$$\therefore \quad RT = \frac{1}{3} M\bar{C}^2$$

$$\therefore \quad \bar{C}^2 = \frac{3RT}{M}$$

$$\therefore \quad \bar{C} = \sqrt{\frac{3RT}{M}}$$



According to kinetic theory, pressure, P exerted by a gas is .

$$P = \frac{1}{3}\rho v^{-2} = \frac{1}{3}(M/V)V^{-2}$$

$$\therefore \quad PV = \frac{1}{3}.Mv^{-2} \qquad 1$$

But at constant temperature total K.E. of gas $\frac{1}{3}(M/V)V^{-2}$ or v^2 will be constant.

∴ At a constant temperature PV = constant. 1

Derivation from K.T. of gas :

a.Boyle's law : For given mass is const. at given temp. So PV is const.

b. Charle's law : $PV = \frac{2\ RT}{3}$; At const P ,V T

c. Avogadro's law : $P_1V_1 = \underline{1\ n_1 m_1 c_1}^2$ and $P_2V_2 = \underline{1\ n_2 m_2 c_1}^2$

$$\text{If, } P_1 = P_{2;} \quad V_1 = V_2$$

$$\mathbf{n_1 = n_2}$$

"There is
no stupid
question;
stupid people
don't ask
questions."

Olivia ◆

THANK YOU