Kinetic Theory

Introduction :

Matter exists in three states : solid, liquid and gas. Gases have large number of molecules. The properties of the gases are entirely different from those of solid and liquid. In case of gases, thermal expansion is very large as compared to solids and liquids .To state the conditions of a gas, its volume, pressure and temperature must be specified.

S.No.	Characteristics	Solid	Liqui Gas
1. Shape/Size	Certain	Uncertain	Uncertain
2. Inter molecular distance	Very small	Small	Large
3. Intermolecular force	Very strong	Weak	Very weak
4. Specific Heat	Unique	Unique	Infinite
5. Density	Large	Small	Very small
6. Expansion by the heating	Very small	Small	Large

– **Intermolecular force (IMF) :–**

Solid > liquid > Real gas > ideal gas (zero)

– **Potential energy (PE) :–**

Solid < liquid < Real gas < ideal gas (zero)

– **At a given temperature :–**

For solid, liquid, real gas, ideal gas

(i) Internal kinetic energy → Same for all

(ii) Internal potential energy
→ Max. for ideal gas (PE=0)
→ Min. for solid (PE=–Ve)

(iii) Internal Energy
→ Max. for Ideal gas
→ Min. for solid

– At same temperature - Rared and compressed gas

(i) Internal kinetic energy → Same

(ii) Internal potential energy → $(PE)_{Rared} > (PE)_{compressed}$

(iii) Internal Energy → $(U)_{Rared} > (U)_{compressed}$

Special Notation :

μ = Molar amount of gas = $M/M_w = N/N_0$

N_0 = Avogadro constant = 6.023×10^{23} molecules/mole

R = Universal gas constant = 8.31 J/mole k

= 1.92 cal/mole-k, [Dimns. = $ML^2T^{-2}\mu^{-1}\theta^{-1}$]

r = Specific constant of gas ($r = R/M_w$)

K = Boltzmann constant = ($K = R/N_0$)

= 1.38×10^{-23} J/kelvin

n = Molecular density ($n = N/V$)

1 litre = 10^{-3} m^3 = 10^3 cm^3

	N.T.P.	S.T.P.
Temperature0°	C = 273.15 K	0.01°C = 273.16K
Pressure	1 atm =1.01325 × 10^5 N/m^2 = 1.01325 × 10^5 Pascal	1 atm
Volume	22.4 lit.	22.4 lit.

Equation of state for Ideal gas :

PV = RT .... For μ = 1 mole

= 1 gm. molecule

PV = μRT .... For μ = Amount of mole

$$PV = \frac{M}{M_w} RT \qquad [M_w = N_0 m]$$

$$PV = \left(\frac{mN}{mN_0}\right) RT \Rightarrow PV = \left(\frac{R}{N_0}\right) NT$$

$$\Rightarrow \boxed{PV = NKT}$$

$$P = K\left(\frac{N}{V}\right) T \Rightarrow \boxed{P = nKT}$$ **Imp.**

$$P = \frac{\rho TK}{m} \text{ or } \boxed{m = \frac{\rho TK}{P}}$$ **Imp.**

$$K = \frac{R}{N_0}$$

$$\frac{N}{V} = n = \frac{\rho}{m}$$

$$\rho = mn$$

Ideal gas concept :

I. Volume of gas molecules is negligible as compared to volume of container,

So volume of gas = volume of container (Except 0K)

II. No intermoleculer force act between gas molecules. i.e. **IMF = 0**

Note : Volume of gas = Free space of contaner in which gas molecules are doing randon motion.

Special point for ideal gas :

1. A gas which follows all gas laws and gas equation at every possible temperature and pressure is known as **ideal** or **perfect gas.**

2. Molecule of gas can do only and only translational Motion and kinetic energy related to this is known as **tanslational kinetic energy**. $\boxed{E_{trans} \propto T}$

3. **Potential energy** of ideal gas is **zero**. so internal energy of ideal gas is perfectly translational K.E. of gas. It is directly proportional to **absolute temperature** So, internal energy depends only its temperature.

For a substance $U = U_{kinetic} + U_{potential}$

U_{KE} – depends only on temperature,

U_{PE} – depends upon intermolecular forces (Always (–) Ve)

Note: By taking same amount of mono atomic gas and diatomic gas and same heat energy is given then rise in temp of mono atomic gas is comparatively more.

$(\Delta T)_{Mono} > (\Delta T)_{dia} > (\Delta T)_{tri}$–

$\because f = 3$ → for monoatomic (100% trans)

$f = 5$ → for diatomic (60% T + 40% R)

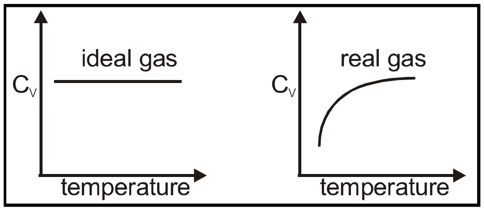
$\boxed{E_{Trans} \propto T}$

$f = 7$ → for tri atomic (T : R : V :: 3 : 2 : 2)

4. According to **Dr. Andrewz ideal** gas cannot be liquidified and solidified. There are **no critical elements** for ideal gas (T_c, P_c, & V_c)

Critical Temperature for CO_2 gas = 31.1^0C

5. **Specific heat** of ideal gas is **constant** quantity and it does not change with temperature



6. All real gases behaves as **ideal gas** at **high temperature** and **low pressure**.

7. Volume expansion cofficient (α) and pressure expansion cofficient (β) is same for a ideal gas and value of each is 1/273 per ^{0}C

$\alpha = \beta = 1/273$ per ^{0}C

8. Gas molecule have point mass and negligible volume and velocity is very high (10^7 cm./sec.).

Properties/Assumptions of Ideal gas :

1. All the molecules of a gas are identical as regards their shape and mass. The molecules of different gases are different.

2. The gas molecules behave as rigid, elastic and smooth spheres. The molecules collide with the walls of the container. These collisions are perfectly elastic i.e., there is no loss of kinetic energy in these collisions.

3. The molecules of a gas are in a state of continuous random motion. They move with all possible velocities in all possible directions. They obey Newton's law of motion.

Mean momentum = 0; Mean velocity = 0.

$< \vec{v} > = 0$; $< v^2 > \neq 0$ (Non zero);

$< v^3 >$ or $< v^5 > = 0$ (may be)

4. The average distance travelled by a molecule between two successive collisions is called as **mean free path** (λ_m) of the molecule.

5. The time during which a collision takes place is negligible as compared to time taken by the molecule to cover the mean free path so NTP ratio of time of collision to free time of motion $\mathbf{10^{-8} : 1}$.

6. When a gas taken into a vessel it is uniformly distributed in entire volume of vessel such that its density, moleculer density, motion of molecules etc. all are identical for all direction, therefore root mean velocity → equal $\overline{v}_x^2 = \overline{v}_y^2 = \overline{v}_z^2$

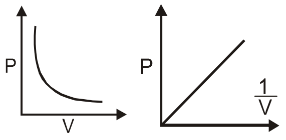
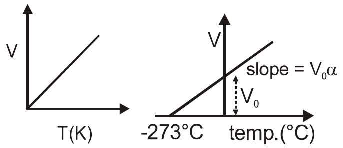
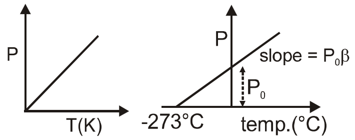
pressure exerted by the gas in all direction

$P_x = P_y = P_z = P \rightarrow$ equal

Note : These assumptions help to keep the mathematical treatment simple.

7. All those assumptions can be justified, if number of gas molecules are taken very large 10^{23} molecules/cm^3.

Gas Law's :

Name of Law	Constant terms	Constant terms	Graph
1. Boyle's Law	(i) Mass of gas (ii) Temperature	PV = constant $V \propto 1/P$ $\boxed{P_1V_1 = P_2V_2}$	
2. Charle's Law	(i) Mass of gas (ii) Pressure	V/T = constant $V \propto T$ $\boxed{\frac{V_1}{T_1} = \frac{V_2}{T_2}}$	 (α → volume expansion coefficient =1/273 per °C)
3. Gay-Lssac's Law	(i) Mass of gas (ii) Volume	P/T = constant $P \propto T$ $\boxed{V_t = V_0(1+\alpha t)}$	 (β→pressure expansion coefficient =1/273 per °C)

4. Avogadro's Law :- At same temperature and pressure equal volumes of all gases contains equal number of moleucles.

$N_1 = N_2$ if P,V, and T are same.

5. Dalton's Law :- According to this law, the pressure exerted by a mixture of several gases equals the sum of the pressure exerted by each component gas present in the mixture i.e.

$P_{mix.} = P_1 + P_2 + P_3$ .... $P = \left(\frac{RT}{V}\right)\mu$ r

$P_{mix.} \propto \mu$ r $P_{mix} = \frac{RT}{V}[\mu_1 + \mu_2 + \mu_3]$

6. Graham's Law of diffusion :– According to this law, at same temperature and pressure, the rate of diffusion of gas is inversly proportional to the square root of the density of gas i.e.

Rate of diffusion $r_d \propto \frac{1}{\sqrt{\rho}}$; $V_{rms} \propto \frac{1}{\sqrt{\rho}}$;

So, $V_{rms} \propto r_d$ [For H_2 gas (Max)]

Solved Examples

Ex.1 By increasing temperature of gas by 5^0C its pressure increases by 0.5% from its initial value at constant volume then what is initial temperature of gas

Sol. $\frac{\Delta T}{T} \times 100 = \frac{\Delta P}{P} \times 100 = 0.5$ r

$T = \frac{5 \times 100}{0.5} = 1000$ K **Ans.**

Ex.2 Calculate the value of universal gas constant at STP ?

Sol. Universal gas constant is given by R = PV/T

Now, one mole of all gases at S.T.P. occupy 22·4 litres.

P = 760 mm of Hg = hρg

$= (760 \times 10^{-3}) \times (13{\cdot}6 \times 10^3) \times (9.80)$ N m^{-2}

$V = 22{\cdot}4$ litre $= 22{\cdot}4 \times 10^{-3}$ m^3 ; T = 273 K

$\therefore R = \frac{760 \times 10^{-3} \times 13.6 \times 10^3 \times 9.80 \times 22.4 \times 10^{-3}}{273}$

$R = 8{\cdot}31$ J mol^{-1} K^{-1} **Ans.**

Ex.3 The pressure of 1 gram molecule of hydrogen and argon in a given container will be as follows

(1) Less in hydrogen (2) More in hydrogen

(3) Equal in both (4) Nothing can be said

Ans. (3)

Ex.4 A sample of oxygen with volume of 500 cc at a pressure of 2 atm is compressed to a volume of 400 cc. What pressure is needed to do this if the temperature is kept constant ?

Sol. Here temperature is constant, So

$$P_1V_1 = P_2V_2 \Rightarrow P_2 = P_1\frac{V_1}{V_2} = 2\left(\frac{500}{400}\right) = 2.5 \text{ atm.}$$

Ex.5 1500 ml of a gas at a room temperature of 23°C is inhaled by a person whose body temperature is 37°C, if the pressure and mass stay constant, what will be the volume of the gas in the lungs of the person. ?

Sol. Here pressure and amount of the gas are kept constant. Therefore,

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

$[T_1 = 273 + 23 = 296 \text{ K}; T_2 = 273 + 37 = 310 \text{ K}]$

$$\therefore \; V_2 = V_1 \times \frac{T_2}{T_1} = 1500 \times \frac{310}{296} = 1570.95 \text{ ml.}$$

Ex.6 A sample of O_2 is at a pressure of 1 atm when the volume is 100 ml and its temperature is 27°C. What will be the temperature of the gas if the pressure becomes 2 atm and volume remains 100 ml.

Sol. $\frac{P_1}{T_1} = \frac{P_2}{T_2} \Rightarrow T_2 = T_1 \times \frac{P_2}{P_1}$

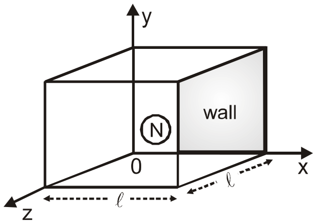
$[T_1 = 273 + 27 = 300 \text{ K}]$

$$T_2 = 300 \times \frac{2}{1} = 600 \text{ K} \Rightarrow T_2 = 600 - 273 = 327° \text{ C}$$

Expression for Pressure of An Ideal gas :

$$\boxed{P = \frac{1}{3}\frac{M}{V}v_{rms}^2 = \frac{1}{3}\rho v_{rms}^2}$$

$$\begin{cases} M = \text{mass of gas} \\ V = \text{volume of gas} \\ \rho = \text{density of gas} \end{cases}$$



Spacial points :

1. Average number of molecules for each direction of wall = N/6

Number of molecules along each axis = N/3

$(N_x = N_y = N_z)$

2. $\overline{v}_x^2 = \overline{v}_y^2 = \overline{v}_z^2 = \frac{\overline{v}_{rms}^2}{3}$

Root mean square velocity along any axis for gas molecule is $(v_{rms})_x = (v_{rms})_y = (v_{rms})_z = \frac{v_{rms}}{\sqrt{3}}$

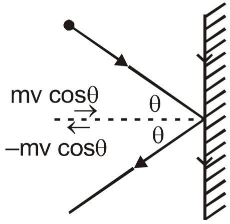
3. Molecules are incident at angle θ with normal change in momentum = –2 mv cos θ

Suppose molecules are incident at surface per second = N/t.

Transfer momentum at surface per second

$$= \frac{N}{t}(2 \text{ mv Cos } \theta)$$

then, $\boxed{P = \frac{(2mv\cos\theta)N}{A \times t}}$



Special Case : It incident molecules are absorbed by wall surface then Pressure $P^1 = \frac{P}{2}$

$$\boxed{P^1 = \frac{(mv\cos\theta)N}{A \times t}}$$

4. All gas laws and gas equation can be obtained by expression of pressure of gas (except Joule's law)

Different K.E. of gas (Internal Energy) :

1. Translatory kinetic energy $(E_T) = \frac{1}{2}Mv_{rms}^2 = \frac{3}{2}PV$

Total internal energy of ideal gas is kinetic i.e.

2. Energy per unit volume or energy density (E_V) : (J/M^3)

$$E_v = \frac{\text{Total Energy}}{\text{Volume}} = \frac{E}{V};$$

$$E_v = \frac{1}{2}\left(\frac{M}{V}\right)v_{rms}^2 ; \qquad E_v = \frac{1}{2}\rho\, v_{rms}^2$$

$\because P = \frac{2}{3}\left[\frac{1}{2}\rho v_{rms}^2\right]$ (By pressure expression)

$P = \frac{2}{3} E_v$; $\boxed{E_V = \frac{3}{2}P}$ **Imp.**

3. Molar K.E. or Mean Molar K.E. (E) :– (K.E. of N_0 molecules or K.E. of M_w grams gas)

$E = \frac{1}{2} M_w v_{rms}^2$ $\boxed{E = \frac{3}{2}RT = \frac{3}{2}N_0KT}$ ......(1)

$[R = N_0K]$

4. Molecular kinetic energy or mean molecular K.E. ($\bar{E}$) :– [K.E. of a gas molecule)

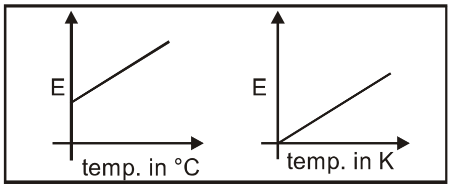
$\bar{E} = \frac{E}{N_0}$; $\bar{E} = \frac{3}{2}\frac{RT}{N_0}$ $\boxed{\bar{E} = \frac{3}{2}KT}$ ....(2)

5. Gram K.E. or Mean gram K.E. (E_m) :-

(K.E. of 1 gram gas)

$E_m = \frac{E}{M_w}$; $\boxed{E_m = \frac{3}{2}\frac{RT}{M_w} = \frac{3}{2}\frac{KT}{m}}$ ....(3)

$\boxed{E_m \propto \frac{1}{M_w}}$



Special point :

(i) Except 0 K, at any temperature T the order of K.E. is $E > E_m > \bar{E}$

(ii) At a common temperature, for all ideal gas E and $\bar{E}$ are same while E_m is different and depends upon nature of gas (M_w or m)

(iii)For Thermal equilibrium of gases. The temperature of each gas is same and this temperature Called as temperature of mixture (T_m) which can be find out on basis of conservation of energy

(All gases are of same atomicity)

(But different atomicity)

$$T_m = \frac{\Sigma NT}{\Sigma N} = \frac{N_1T_1 + N_2T_2 + ...+ N_nT_n}{N_1 + N_2 ...... N_n}$$

$$T_m = \frac{f_1N_1T_1 + f_2N_2T_2 + ...}{f_1N_1 + f_2N_2 ......}$$

(iv) When atomicity nature of gas or total K.E. is given then use f in placed of 3

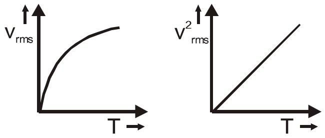
(a) for 1 mole of gas → f/2 RT

(b) for 1 molecule of gas → f/2 KT

(Where f → degree of freedom)

RMS. Velocity :

$$\boxed{v_{rms} = \sqrt{\frac{3P}{\rho}} = \sqrt{\frac{3RT}{M_w}} = \sqrt{\frac{3KT}{m}}}$$



so, $\boxed{v_{rms} \propto \sqrt{T}}$ **Imp.**

Ideal gas at absolute zero temp :–

In this position

Motion of molecule → zero

v_{rms} → zero

K.E. of molecule → zero **Imp.**

Internal energy of gas → zero

Pressure of gas → zero

Volume of gas → zero

(in effective form)

Different speeds of gas molecules :

1. Average velocity :– ($<\bar{v}>$)

$$<\bar{v}> = \frac{\bar{v}_1 + \bar{v}_2 + ...+ \bar{v}_N}{N} = 0$$

Because molecules are in random motion in all possible direction in all possible velocity. Therefore, the velocity of the gas container is zero.

2. Rms speed of molecules :– (v_{rms})

$$v_{rms} = \sqrt{\frac{3P}{\rho}} = \sqrt{\frac{3RT}{M_w}} = \sqrt{\frac{3KT}{m}}$$

$$= 1.732\sqrt{\frac{KT}{m}} \quad ....(1)$$

3. Mean speed of molecules :– (By maxwell's velocity distribution law) (v_M or $< |\bar{v}| >$)

$$v_{Mean} = \sqrt{\frac{8}{\pi}\frac{P}{\rho}} = \sqrt{\frac{8RT}{\pi M_w}} = \sqrt{\frac{8KT}{\pi m}}$$

$$= 1.595\sqrt{\frac{KT}{m}} \quad ....(2)$$

$$< |\bar{v}| > = v_{mean} = \frac{|\bar{v}_1| + |\bar{v}_2| + ... + |\bar{v}_n|}{N}$$

4. Most probable speed of molecules :- (v_{mp})

At a given Temperature the speed to which maximum number of molecules belongs is called as most probable speed (v_{mp})

$$v_{mp} = \sqrt{\frac{2P}{\rho}} = \sqrt{\frac{2RT}{M_w}} = \sqrt{\frac{2KT}{m}} = 1.414\sqrt{\frac{KT}{m}} \quad ----------- (3)$$

5. Velocity of sound in gas medium :- (v_s)

$$v_{sound} = \sqrt{\frac{\gamma P}{\rho}} = \sqrt{\frac{\gamma RT}{M_w}} = \sqrt{\frac{\gamma KT}{m}}$$

[$\because 1 < \gamma < 2$]

Special points :-

1. At any temprature (always)

$v_{rms} > v_{Mean} > v_{mp} > v_{sound}$

2. For a gas at any temprature (T)

$$\frac{v_{rms}}{v_{sound}} = \sqrt{\frac{3}{\gamma}} \quad , \quad \frac{v_{rms}}{v_{mp}} = \sqrt{\frac{3}{2}}$$

3. A temp is not possible at which above order can be changed

Always $v_{rms} \neq v_{Mean} \neq v_{mp} \neq v_{sound}$

4. At any given temprature

Any speed $\propto \sqrt{T}$; $\boxed{\text{graph } v_{r.m.s.} \text{ v/s T} \rightarrow \text{parabola}}$

Solved Examples

Ex.7 The velocities of ten particles in ms^{-1} are 0, 2, 3, 4, 4, 4, 5, 5, 6, 9. Calculate

(i) Average speed and (ii) r.m.s. speed

(iii) most probable speed.

Sol. (i) Average speed, V_{av}

$$= \frac{0+2+3+4+4+4+5+5+6+9}{10} = \frac{42}{10} = 4 \cdot 2 \text{ ms}^{-1}$$

(ii) R.M.S. speed,

$V_{r.m.s}$

$$= \left(\frac{(0)^2+(2)^2+(3)^2+(4)^2+(4)^2+(4)^2+(5)^2+(5)^2+(6)^2+(9)^2}{10}\right)^{1/2}$$

$$= \left(\frac{228}{10}\right)^{1/2} = 4.77 \text{ ms}^{-1}$$

(iii) most probable speed V_{mp} = 4 m/s

Ex.8 At what temperature, will the root mean square velocity of hydrogen be double of its value at S.T.P., pressure remaining constant ?

Sol. Let V_1 be the r.m.s. velocity at S.T.P. and V_2 be the r.m.s. velocity at unknown temperature T_2.

Here T_1 = 273 K, T_2 = ? $\frac{V_2}{V_1} = 2$ We know, $V^2 \propto T$

$$\therefore \frac{V_1^2}{V_2^2} = \frac{T_1}{T_2} \text{ or } T_2 = T_1\left(\frac{V_2}{V_1}\right)^2 = 273 \times (2)^2$$

= 273 × 4 = 1092 K

T_2 = (1092 – 273) = 819°C **Ans.**

Ex.9 Calculate rms velocity of oxygen molecule at 27°C

Sol. Temperature, T = 27° C $\Rightarrow$ 273 + 27 = 300 K,

$\therefore$ Molecular weight of oxygen = 32×10^{-3} kg,

$R = 8 \cdot 31 \text{ J mol}^{-1} \text{ K}^{-1}$

Now, r.m.s. velocity is $V = \sqrt{\frac{3RT}{M}}$

$$= \sqrt{\frac{3 \times 8 \cdot 31 \times 300}{32 \times 10^{-3}}} = 483 \cdot 5 \text{ ms}^{-1}$$ **Ans.**

Ex.10 Calculate the kinetic energy of a gram moelcule of argon at 127°C.

Sol. Temperature, T = 127°C = 273 + 127 = 400 K,

R = 8.31 J/mol K

Now, K.E. per gram molecule of argon = $\frac{3}{2}$ RT

$$= \frac{3}{2} \times 8.31 \times 400 \text{ J} = 4986 \text{ J}$$ **Ans.**

Degree of freedom (f) :

(i) The number of independent ways in which a molecule or an atom can exhibit motion is called it's degrees of freedom.

(ii) The number of independent coordinates required to specify the dynamical state of a system is called it's degrees of freedom.

(iii) The degrees of freedom are of three types :

(a) Translational Degree of freedom :–

Maximum three degree of freedom are there corresponding to translational motion.

(b) Rotational Degree of freedom :–

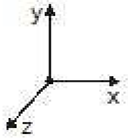
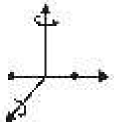
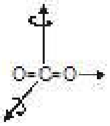
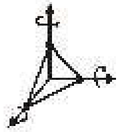
The number of degrees of freedom in this case depends on the structure of the molecule.

(c) Vibrational Degree of freedom :–

It is exhibited at high temperatures.

(iv) Degree of freedom for different gases :– (Acc. to atomicity of gas)

Degree of freedom (f)

Atomicity of gas		Translational	Rotational	Vibrational	Total	Graphically
Monoatomic eg. He, Ar, Ne, Ideal gas etc		3	0	0	3	
Diatomic eg. H_2, O_2, Cl_2, N_2 etc.		3	2	0	5	
Triatomic or Polyatomic	(linear) eg. CO_2, C_2H_2	3	2	2	7	
	Triangular (non-linear) eg. H_2O, O_3, SO_2 NH_3, CH_4 etc.	3	3	0	6	

Relation between degree of freedom & specific heat of gas.

Energy related with each degree of freedom = RT/2

Energy related with all degree of freedom = fRT/2

Internal Energy of one Mole of Ideal gas (Total K.E.)
U = fRT/2 [ΔU = fRΔT/2]

$$C_V = \frac{\Delta U}{\Delta T}\ ;\ \boxed{C_v = \frac{f}{2}R = \frac{R}{\gamma - 1}}\ ;\ C_p = C_V + R$$

$$= \left(\frac{f}{2} + 1\right)R$$

$$\boxed{C_p = \frac{\gamma R}{\gamma - 1}}\ ;\quad \gamma = \frac{C_P}{C_V} = 1 + \frac{2}{f}\ ;\quad \boxed{\gamma = 1 + \frac{2}{f}}$$

Atomicity of gas		f	C_v	C_P	g V.Imp
Monoatomic		3	$\frac{3}{2}R$	$\frac{5}{2}R$	$\frac{5}{3}=1.67$
Diatomic		5	$\frac{5}{2}R$	$\frac{7}{2}R$	$\frac{7}{5}=1.4$
Triatomic or Poly atomic	Triatomic linear	7	$\frac{7}{2}R$	$\frac{9}{2}R$	$\frac{9}{7}=1.28$
	Non-linear	6	$\frac{6}{2}R=3R$	$\frac{8}{2}R=4R$	$\frac{4}{3}=1.33$

Note :-

1. Atomicity ↑, f↑, γ↓ For mono atomic gas $f_{\min} = 3$, But $\gamma = 1.67$ (max)

2 U, C_P, C_V and γ is same for gas mixture. If atomicity of gases is same.

3 If in a gas mixture gases are of different atomicity, then for gas mixture γ changes according to following condition. diatomic $\gamma_1 \le$ mixture $\le \gamma_2$ mono Atomic where $\gamma_1 < \gamma_2$

Maxwell's law of equipartition of energy :

The total kinetic energy of a gas molecules is equally distributed among its all degree of freedom and the energy associated with each degree of freedom at absolute temperature T is 1/2 KT

Special point :-

1. At T = 0K, energy of each degree of freedom is 0.

2. At T K, energy of each degree of freedom is KT/2.

3. If 'f' is the degree of freedom per molecule for a gas, then

(i) Total energy of each **molecule** = fKT/2

(ii) Total energy per **mole** of gas = fRT/2

4. For 'μ' mole of a gas

Internal energy at temperature TK is

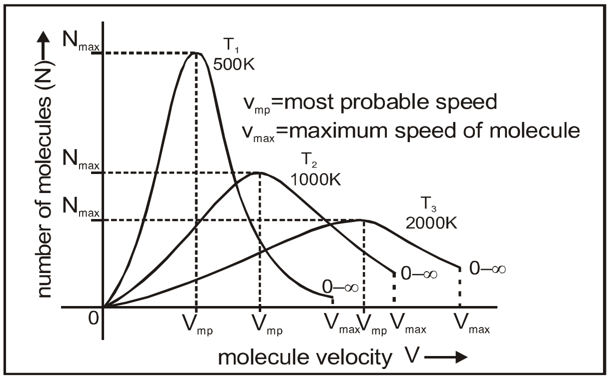
$$U = \frac{\mu fRT}{2} = \mu C_v T$$ **Imp.**

5. Change is internal energy is given by

$$\Delta U = \frac{\mu fR}{2}(\Delta T) = \mu C_v \Delta T$$

This change is process independent.

Maxwell's law of distribution of velocities :



Special point :-

1. At any given temperature graph drawn in between molecular velocity & number of molecules is known as velocity distribution curve (v.d.c.)

2. The velocities of molecules of a gas are in between zero and infinity (0 - ∞)

3. With the increase in the temperature, the most probable velocity and maximum molecule velocity are increases.

4. The number of molecules within certain velocity range is constant although the velocity of molecule changes continuously at particular temperature

5. The area enclosed between the (N – v) curve and the velocity axis presents the total number of molecules.

Special Conclusion :–

On the basis of velocity distribution Maxwell's gives the law of equipartition of energy for gases of any temperature

Mean free path of gas molecules :

"The distance between any two consecutive collision is called free path. The average distance travelled by a molecule between successive collision is called the mean free path".

From kinetic Theory of gases

PMT-95 → $l_m = \frac{1}{\sqrt{2}\,\pi d^2 n}$

$$\lambda_m = \frac{m}{\sqrt{2}\,\pi d^2 (mn)}$$

$$\lambda_m = \frac{m}{\sqrt{2}\,\pi d^2 \rho}$$

$$\lambda_m = \frac{V}{\sqrt{2}\,\pi d^2 N}$$

$$\lambda_m = \frac{KT}{\sqrt{2}\,\pi d^2 P}$$

d = diameter of molecule

n = molecular density $n = \frac{N}{V}$

ρ = density of gas = $\rho = \frac{M}{V} = \frac{mN}{V} = mn$

$PV = NKT \quad \Rightarrow \quad \frac{V}{N} = \frac{KT}{P}$

Special point :-

1 At equal temperature pressure condition mean free path will be maximum for moleculer of lightest gas (H_2)

2 By increasing amount of gas in a container of definite volume then λ_m decreases.

3 If pressure reduces by taken out some gas from container then λ_m increases.

Specific Cofficient of gas :-

1. Thermal conductivity cofficient $K = \frac{1}{3} C_v \rho v_{rms} \lambda_m$

2. Viscosity cofficient of gas

$$n = \frac{1}{3}\rho v_{rms}\lambda_m \qquad \boxed{\lambda_m \propto \frac{1}{v_{rms}}}$$

3. Diffusion cofficient of gas $D = \frac{1}{3} v_{rms}\lambda_m$

Specific heat :

The specific heat of a substance is the amount of heat required to raise the temperature of a unit mass of the substance through 1 K or 1° C.

The SI unit of specific heat is J kg^{-1} K^{-1}

$$c = \frac{1}{m}\frac{\Delta Q}{\Delta T}$$

The heat required to increase the temperature of a body mass m from T_i to T_f is given by

$$Q = m\int_{T_i}^{T_f} c \, dT$$

where c is the specific heat of the material of the body. It may considered c as **thermal inertia**.

C_p is greater than C_υ. If a gas is heated at constant volume, the gas does no work against external pressure. In this case, the whole of the heat energy supplied to the gas is spend in raising the temperature of the gas.

If a gas is heated at constant pressure, its volume increases. In this case, heat energy is required for the following two purpose :

(i) To increase the volume of the gas against external pressure.

(ii) To increase the temperature of 1 mole of gas through 1 K.

Thus, more heat energy is required to raise the temperature of 1 mole of gas through 1 K when it is heated at constant pressure than when it is heated at constant volume.

$\therefore\ C_p > C_\upsilon$

The difference between C_p and C_υ is equal to thermal equivalent of the work done by the gas in expanding against external pressure.

FIRST LAW OF THERMODYNAMICS (FLOT) ($\delta Q = \delta W + dU$)

Process	**Constant**	**δQ**	**δW**	**ΔU**	**Specific heat**
Isobaric	P (Pressure)	$\mu C_P \Delta T$	$PdV = \mu R \Delta T$	$\mu C_V \Delta T$	C_P
Isochoric	V (Volume)	$\mu C_V \Delta T$	0	$\mu C_V \Delta T$	C_V
Isothermal (for ideal gas)	T (Temperature)	δW	$2.303 \mu RT \log_{10} \frac{V_2}{V_1}$	0	∞
Adiabatic (for ideal gas)	Q (Heat)	0	$\frac{\mu R(T_1 - T_2)}{\gamma - 1}$	$\mu C_V dt$	0

REAL GAS

(A) Vanderwaal's Equation :– (For real gas)

Ideal gas equation PV = RT

two correction are made in ideal gas model

1. Volume correction (Due to finite size of molecules) :–

$V_{real} = V - b$

b = decrease in volume for 1 mole gas

2. Pressure correction (Due to inter molecular forces) :-

(i) Pressure decreases α (density)^2

(ii) $P_{real} = \frac{RT}{V-b} - \frac{a}{V^2}$

$\boxed{\left(P_{real} + \frac{a}{V^2}\right)(V_{Ideal} - b) = RT}$ → For one mole real gas

$\boxed{\left(P_{real} + \mu^2 \frac{a}{V^2}\right)\left(V_{ideal} - \mu b\right) = \mu RT}$ →

For μ mole of real gas

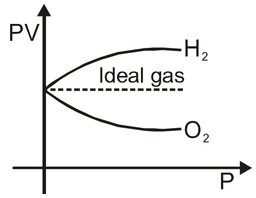
$b \rightarrow m^3 \rightarrow M^0 L^3 T^0$

$a \rightarrow Nm^4 \rightarrow ML^5 T^{-2}$

(a & b Vanderwaal's gas constant)

(B) Amaghat Experiment :-

At low temperature and high pressure gases shows deviation from Boyle's law.



Graphs are drawn between PV and P at 0^0 C for H_2 and O_2

Conclusions :–

(1) All real gases shows deviation at high pressure and low temperature, deviation of Co_2 gas is max.

(2) According to **Amaghat** every real gas has definite and specific temperature at which it follows Boyle's law this is known as Boyle's temperature of real gas

Boyle's coefficients :- $\boxed{T_B > T_C}$ [T_B = Boyle's temperature, T_C = Critical temperature] $\boxed{T_B = \frac{a}{Rb}}$

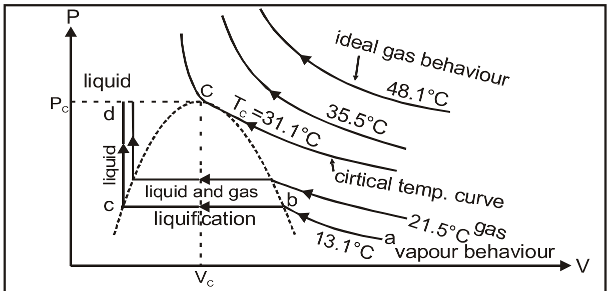
where a & b are Vanderwaal's constant for real gas.

(C) Dr. Andrewz's Experiment :–

(Isothermal curve of real gas)

Dr. Andrewz drawn graphs in between volume and pressure for different constant temperature and curves are obtained these curves are known as isothermal curves

Example :– CO_2 curves at different temperature



(Isothermal curves for CO_2 gas at different temperature)

Special points :-

(1) By meeting edge of horizontal part of these curve parabola is obtained. It peak point is known as critical point

(2) Thermodynamic element corresponding to critical point is known as critical parameters (T_C, V_C, P_C)

(i) **Critical temp (T_C)** - It is that temperature below which a gas can be liquified only by increase in pressure and above which no liquification is possible whatever the pressure may be increased.

Real gas		**T_C**
He	→	-268^0 C
H_2	→	-240^0 C
N_2	→	-147^0 C
O_2	→	-118^0 C
CO_2 (CPMT-94)	→	31.1^0
Steam	→	$+365\ ^0$ C

(ii) **Critical pressure :– (P_C)**

Minimum pressure required to liquify a gas when it is at critical temperature is called critical pressure

For He P_C = 2 atmospheric pressure

For CO_2 P_C = 76 atmospheric pressure

For O_2 P_C = 49.7 atmospheric pressure

(iii) **Critical volume :– (V_C)**

At critical pressure and temperature the volume of one mole of gas is called its critical volume (V_C). Critical volume for CO_2 gas $= 95 \times 10^{-6}\ m^3$

Special Results :

1. $\boxed{V_C = 3b\ ;\ T_C = \frac{8a}{27Rb}\ ;\ P_C = \frac{a}{27b^2};}$ $\boxed{T_C = \frac{8}{27}T_B}$

2. $\frac{P_C V_C}{RT_C} = \frac{3}{8}$

3. Critical element of gas are derive from vanderwall's gas equation at critical position for which.

$$\left(\frac{dP}{dV}\right)_{critical} = 0$$

$\boxed{\text{At critical point, slope of the graph is zero.}}$

Sp. Results for Real gas :–

1. All real gases follows Vanderwaal's gas equation at every possible temperature and pressure so these are known as vanderwaal's gases.

2. At a given temperature volume and pressure for real gas are comparetively low than for ideal gas.

3. Internal energy of real gas depends upon its temperature pressure and volume

If ΔU → Change in Internal energy

μ = 1 mole

ideal gas $\Delta U = c_V\,\Delta T$

$U = f\,(T)$

Real gas

$$(\Delta U)_{Real} = C_V\,\Delta T + \frac{a}{V^2}\,\Delta V$$

$$U_{Real} = f\,(T, P, V)$$

4. Internal Energy of Real gas is always (–ve) at absolute zero temperature.

5. Specific heat of Real gas increases By increasing temperature and decreases By decreasing temperature.

MEMORY TIPS

1. An ideal gas is assumed to have following properities:

(a) It strictly obeys gas laws under all the conditions of temperature and pressure.

(b) It has got exactly equal pressure coefficient and volume coefficient.

(c) Its molecules exert no attractive force on each other. Hence , an ideal gas can not be converted into liquid or solid state, because a force of attraction is necessary between the molecules in the liquid or solid state.

(d) Its molecules are infinitesimally small.

2. Perfect gas equation:-

(a) PV= RT (For one gram molecule of a gas)
(b) PV= (R/M_w)T (For one gram of any gas)
(c) PV= (M/M_w)RT (For M gram of a gas)

3. R= 8.31 Joules/mole-K

4. The pressure of a gas is given by

$$P = \frac{1}{3}\frac{mN}{V}\,\overline{V}^2 = \frac{1}{3}\rho\overline{V}^2$$

Where ρ is the density of gas, M = mN is the mass of the gas, V is the volume and $\overline{V}^2$ is the mean square velocity of the gas.

5. Root mean square velocity is related with temperature as:

$$V_{rms} = \sqrt{\left(\frac{3PV}{M}\right)} = \sqrt{\frac{3RT}{M_w}} \text{ or } V_{rms} \propto \sqrt{T}$$

When M_w is the molecular weight of the gas.

6. Kinetic energy per mole of ideal gas is 3/2RT, and that of one molecule of gas is 3/2 KT.

7. Boyle's law: PV = Constant

8. Charle's law: V/T = Constant

9. Grahm's law of diffusion: Rate of diffusion of a gas is inversely proportional to the square root of the density of gas.

10. Dalton's law of partial pressure : The pressure exerted by a mixure of several gases equals the sum of the pressure exerted by each gas occupying the same volume as that of mixure.

$P_m = P_1 + P_2 + P_3 + \ldots\ldots\ldots$

11. Mean free path $\lambda_m = \dfrac{1}{\sqrt{2}\,\pi d^2 n}$

12. For real gas

(a) Vanderwaals' equation : $\left(P + \dfrac{\mu^2 a}{V^2}\right)(V - \mu b)$

$= \mu RT$ [for μ - mole]

where a & b are Vanderwaal's constant

(b) Boyle's temperature $T_B = \dfrac{a}{Rb}$

(c) Critical parameter : (P_c, V_c, T_c) $P_c = \dfrac{a}{27b^2}$,

$T_c = \dfrac{8}{27}\dfrac{a}{Rb}$, $V_c = 3b$