STATES OF MATTER

REAL GAS EQUATION

❖ KINETIC THEORY OF GASES

The theoretical model for all the experimental gas laws can be analys with the help of kinetic theory of gases which is based on following assumptions:

(a) All the gases consists of very small molecules or atoms whose volume is negligible compared to volume of container (in case volume of container is very small, then this assumption will be violated)

(b) There is no interaction between gaseous particles (the interaction may appreciably affected under certain conditions of temperature and pressure).

(c) The gaseous molecules are under a continuous state of motion which is unaffected by gravity (the random straight-line motion is known as brownian motion)

(d) Due to the continuous motion, collision between gaseous molecules with the wall of cantainer occurs. The collision with the wall of container are responsible for pressure exerted by the gas on the wall of container.

(e) The molecule moves with different speed, however the speed of each molecule keep on changing as the collision occur.

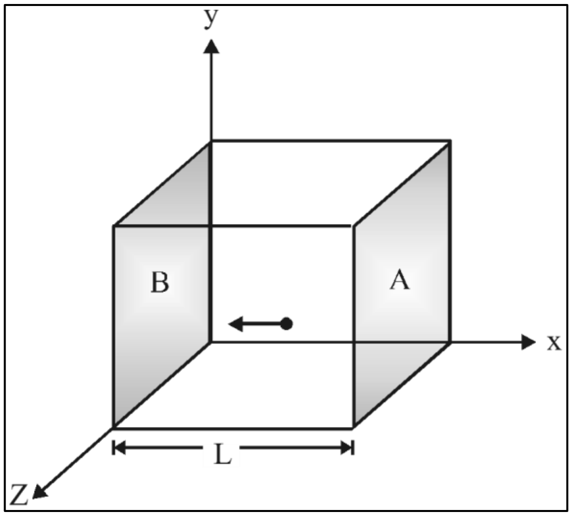
(f) All the collision occurring are considered to be perfectly elastic which implies that there is no loss of energy.

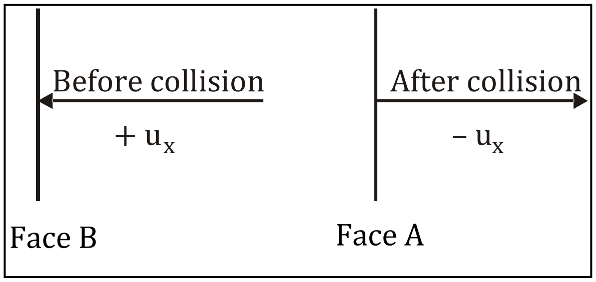
(g) The average kinetic energy of gas will depends on absolute temperature only.

Derivation of Equation for Kinetic Molecular Theory

Let us consider a cube of side L, that has N_0 molecules each of mass m moving with velocity u in all direction and thus colliding with one each other and against sides of the container. Velocity u can be resolved into three components u_x, u_y and u_z along their axes such that

$$u^2 = u_x^2 + u_y^2 + u_z^2 \text{ (assume velocity in ms}^{-1}\text{ and distance in meter)}$$





For a simplest case we consider motion of a molecule along x-axis only in which it moves towards face B with velocity u_X. After collision against face B it moves towards face A with velocity ($-u_X$) collisions being elastic (which results in change in direction but not velocity)

$\therefore$ Momentum before collision on face B $= mu_X$

Momentum after collision on face B $= -mu_X$

Change in momentum due to one collision on face B

$$= mu_X - (-mu_X) = 2mu_X$$

To strike face B again distance travelled = 2L

Time taken to strike face B again $= \frac{2L}{u_x}$seconds

$\therefore$ Number of collisions per second on face B along x-axis $= \frac{u_x}{2L}$

$\therefore$ Change in momentum due to $\frac{u_x}{2L}$ collisions per second on face B along x-axis

$= 2mu_X \cdot \frac{u_x}{2L} =$

Change in momentum per second due to collisions of one molecule on opposite faces A and B along x-axis $= \frac{mu_x^2}{L}$

Similarly for y-axis change in momentum per second = $\frac{2mu_y^2}{L}$ and for z-axis =$\frac{2mu_z^2}{L}$

Total change in momentum per second due to collisions of a single molecule on six faces along three axes

$$= \frac{2mu_x^2}{L} + \frac{2mu_y^2}{L} + \frac{2mu_z^2}{L}$$

$$= \frac{2m}{L}(u_x^2 + u_y^2 + u_z^2) = \frac{2mu^2}{L}$$

But rate of change in momentum per second = Force

$\therefore$ Force = $\frac{2mu^2}{L}$

$\therefore$ Pressure = $\frac{\text{Force}}{\text{Area of six faces}} = \frac{\frac{2mu^2}{L}}{6\ L^2} = \frac{mu^2}{3\ L^3} = \frac{mu^2}{3\ V}$ $[L^3 = \text{volume } V]$

$\therefore$ Pressure due to collisions of N_0 molecules on six faces of a cube = $\frac{1}{3}mN_0u^2$

$$PV = \frac{1}{3}\ mN_0u^2 = \frac{1}{3}\ Mu^2$$

$mN_0 = M$ (molar mass)

N_0 = Avogadro's number

u = root mean square velocity (U_{rms})

Translational Kinetic Energy of n Moles

$$\frac{1}{2}Mu^2 = \frac{3}{2}PV = \frac{3}{2}\ nRT$$

Average Translational Kinetic Energy Per Molecule

$$= \frac{3}{2}\frac{RT}{N_0} = \frac{3}{2}KT$$

Where $K(= \frac{R}{N_0})$ is called Boltzmann's constant.

Its numerical value is 1.38×10^{-16} erg K^{-1} molecule^{-1}

Thus average K.E. is proportional to absolute temperature.

If T = 0 K (i.e., – 273.15ºC), then average KE = 0

Thus, absolute zero (0 K) is the temperature at which molecular motion ceases.

DIFFERENT TYPES OF MOLECULAR VELOCITIES

- $PV = \frac{1}{3}MU_{rms}^2$

(i) **Root mean square velocity (U_{rms})** : It is defined as the square root of the mean of the squares of the velocities possessed by all the molecules present in the given sample of gas

$$U_{rms} = \sqrt{\frac{U_1^2 + U_2^2 + \cdots U_n^2}{N}}$$

∴ U_{rms} (root mean square velocity) $= \sqrt{\frac{3PV}{M}} = \sqrt{\frac{3RT}{M}} = \sqrt{\frac{3P}{d}}$

Where d is the density.

◆ If N_1 molecules have velocity u_1 and N_2 molecules have velocity u_2, then

$$U_{rms} = \sqrt{\frac{N_1 u_1^2 + N_2 u_2^2}{N_1 + N_2}}$$

(ii) Average velocity (U_{av}) : It is given by the arithmetic mean of square of the different velocities possessed by the molecules of the gases at a particular temperature.

$$U_{av} = \frac{U_1^2 + U_2^2 + \cdots U_n^2}{n}$$

◆ U_{av} (average velocity) $= \sqrt{\frac{8RT}{\pi M}}$

(iii) Most probable velocity (U_{mp}) : It is defined as the velocity possessed by the maximum number of molecules of a gas at a given temperature.

◆ U_{mp} (most probable velocity) $= \sqrt{\frac{2RT}{M}}$

◆ If P and T both are given, use equation in terms of temperature i.e., use

$$U_{rms} = \sqrt{\frac{3RT}{M}} \text{ and not } \sqrt{\frac{3pv}{M}}$$

◆ To have velocity in ms^{-1} (MKS) take $R = 8.314\ J\ mol^{-1}K^{-1}$, M in kg.

◆ If density is in $kg\ m^{-3}$ and P in $N\ m^{-2}$, velocity will be in ms^{-1}.

Relation between rms velocity, average velocity and most probable velocity.

◆ $U_{rms} : U_{av} : U_{mp} = \sqrt{\frac{3RT}{M}} : \sqrt{\frac{8RT}{\pi M}} : \sqrt{\frac{2RT}{M}} = \sqrt{3} : \sqrt{\frac{8}{\pi}} : \sqrt{2} = 1.2248 : 1.1284 : 1$

$$U_{rms} = 1.2248\ U_{mp}$$

$$U_{av} = 1.1284\ U_{mp}$$

$$U_{mp} = 1.0854\ U_{av}$$

Distribution of Molecular Speeds

(a) The speed of a molecule of a gas changes continuously as a result of collisions with other molecules and with the walls of the container. Thus, the net result is that we cannot speak of the speed of individual molecule; hence must consider the statistical averages of the speeds of the whole collection of gas molecules.

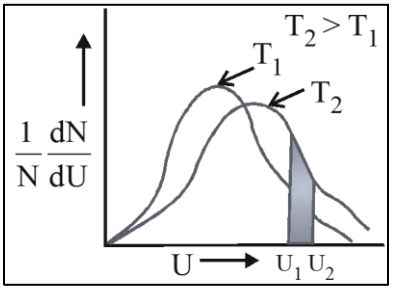
(b) The manner in which the molecules of a gas are distributed over the possible speed ranges, from zero to very high values, was first investigated by Maxwell using the theory of probability. His results are expressed as the law of distribution of molecular speeds, one form of which is

$$dN = 4\pi N\left(\frac{m}{2\pi KT}\right)^{3/2} e^{-\frac{mu^2}{2\pi KT}} u^2 du$$

(c) The above expression gives the no. of molecules dN having speeds between U and U + du in terms of total no. of molecules, N present in the gas m is mass of single gas molecule and T is the absolute temperature of gas.

(d) The Maxwell distribution of speeds is customarily plotted with the fraction as $\frac{1}{N}\left(\frac{dNu}{dU}\right)$ the ordinate and U as the abscissa.

$$\frac{1}{N}\left(\frac{dN}{dU}\right) = \frac{1}{du}\left(\frac{dN}{dU}\right)$$



So, the term, $\frac{1}{N}\frac{dN}{dU}$

represents the fraction of molecules in the speed range of u to u + du per unit interval of speed. Roughly speaking, this gives the probability of finding a molecule with a speed between u and (u + du). The distribution of two temperatures is shown in the fig.

(e) The curve at any temperature is parabolic near the origin, since the factor u^2 is dominant in this region, the exponential function being approximately equal to unity. At high values of u, however, the exponential factor dominates the behaviour of the function, causing it to decrease rapidly in value. As a consequence of the contrasting behaviour of two factors, the product function passes through a maximum at a speed known as the most probable speed (U_{mps}). Thus, the most probable speed is the speed possessed by the maximum fraction of the molecules.

(f) It can be seen from the given figure, that the fraction of molecules having either very low speeds or very high speeds are small in numbers. The total area under the curve gives the total no. of molecules in the collection i.e. the no. of molecules comprising of all speeds. The area under the curve between any two speeds, for example, U_1 and U_2, gives the total no. of molecules having speed between these two values.

(g) The given figure illustrates the distribution of speeds at two temperatures T_1 and T_2. Since the total no. of molecules is the same at both temperatures, increases the K.E. of the molecules, it follows that fraction of molecules having lower speed range decreases whereas fraction of molecules having higher speed range increases on increasing the temperature.

(h) Also, the curve at the higher temperature T_2 has its U_{mps} shifted to a higher value compared with that for T_1, whereas corresponding fraction of molecules has decreased. But at the same time, the curve near U_{mps} has become broader at the higher temperature indicating the more molecules possess speeds near to most probable speed.

(i) The value of U_{mps} can be calculated easily, based on the concept of maximum or minimum value of a function.

$$dN = 4\pi N(\frac{m}{2\pi RT})^{3/2} e^{-mU^2/2kT} u_{u^2 du}$$

$$\text{or} \qquad \frac{1}{N}\frac{dN}{du} = 4\pi(\frac{m}{2\pi RT})^{3/2} e^{-mu^2/2kT} u^2$$

Differentiating both sides with respect to U

$$\frac{d}{du}(\frac{1}{N}\frac{dN}{du}) = 4\pi(\frac{m}{2\pi RT})^{3/2}[2ue^{-mu^2/2KT} + u^2(-\frac{2mu}{2KT})e^{-mm^2/2KT}]$$

For maximum

$$\frac{d}{du}(\frac{1}{N}\frac{dN}{du})_{=0}$$

$$\therefore \qquad 4\pi(\frac{m}{2\pi RT})^{3/2}[2ue^{-mu^2/2KT} + u^2(-\frac{2mu}{2KT})e^{-mu^2/2KT]} = 0$$

$$\text{or} \qquad 2ue^{-mU^2/2KT}[1 - \frac{mu^2}{2KT}] = 0$$

Now at the condition of mps, $U \neq 0$ and $= 0$ when $U = \infty$,

but at the condition of U_{mps}, $U \neq \infty$.

$$\therefore \qquad e^{-mU^2/2KT} = 0$$

∴ $1 - \frac{mU^2}{2KT} = 0 \Rightarrow \frac{mU^2}{2KT} = 1$

or $U = \sqrt{\frac{2KT}{m}}$

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

- **Maxwell Distribution Curve for Energy**

$$E = \frac{1}{2}MU^2$$

$$U = \sqrt{\frac{2E}{M}}$$

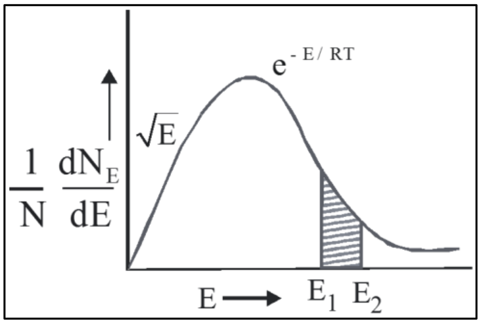
$$dE = \frac{1}{2}M \times 2\,UdU$$

$$dE = MU\,dU$$

$$UdU = \frac{dE}{M}$$

By Maxwell equation :

$$dN = 4\pi\,N\,\left(\frac{M}{2\pi RT}\right)^{3/2} \cdot e^{\frac{-Mu^2}{2RT}}\,U.\,UdU$$



$$dN_E = 4\pi N\,\left(\frac{M}{2\pi RT}\right)^{3/2} \cdot e^{-\left(\frac{E}{RT}\right)}\sqrt{\frac{2E}{M}}\,\frac{dE}{M}$$

$$dN_E = 2\pi N\left(\frac{1}{\pi RT}\right)^{3/2} \cdot e^{\frac{-E}{RT}}\sqrt{E}\,dE$$

$$\frac{1}{N}\left(\frac{dN_E}{dE}\right) = 2\pi\left(\frac{1}{\pi RT}\right)^{3/2}\sqrt{E}e^{-E/RT}$$

The shaded area of this graph indicates the fraction of particle having energy between E_1 and E_2. From maxwell equation we are able to calculate the total no. of particles which are having energy greater than threshold energy (Activation energy) [for a chemical reaction to occur, reactant need some minimum amount of energy which is called as threshold energy or activation energy].

$$\mathrm{dN_E} = 2\pi\mathrm{N}$$

$$\left(\frac{1}{\pi RT}\right)^{3/2} \int_{E_a}^{\infty} \sqrt{E}\, e^{-\sqrt{\frac{E}{RT}}} dE$$

From the above equation we calculate the total no. of particles which will participate in chemical reaction.