Physics I

Kinetic Theory of Gases

Fundamental assumptions of the Kinetic Theory of gases (Clausius theory in 1860.)

i. A gas consists of minute particles called molecules for everyone chemical spaces these are identical.
ii. The molecules are like perfectly rigid spheres like a steel ball bearing obey Newton's law of motion.
iii. There is no attraction or repulsion between two molecules. So they obey Newton's law.
iv. They have no potential energy but have only Kinetic Energy.
v. The size of a molecule is infinitesimally small.
vi. The molecules are very small dimensions

- **Charles law → P constant.** $\mathbf{V \propto T}$
- **Boyle's law → T constant.** $\mathbf{V \propto \frac{1}{P}}$
- **R → gram molecular gas constant** $\mathbf{= 8.31 \times 10^7\ erg/mole/k}$
- **Avogadro's no** $\mathbf{= N = \frac{M}{m} = \frac{Molecular\ weight\ in\ gm}{weight\ of\ a\ molecule}}$.

$$= \frac{2}{3.32 \times 10^{-24}}$$

$$= 6.02 \times 10^{23} \text{ per gm molecule.}$$

- Boltzmann's constant,

$$k = \frac{R}{N}$$

$$\Rightarrow k = \frac{8.31 \times 10^7}{6.02 \times 10^{23}} = 1.38 \times 10^{-23}\ J/k$$

- **Degrees of freedom:** The total no. of independent coordinates needed to describe completely the position and state/configuration of a dynamical system.

$$\upsilon = \frac{C_p}{C_v} = \frac{\text{molar specific heat at constant pressure}}{\text{molar specific heat at constant volume}}$$

Expression for pressure exerted by a gas:

Consider certain quantity of gas confined in a cube of each side l. No. of molecules be n of mass m of each. The molecules are moving at random with average speed c.

Consider the components of the velocity of a molecule c are u, v, w along x, y and z directions.

The component u is parallel to AB with in the wall ACED. So, no effect to other walls. Since, u hits with the same momentum $-$mu.

The change of momentum per collision

$$= \textbf{Original momentum} - \textbf{final momentum}$$

$$= \mathbf{mu} - (-\mathbf{mu})$$

$$= \mathbf{2mu}$$

The distance between two opposite walls is l. Total no. of collisions per second is $\frac{u}{l}$

∴ Total change of momentum for $\mathbf{u} = \frac{\textbf{change of momentum per collision}}{\textbf{total no of collision}}$

$$=> 2mu \times \frac{\mathbf{u}}{\mathbf{l}} = \frac{\mathbf{2mu^2}}{\mathbf{l}}$$

Similarly, $\frac{2mv^2}{l}, \frac{2mw^2}{l}$ for v and w components.

∴ Total change of momentum per molecule/second is

$$\frac{\mathbf{2mu^2}}{\mathbf{l}} + \frac{\mathbf{2mv^2}}{\mathbf{l}} + \frac{\mathbf{2mw^2}}{\mathbf{l}}$$

$$= \frac{\mathbf{2m}}{\mathbf{l}}(\mathbf{u^2} + \mathbf{v^2} + \mathbf{w^2})$$

$$= \frac{\mathbf{2m}}{\mathbf{l}}\mathbf{c^2}$$

There is *n* molecule. So, total change in momentum for all molecules

$$\frac{\mathbf{2mc^2}}{\mathbf{l}} \times \mathbf{n}$$

$$= \frac{\mathbf{2mnc^2}}{\mathbf{l}}$$

Now, total pressure on the 6 walls of the cube is

$$\mathbf{6l^2} \times \mathbf{P}$$

P is the force per unit area

$\mathbf{l^2}$ **area of each wall**

According to 2nd law of motion the impressed force is numerically equal to the rate of change of momentum.

$$\frac{\mathbf{2mnc^2}}{\mathbf{l}} = \mathbf{6l^2 \times P}$$

$$=> P = \frac{\mathbf{mnc^2}}{\mathbf{3l^2}}$$

$\therefore P = \frac{1}{3}\frac{mn}{V}^2$ which is the required pressure exerted by gas molecules on the walls of a cube/vessel.

$$\mathbf{C = \sqrt{\frac{3P}{\rho}}}$$

Where, $\mathbf{P = \frac{1}{3V}\ mnc^2}$

$\boldsymbol{\rho = \frac{M}{V}}$, density of gas.

$\mathbf{C}$ = root mean square velocity

Example 16.1: Calculate the root mean square (r.m.s) velocity of the molecule of hydrogen, oxygen and air at 0^o C and at atm pressure.

Solution: We know,

1. $C = \sqrt{\frac{3P}{\rho}}$

$=> C = \sqrt{\frac{3\times76\times13.6\times981}{0.000089}}$

$\therefore\ \ C = 1.84 \times 10^5\ \text{cm/s}$

At NTP the density of H_2 is $\rho = 0.000089\ \text{gm/cc}$

Atmospheric pressure,

$P = 76 \times 13.6 \times 981\ \text{dyne}/\mathbf{cm^2}$

2. $C = \sqrt{\frac{3\times76\times13.6\times981}{16\times0.000089}}$

$= 4.6 \times 10^4\ \text{cm/s}$

For oxygen then density at NTP $\rho = 16 \times 0.000089$

3. $C = \sqrt{\frac{3\times76\times13.6\times981}{0.001293}}$

$= 4.850 \times 10^4\ \text{cm/s}$

For air the density at NTP is $\rho = 0.001293\ \text{gm/cc}$

Example 16.2: A kg-mole of H_2 occupies a volume of 22.4 m^3 at NTP. Calculate the r.m.s velocity of the molecules at NTP.

Solution:

$$PV = \frac{1}{3}mnc^2$$

Again, $PV = RT$

So, $\frac{1}{3}Mc^2 = RT$

$$=> c = \sqrt{\frac{3RT}{M}}$$

$$\therefore \quad R = \frac{1.013\times10^5\times22.4}{273}$$

$$= 8310 \text{ J/kg} - \text{mole} - \text{K}$$

$$\therefore \quad c = \sqrt{\frac{3\times8310\times273}{2}}$$

$$= 1845 \text{ m/s}$$

M= molecular weight of H_2 in kg.

R= kg molecular gas constant

$$PV = RT$$

$$=> R = \frac{PV}{T}$$

$$P = .76 \times 13.6 \times 9.8 \times 10^3$$

$$= 1.013 \times 10^5 \text{ N/m}^2$$

T=273 K

$V = 22.4 \text{ m}^3$

Example 16.6: Calculate the Kinetic Energy of $H_2/gm - \text{molecule}$ at 0^o C. $[R = 8.3 \times 10^7 ergs/gm - \text{mol}]$

Solution: We know,

$$\frac{1}{2}Mc^2 = \frac{3}{2}RT$$

$$= \frac{3}{2} \times 8.3 \times 10^7 \times 273$$

$$= 3.4 \times 10^{10} \text{ ergs}$$

Example 16.7: Calculate the molecular Kinetic Energy of 1 gm of H_2 gas at 50^o C. [Molecular weight of hydrogen, $M = 2, R = 8.3 \times 10^7 ergs/gm - molecule$]

Solution: For 1 gm molecule

$$\frac{1}{2}Mc^2 = \frac{3}{2}RT$$

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

$$= \frac{3}{2} \times \frac{8.3\times10^7\times323}{2}$$

$$= 2.01 \times 10^{10} \text{ ergs.}$$

$$T = 50^o \text{ C} = (273 + 50)$$

$$= 323 \text{ K}$$

Mean free path: According to kinetic theory between two consecutive collisions the molecules move with constant speed along a straight line. This distance between any two consecutive collisions is known as mean free path. The average distance between two collisions is called mean free path λ. If S is the total distance travelled during N collisions then, $\lambda = {}^{S}/_{N}$.

Expression for Mean free path:

Let n be the no. of molecules per unit volume of the gas. The no. of molecules lying within a volume in the cylinder $= \pi d^2 c\, n$. So the no. of collisions made by the molecule A in one second is also $\pi\, d^2 c\, n$. So one collision take place by $\frac{1}{\pi d^2 c\, n}$ second. Time interval between two successive collisions is $\frac{1}{\pi d^2 c\, n}$ second.

So, distance travelled between two successive collisions = $speed \times time = c \times \frac{1}{\pi d^2 c\, n} = \frac{1}{\pi d^2 n} = \frac{m}{\pi d^2 m\, n} = \frac{m}{\pi d^2 \rho}$ where m is the mass of a single molecule & $\rho = mn$ is the density or total mass per unit volume.

A quantitative calculation taking into account the actual speed distribution of the molecules gives mean relative speed $c_{rel} = \sqrt{2}$c.

Hence the mean free path λ reduces to

$$\lambda = \frac{c}{\pi d^2 n\, \sqrt{2}c} = \frac{1}{\sqrt{2}\, \pi d^2 n}$$

Ex. 16.8 Calculate the average K.E. of molecule of a gas at a temp of 300k.

Solution

We know,

The average K.E. of a gas

$$\frac{1}{2}\, \mathrm{mc}^2 = \frac{3}{2}\, \mathrm{KT} = \frac{3}{2}\frac{R}{N}\mathrm{T}$$

$$= \frac{3}{2}\frac{3 \times 8.3 \times 10^7 \times 300}{6.023 \times 10^{23}} = 6.2 \times 10^{-24} ergs.$$

The average K.E. of a molecule of any gas H_2, O_2, He is the same at same temperature.

Ex. 16.10 the kinetic energy of a molecule of Hydrogen at 0 degree C is 5$.64 \times 10^{-14} ergs$ and the molecular Gas constant 8.3×10^7 ergs/gm-mole-K. Calculate the Avogadro's number.

Solution

We know,

The average K.E. of a gas

$$\frac{1}{2}\,\mathrm{mc}^2 = \frac{3}{2}\,\mathrm{KT} = \frac{3}{2}\frac{R}{N}\mathrm{T}$$

$$or, N = \frac{\frac{3}{2}\mathrm{RT}}{\frac{3}{2}\,\mathrm{KT}} = \frac{\frac{3}{2}\times 8.3\times 10^{7}\times 300}{\mathbf{5}.64\times 10^{-1}}$$

$$= 6.08\times 10^{23}$$

Ex. 16.11 Show that n, the no. of molecules per unit volume of an ideal gas is given by $\boldsymbol{n = \frac{PN}{RT}}$ where n is the Avogadro's number.

Solution

For one gm-molecule of an ideal gas $\boldsymbol{PV = RT = NKT}$

Let n be the no. of molecules per c.c.

i.e. $\boldsymbol{N = n}$ when V =1c.c.

then $\boldsymbol{P = nKT}$

or, $\boldsymbol{n = \frac{P}{KT} = \frac{P}{\frac{R}{N}\times T} = \frac{PN}{RT}}$

- **In one cubic meter the no. of molecules will be**
  $\boldsymbol{x = n\times 10^{6} = \frac{PN}{RT}\times 10^{6} = 2.688\times 10^{25}}$

Ex. 16.17 Calculate the mean free path and collision frequency for air molecules at $\boldsymbol{0°C}$ and 1 atm pressure. Given that the effective diameter of air molecule = 2Anstrom. The r.m.s of air molecule at NTP is about $\boldsymbol{1\times 10^{5}\,cm/s}$ and the air molecules per cc = $\boldsymbol{3\times 10^{19}}$.

Solution

Using Maxwell's relation the mean free path

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

$$= \frac{1}{\sqrt{2}\times 3.14\times(2\times10^{-8})^2\times 3\times 10^{19}} = 1.9\times 10^{-5}$$

The collision frequency is $\frac{c}{\lambda} = \frac{1\times 10^{5}}{1.9\times 10^{-5}} = 5.2\times 10^{9}/sec$

Thus on the average each molecule make 5.2 billion collisions per second.

Ex. 16.18 Calculate the no. of molecules per c.c. of a gas if the mean free path of the molecules is $\mathbf{2}.4\times 10^{-6}cm$ and the molecular diameter is equal to $2\times 10^{-8}cm$. What will be the collision frequency if the r.m.s.= $1\times 10^{5}\,cm/s$?

Solution

Using Maxwell's relation the mean free path

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

$$= \frac{1}{\sqrt{2}\times 3.14\times\ 2.4\times 10^{-6}\times(2\times 10^{-8})^2}$$

$=(2.345\times 10^{20})\ molecules/c.c.$

Collision frequency = r.m.s velocity/ mean free path

$$= \frac{(1\times 10^5)}{(\mathbf{2}.4\times 10^{-6})} = 41.66\times 10^9/s$$

Ex. There is helium gas in a container at 27 degree C. Find the average kinetic energy and r.m.s. velocity of the He molecule. Mass of the He molecule is $\mathbf{6}.68\times 10^{-27}kg.$

Solution

We know the average value of kinetic energy of Helium molecule,

$$E = \frac{3}{2}KT = \frac{3}{2}\times 1.38\times 10^{-23}J/K\ \times 300K = 6.21\times 10^{-21}J$$

Root mean square velocity

$$C = \sqrt{\frac{3K}{m}}$$

$$= \sqrt{\frac{3\times 1.38\times 10^{-2}\ \ J/K\times 300K}{\mathbf{6}.68\times 10^{-27}kg}}$$

$= \mathbf{1}.36\times 10^3 m/s$