

*. Distribution of velocities of gases :-

Maxwell distribution law of velocities :-

Gaseous molecules are colliding with themselves randomly thereby changing the molecular velocity.

Let us consider a gas molecule of mass 'm' having a velocity component 'u'. Then, the kinetic energy 'E' associated with this velocity component is $\frac{1}{2} mu^2$. The probability that this molecule has its velocity component between u and u+du is given by P(u). Boltzmann had shown that the probability for a molecule to have an energy 'E' was proportional to $e^{-E/KT}$.

$$P(u) \propto e^{-E/KT} \propto e^{-mu^2/2KT}$$
$$\propto P(u) du = A e^{-mu^2/2KT} du \quad \text{--- (1)}$$

where, 'A' is the constant of proportionality.

This constant can be evaluated by requiring that the total probability must be unity. Thus,

$$\int_{-\infty}^{+\infty} P(u) du = A \int_{-\infty}^{+\infty} e^{-mu^2/2KT} du = 1 \quad \text{--- (2)}$$

The range of integration + ∞ to - ∞ (velocity component u) has both magnitude and direction. This eqn - (2) is simplified as -
putting $m/2KT = a$.

$$\int_{-\infty}^{+\infty} e^{-au^2} du = \left(\frac{\pi}{a}\right)^{1/2} = \left(\frac{2\pi KT}{m}\right)^{1/2} \quad \text{--- (3)}$$

from eqn - (2) & (3) we have $A \left(\frac{2\pi KT}{m}\right)^{1/2} = 1$

$$\text{So, } A = \left(\frac{m}{2\pi kT}\right)^{1/2} \quad \text{--- (4)}$$

Now substituting for A in eqⁿ - (1) we get.

$$P(u) du = \left(\frac{m}{2\pi kT}\right)^{1/2} e^{-mu^2/2kT} du \quad \text{--- (5)}$$

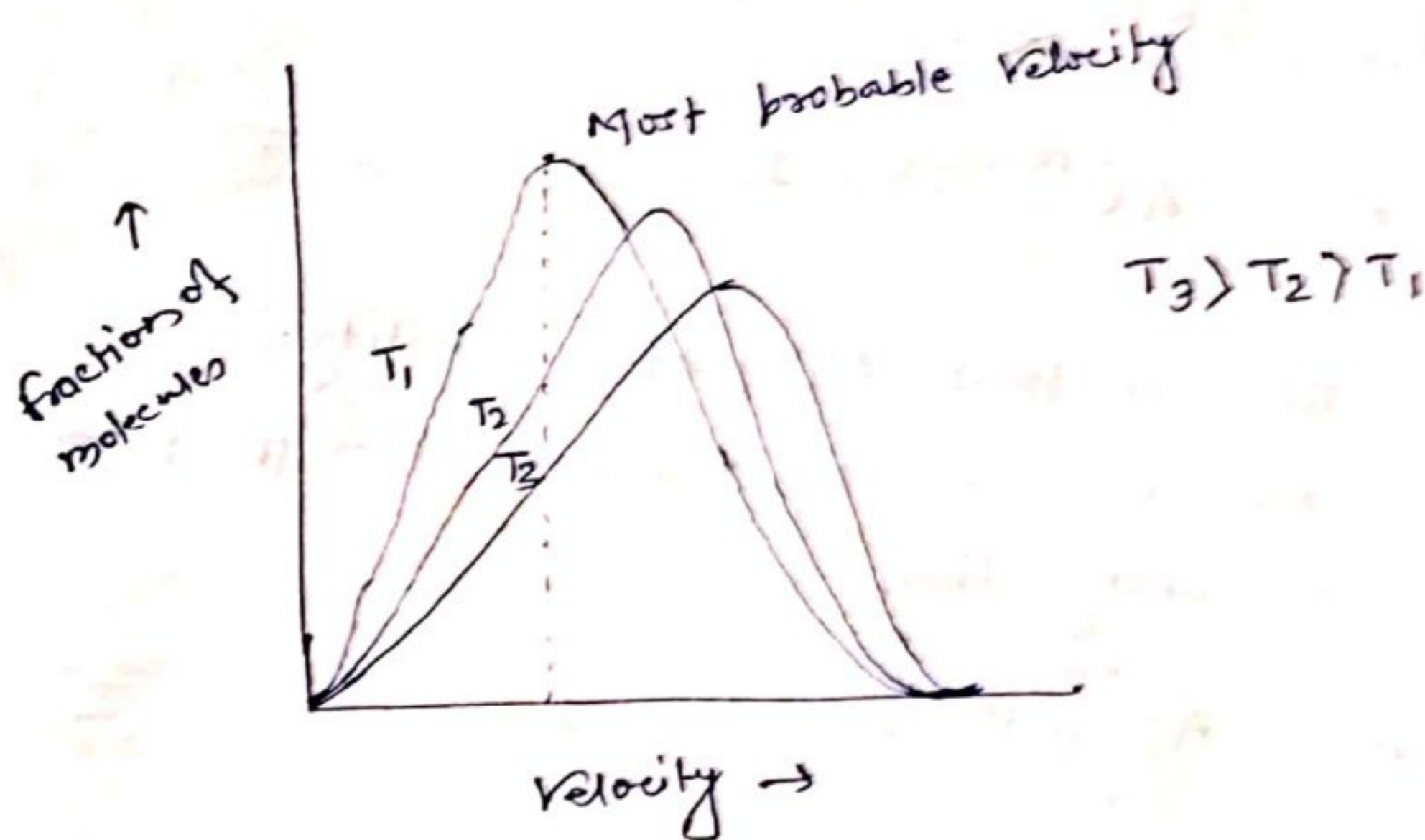
Eqⁿ - (5) is called Maxwell distribution of molecular velocities in one dimension.

In three dimension, the eqⁿ - (5) is written as -

$$P(c) dc = 4\pi \left(\frac{m}{2\pi kT}\right)^{3/2} c^2 \exp(-mc^2/2kT) dc \quad \text{--- (6)}$$

$$\therefore \frac{dNc}{N} = 4\pi \left(\frac{M}{2\pi RT}\right)^{3/2} c^2 \exp\left(-\frac{Mc^2}{2RT}\right) dc \quad \text{--- (7)}$$

This may be plotted as:-



At higher temperature, the whole curve shifts to the right. This shows that at higher temperature more molecules have higher velocity and fewer molecules have lower velocity.

Dr. A.K. Gupta.
Chemistry (L.S. College)

1). Most Probable velocity:-

It is defined as the velocity of gas possessed by maximum no. of molecules at a given temperature.

The equation for Maxwell distribution of velocities may be written as -

$$\frac{N}{dU_x} = 4\pi \left(\frac{M}{2\pi RT} \right)^{3/2} \exp\left(-\frac{MU_x^2}{2RT}\right) U_x^2 \quad \text{--- (1)}$$

for maxima & minima conditions, this equation is differentiated w.r.t U_x and equated to zero. Thus we get -

$$\left(1 - \frac{MU_x^2}{2RT}\right) U_x \exp\left(-\frac{MU_x^2}{2RT}\right) = 0.$$

Since, $U_x \exp\left(-\frac{MU_x^2}{2RT}\right) \neq 0.$

Then, $1 - \frac{MU_x^2}{2RT} = 0.$

or $\frac{MU_x^2}{2RT} = 1$

$$MU_x^2 = 2RT$$

$$U_x = \sqrt{\frac{2RT}{M}}$$

where, ' U_x ' is the most probable velocity. M = Mol. mass of the gas.