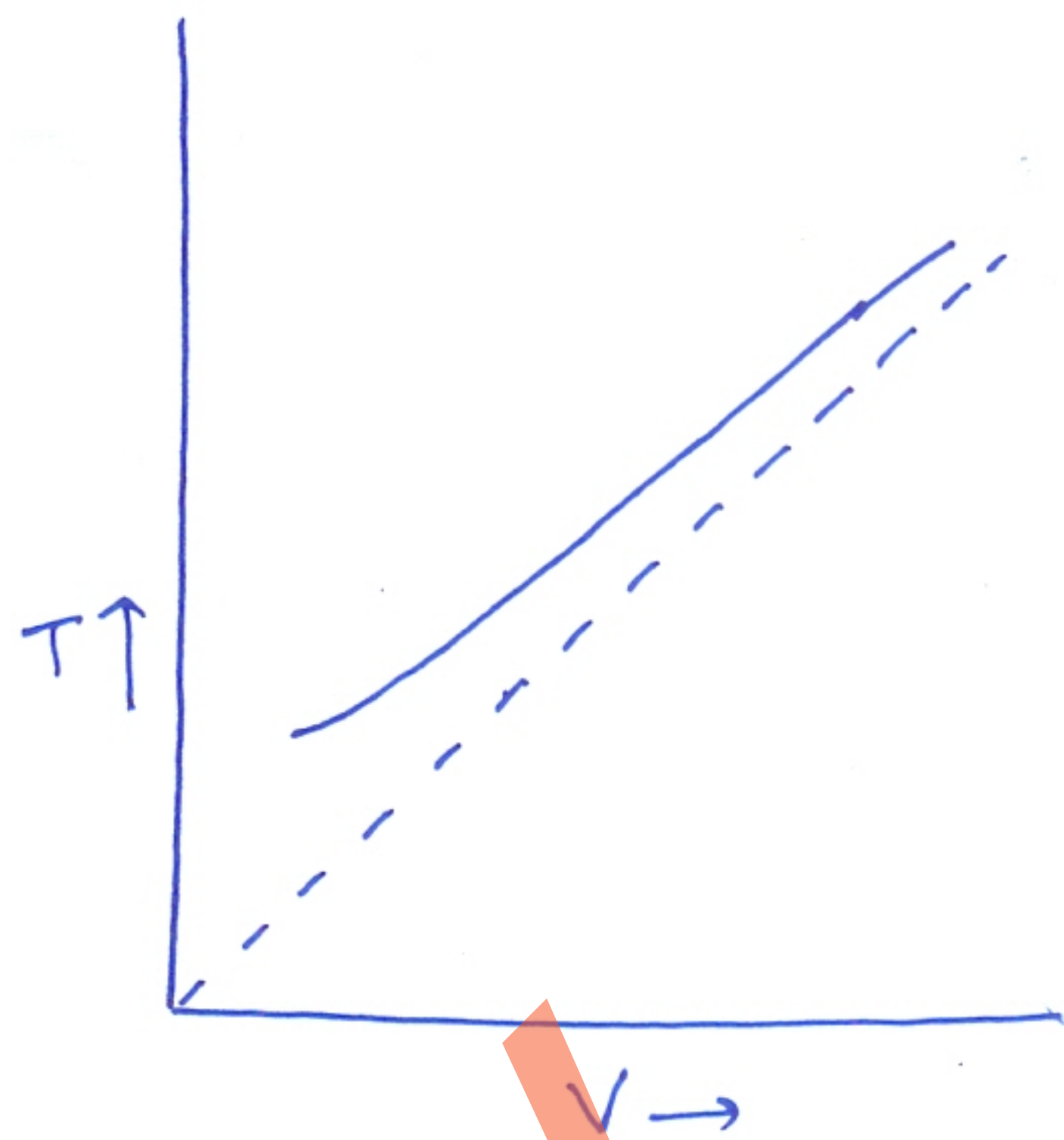


→ At low tem. the deviation of the experimental & theoretical graph is more pronounced.

→ At a high tem., the experimental & the theoretical graphs are found to be in close agreement with each other.



Gay Lussac law

"The volume remaining constant, the pressure of a given mass of a gas is directly proportional to its absolute tem."

Mathematically, at const. volume

$$P \propto T$$
$$\boxed{\frac{P}{T} = \text{const}}$$

Perfect gas equation

Consider 1 mole of a perfect gas.

Let P_1, V_1, T_1 - initial pressure, volume & tem.

P_2, V_2, T_2 - final " " "

The change of the state of gas from (P_1, V_1, T_1) to (P_2, V_2, T_2) may be supposed to be taking place in the following 2 steps:

Step 1

Suppose that the tem. of gas remains constant at T_1 & the pressure is changed from P_1 to P_2 so that volume of gas changes from V_1 to V'

As tem. is constant, so acc. to Boyle's law

$$P_1 V_1 = P_2 V' \quad \text{--- (1)}$$

Step 2

Suppose that the pressure of the gas is kept constant at P_2 & temp. is changed from T_1 to T_2 so that volume changes from V_1 to V_2

Since the pressure of the gas remains constant, so from Charles's law

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

$$V_1 = V_2 \times \frac{T_1}{T_2} \quad \text{put in eqn (1)}$$

$$P_1 V_1 = P_2 \left(V_2 \times \frac{T_1}{T_2} \right)$$

$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$$

$$\frac{PV}{T} = R(\text{const.})$$

If the mass of the gas is n moles, then

$$PV = nRT$$

Universal gas constant (R)

$$R = \frac{PV}{nT}$$

$$hP = 760 \text{ mm of mercury} = 760 \times 10^{-3} \text{ m of mercury}$$

$$\rho_{\text{mercury}} = 13,600 \text{ kg m}^{-3}$$

$$\therefore P = \rho gh = 760 \times 10^{-3} \times 13,600 \times 9.8$$

$$\text{Standard temp. } T = 273.15 \text{ K}$$

At S.T.P., molar volume of 1 mole of gas, $V = 22.4 \times 10^{-3} \text{ m}^3$

$$\therefore R = \frac{760 \times 10^{-3} \times 13600 \times 9.8 \times 22.4 \times 10^{-3}}{273.15} = 8.31 \text{ J mol}^{-1} \text{ K}^{-1}$$

$$\text{In c.g.s system, } R = \frac{8.31}{4.2} \text{ cal mol}^{-1} \text{ } ^\circ\text{C}^{-1} = 1.98 \text{ cal mol}^{-1} \text{ } ^\circ\text{C}^{-1}$$

Kinetic Theory of Gases

Rudolph Clausius & James Maxwell developed the kinetic theory of gases to explain gas laws in terms of the motion of the gas molecules.

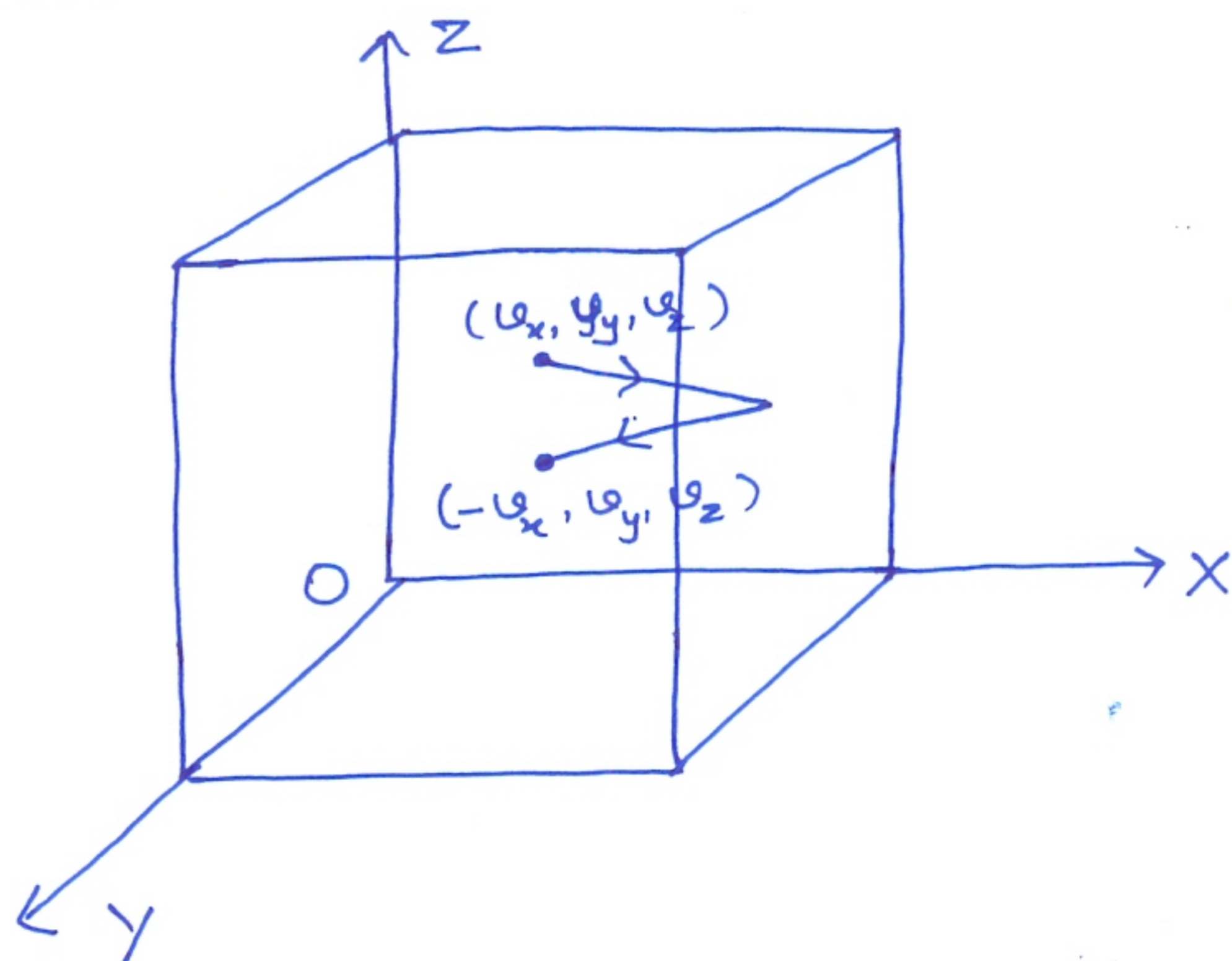
Assumptions

1. All gases consist of molecules. The molecules of a gas are all alike & differ from those of other gases.
2. The molecules of a gas are very small in size as compared to the distance betⁿ them.
3. The molecules of a gas behave as perfect elastic spheres.
4. The molecules are always in random motion.
5. During their random motion, the molecules collide against one another & walls of the containing vessel & the collisions are perfectly elastic.
6. Between 2 collisions, a molecule moves along a straight line.
7. The collisions are almost instantaneous.
8. The molecules do not exert any force on each other except during collisions.

Pressure exerted by a gas

Consider an ideal gas enclosed in a cube of side 'l'.

Consider a gas molecule of mass 'm' moving with velocity (u_x, u_y, u_z) hitting the wall of area A, parallel to Y-Z plane



As the collision is perfectly elastic, the molecule rebounds with the same velocity.

The change in linear momentum of the molecule is
 $= -m u_x - m u_x = -2m u_x$

So, the momentum imparted to the wall of the cube
in one collision $= +2m u_x$

In any small interval Δt , a molecule with velocity u_x
will hit the wall if it is within distance $(u_x \cdot \Delta t)$
from the wall.

\therefore All molecules lying in the volume $(A u_x \Delta t)$ can hit the
wall in time Δt .

If n is the no. of gas molecules per unit volume, then
total number of gas molecules in volume $(A u_x \Delta t)$
 $= (A u_x \Delta t) n$.

But, on the average, half of these molecules are moving
towards the wall & the other half, away from the wall.

\therefore Effective no. of molecules hitting the planar wall in
time Δt
 $= \frac{1}{2} (A u_x \Delta t) n$

As collision of one molecule with the wall imparts a
momentum $(2m u_x)$ to the wall, so total momentum
transferred to the wall in time Δt is

$$= \frac{1}{2} (A u_x \Delta t) n \times 2m u_x$$

$$= m n A u_x^2 \Delta t$$

\therefore force on the wall exerted by these molecules

$$f = \frac{\text{momentum transferred}}{\text{time taken}} = \frac{m n A u_x^2 \Delta t}{\Delta t} = m n A u_x^2$$

Pressure exerted by these molecules on the wall

$$p = \frac{f}{A} = \frac{m n A u_x^2}{A} = m n u_x^2$$

Since all molecules in a gas don't have the same velocity so, u_x^2 is replaced by $\overline{u_x^2}$ (average velocity)

∴ Total pressure of all molecules is

$$P = mn\overline{u_x^2}$$

Pressure along x-axis, $P_x = mn\overline{u_x^2}$

Y-axis, $P_y = mn\overline{u_y^2}$

Z-axis, $P_z = mn\overline{u_z^2}$

Since gas molecules have same properties in all directions

so, $P_x = P_y = P_z = P$

or $P = \frac{1}{3}(P_x + P_y + P_z)$

$$= \frac{1}{3}(mn\overline{u_x^2} + mn\overline{u_y^2} + mn\overline{u_z^2})$$

$$= \frac{1}{3}mn(\overline{u_x^2} + \overline{u_y^2} + \overline{u_z^2})$$

$$P = \frac{1}{3}mnC^2$$

where C - rms speed of the molecules of the gas

Now, $m \times n = \text{mass of 1 molecule} \times \frac{\text{no. of molecules}}{\text{volume}}$

$$= \frac{M}{V} = \rho$$

$$\therefore P = \frac{1}{3}\rho C^2$$

* Relation betⁿ Pressure & K.E. of gas

$$P = \frac{1}{3}\rho C^2$$

Mean K.E. of translation per unit volume of gas, $E = \frac{1}{2}\rho C^2$

$$\therefore \frac{P}{E} = \frac{\frac{1}{3}\rho C^2}{\frac{1}{2}\rho C^2}$$

$$P = \frac{2}{3}E$$

Average kinetic energy per molecule of gas

Consider 1 gm mole of an ideal gas having volume V at tem. T .

The total mass of the gas is $M = m \times N$ | N - Avagadro No.

The pressure exerted by ideal gas is given by

$$P = \frac{1}{3} \rho c^2$$

$$P = \frac{1}{3} \frac{M}{V} c^2$$

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

$$RT = \frac{1}{3} M c^2$$

$$\frac{1}{2} M c^2 = \frac{3}{2} RT \quad \text{--- (1)}$$

$$\frac{1}{2} m \times N \times c^2 = \frac{3}{2} RT$$

$$\frac{1}{2} m c^2 = \frac{3}{2} \frac{R}{N} \cdot T$$

$$\boxed{\frac{1}{2} m c^2 = \frac{3}{2} k_B T} \quad \text{--- (2)}$$

[k_B - Boltzmann const]

Kinetic interpretation of temperature

From the eqⁿ $\frac{1}{2} m c^2 = \frac{3}{2} k_B T$, we can say

$$\frac{1}{2} m c^2 \propto T$$

So, average kinetic energy of translation per molecule of a gas is directly proportional to absolute tem. of the gas.

From (1), when $T = 0$, $c = 0$

So, absolute zero of tem. is defined as that tem. at which the r.m.s. velocity of the gas reduces to zero.

Equip

Law of equipartition of energy

For any dynamical system in thermal equilibrium, the total energy is distributed equally amongst all the degrees of freedom, and the energy associated with each molecule per degree of freedom is $\frac{1}{2}k_B T$.

Specific heat capacity of monoatomic, diatomic & triatomic gases

(a) Mono atomic gases

Average energy per molecule with 3 d.o.f = $\frac{3}{2}k_B T$

Total internal energy, $U = \frac{3}{2}k_B T \times N = \frac{3}{2}RT$

$$C_v = \frac{dU}{dT} = \frac{d}{dT} \left(\frac{3}{2}RT \right) = \frac{3}{2}R = \frac{3}{2} \times 1.98 \approx 2.98 \text{ cal. mole}^{-1} \text{ K}^{-1}$$

$$C_p = C_v + R = \frac{3}{2}R + R = \frac{5}{2}R = \frac{5}{2} \times 1.98 \approx 4.96 \text{ cal mol}^{-1} \text{ K}^{-1}$$

$$\gamma = \frac{C_p}{C_v} = \frac{\frac{5}{2}R}{\frac{3}{2}R} = \frac{5}{3} = 1.67$$

(b) Diatomic gases

$$U = \frac{5}{2}RT$$

$$C_v = \frac{dU}{dT} = \frac{d}{dT} \left(\frac{5}{2}RT \right) = \frac{5}{2}R = \frac{5}{2} \times 1.98 \approx 4.96 \text{ cal mol}^{-1} \text{ K}^{-1}$$

$$C_p = C_v + R = \frac{5}{2}R + R = \frac{7}{2}R = \frac{7}{2} \times 1.98 \approx 6.95 \text{ cal. mol}^{-1} \text{ K}^{-1}$$

$$\gamma = \frac{C_p}{C_v} = \frac{\frac{7}{2}R}{\frac{5}{2}R} = \frac{7}{5} = 1.4$$

(C) Triatomic gases

(i) linear triatomic molecule

$$U = \frac{7}{2} RT$$

$$C_v = \frac{dU}{dT} = \frac{d}{dT} \left(\frac{7}{2} RT \right) = \frac{7}{2} R = \frac{7}{2} \times 1.98 \approx 6.95 \text{ cal mol}^{-1} \text{K}^{-1}$$

$$C_p = C_v + R = \frac{7}{2} R + R = \frac{9}{2} R = \frac{9}{2} \times 1.98 \approx 8.9 \text{ cal mol}^{-1} \text{K}^{-1}$$

$$\gamma = \frac{C_p}{C_v} = \frac{\frac{9}{2} R}{\frac{7}{2} R} = \frac{9}{7} = 1.28$$

(ii) non-linear triatomic molecule

$$U = 3RT$$

$$C_v = \frac{dU}{dT} = \frac{d}{dT} (3RT) = 3R = 3 \times 1.98 \approx 5.96 \text{ cal mol}^{-1} \text{K}^{-1}$$

$$C_p = C_v + R = 3R + R = 4R = 4 \times 1.98 \approx 7.94 \text{ cal mol}^{-1} \text{K}^{-1}$$

$$\gamma = \frac{C_p}{C_v} = \frac{4R}{3R} = \frac{4}{3} = 1.33$$

Degree of freedom

The total number of co-ordinates or independent quantities required to describe completely the position & configuration of the system.

* For a point mass (it doesn't undergo rotation) only translatory motion is possible & so it has only translatory degree of freedom.

eg: particle moving in straight line - 1 translatory d.o. freedom
" " " a plane - 2 " "
" " " space - 3 " "

* For a rigid body, degree of freedom is due to translatory as well as rotatory motion.

eg: Consider 2 point mass objects. Individually both have 3 degree of freedom but 1 is common in both so total degree of freedom = $6 - 1 = 5$

* General formula to find degree of freedom

$$N = 3A - R$$

N - No. of degrees of freedom of the system

A - No. of particles in the system

R - No. of independent relations among particles

(a) Monoatomic gases (Ne, Ar, He)

$$N = 3 \times 1 - 0 = 3$$

(b) Diatomic gases (H_2 , O_2 , N_2)

$$N = 3 \times 2 - 1 = 5$$

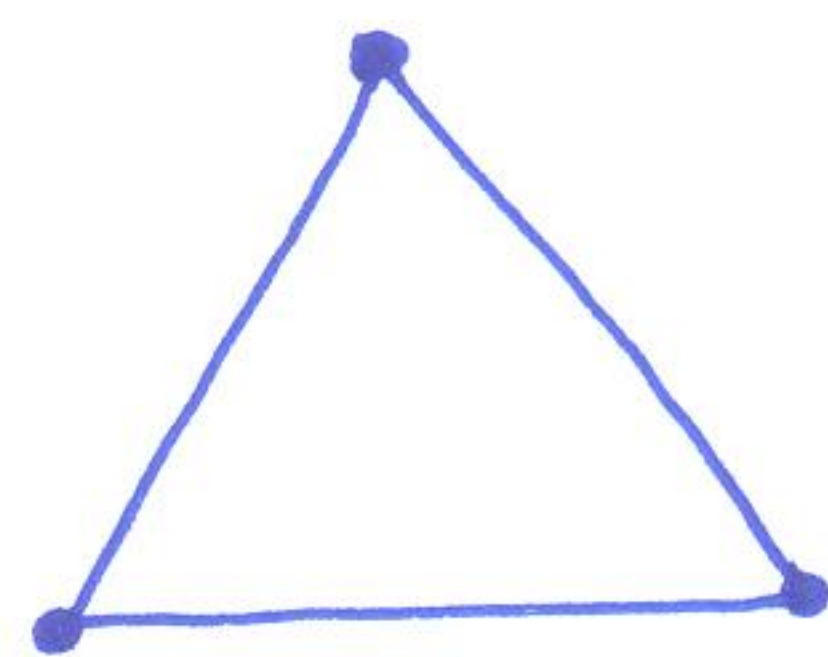
(c) Triatomic gases (SO_2 , H_2S)

(i) linear molecule

$$N = 3 \times 3 - 2 = 7$$

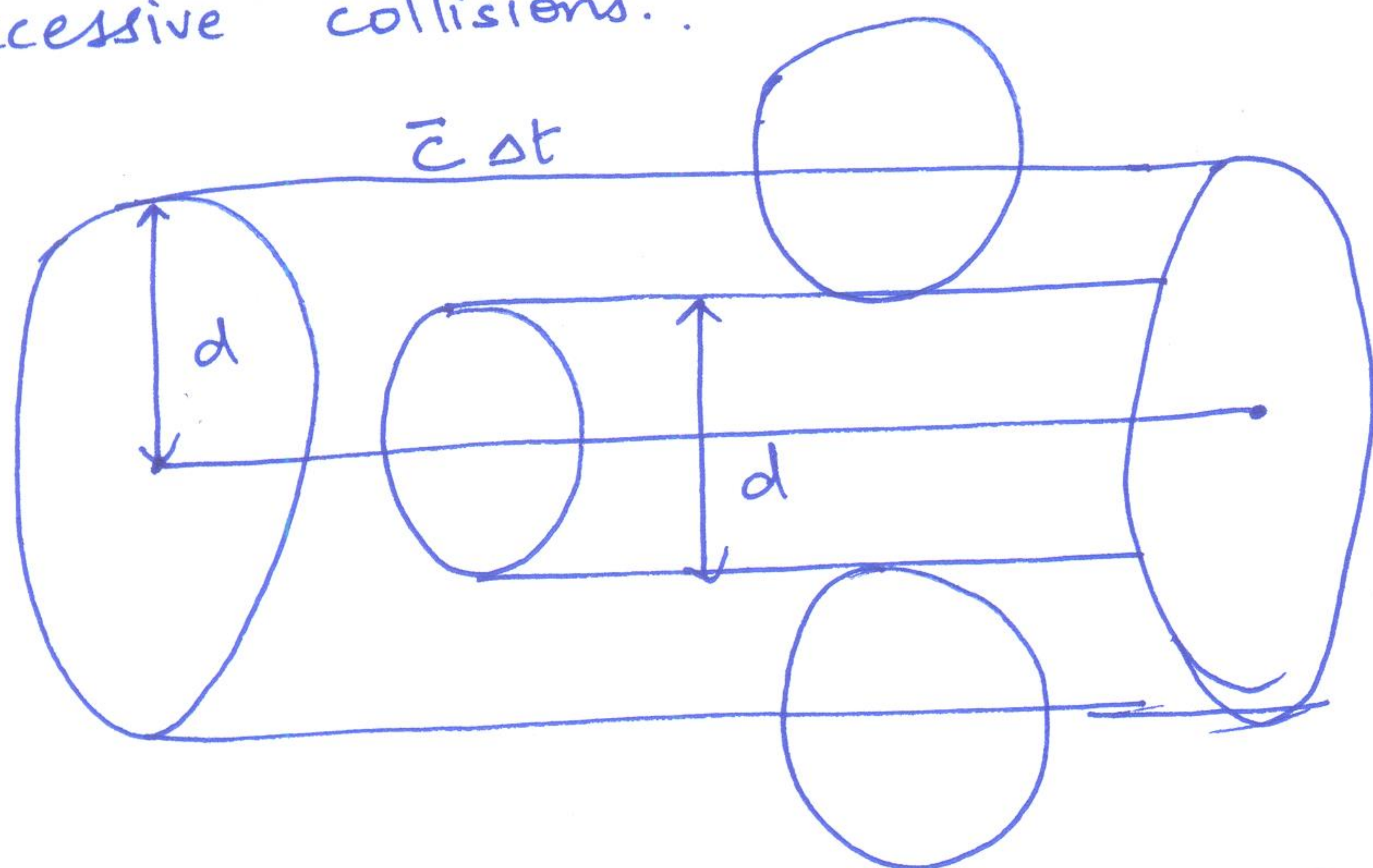
(ii) Non-linear molecule

$$N = 3 \times 3 - 3 = 6$$



Mean free path (λ)

It is the average distance travelled by a molecule betⁿ & successive collisions.



Consider 'd' to be the diameter of each molecule of gas. A molecule will suffer collision with any molecule that comes within a distance 'd' betⁿ the centres of 2 molecules.

Volume swept the molecule in time Δt is

$$V = \pi d^2 (\bar{c}) \Delta t$$

[\bar{c} - average speed of molecule]

No. of collisions suffered by the molecule in time Δt

$$= \pi d^2 (\bar{c}) \Delta t \times \eta \quad \left[\eta - \text{no. of molecules per unit volume} \right]$$

$$\text{No. of collisions per sec} = \frac{\pi d^2 (\bar{c}) \Delta t \times \eta}{\Delta t} = \eta \pi d^2 (\bar{c})$$

$$\text{Average time betⁿ & successive collisions } \tau = \frac{1}{\eta \pi d^2 (\bar{c})}$$

$$\begin{aligned} \text{Now, } \lambda &= \text{average distance betⁿ & successive collisions} \\ &= \text{mean velocity} \times \text{average time} \\ &= \bar{c} \times \frac{1}{\eta \pi d^2 \bar{c}} \end{aligned}$$

$$\lambda = \frac{1}{\eta \pi d^2}$$

In the above treatment, all other molecules were imagined at rest. If that is not the case then

$$\lambda = \frac{1}{\sqrt{2} \eta \pi d^2}$$