

Effect of temperature in distribution of molecular velocities:-

The most probable velocity increase with rise in temperature as mentioned in the previous plot. There is a shifting in the entire curve.

The rise in temperature increases the number of molecules having high velocities.

According to equation

$$P(c)dc = 4\pi \left( \frac{m}{2kTn} \right)^{3/2} c^2 \exp\left( -\frac{mc^2}{2kT} \right) dc \quad \text{--- (1)}$$

The exponent has negative sign and temperature  $T$  in the denominator. The factor that increases in temperature. This is known as Boltzmann factor.

$$\text{Since } \frac{1}{2} mc^2 = K.E = E \quad \text{--- (2)}$$

$$\exp\left( -\frac{mc^2}{2kT} \right) = \exp\left( -\frac{E}{kT} \right) \quad \text{--- (3)}$$

$E = K.E$  of the molecule of the gas.

The greater the temperature, the greater is the value of  $e$ . Hence there is increase of Boltzmann factor with the increase in temperature.

This conclusion finds application in the theory of reaction rates.

Maxwell distribution of molecular kinetic energies:-

The fraction of molecules having kinetic energies in the range of  $\epsilon$  and  $\epsilon + d\epsilon$  viz  $\frac{dN_\epsilon}{N}$  can be determined as follows:-

$$\epsilon = \frac{1}{2} mc^2 \quad \text{--- (1)}$$

$$c^2 = \frac{2\epsilon}{m} \quad \text{--- (2)}$$

$$2c dc = \left(\frac{2}{m}\right) d\epsilon$$

$$\text{or } c dc = \frac{d\epsilon}{m} \quad \text{--- (3)}$$

Then,

$$\begin{aligned} c^2 dc &= c \frac{d\epsilon}{m} \\ &= \left(\frac{2\epsilon}{m}\right)^{1/2} \left(\frac{d\epsilon}{m}\right) \end{aligned}$$

$$c^2 dc = \frac{\sqrt{2\epsilon}}{(m)^{3/2}} d\epsilon \quad \text{--- (4)}$$

Replacing  $c^2 dc$  using equation for Maxwell molecular velocity distribution, we have

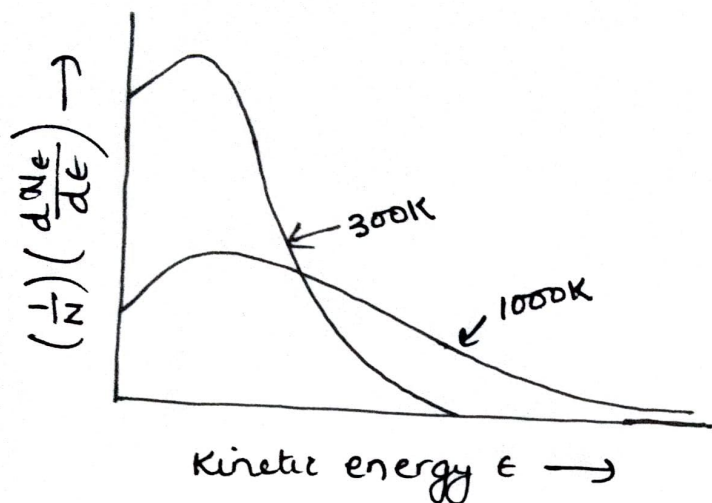
$$p(c)dc = \frac{dN_\epsilon}{N} = 4\pi \left(\frac{m}{2kT\pi}\right)^{3/2} \left(\frac{\sqrt{2\epsilon}}{m^{3/2}}\right) d\epsilon \exp\left(-\frac{\epsilon}{kT}\right)$$

$$p(c)dc = \frac{2\sqrt{\epsilon}}{\sqrt{\pi} (kT)^{3/2}} \exp\left(-\frac{\epsilon}{kT}\right) d\epsilon \quad \text{--- (5)}$$

Maxwell distribution of molecular kinetic energy



The Maxwell distribution of kinetic energy at two different temperature can be represented as



According to the plot the probable K.E. increases with the increase in temperature.

The maximum in the probability function corresponds to the most probable kinetic energy.

From the equation (5)

(i) The most probable kinetic energy is given by  $kT/2$  per molecule or  $\frac{RT}{2}$  per mole of the gas

(ii) The average kinetic energy per mole is given by  $\left(\frac{3}{2}\right) N_A kT = \left(\frac{3}{2}\right) RT$ .

Above two relations are in agreement with that obtained from the kinetic theory.

## Types of molecular velocities:-

Three types of molecular velocities are reckoned with in the study of gases. These are:-

- ① The most probable velocity,  $c_p$ .
- ② The average velocity  $\langle c \rangle$
- ③ The root mean square velocity  $\langle c^2 \rangle^{1/2}$

The most probable velocity is defined as the velocity possessed by maximum number of molecules of a gas at a given temperature.

Average Velocity:- The velocity possessed by maximum number of molecules

Average Velocity:- The arithmetic mean of different velocities possessed by the molecules of the gas at a given temperature.

If  $c_1, c_2, c_3, \dots, c_n$  are individual <sup>velocities</sup> possessed by the gas molecules. And  $n$  is their total number

Average velocity

$$\langle c \rangle = \frac{c_1 + c_2 + c_3 + \dots + c_n}{n}$$

If  $c_1, c_2, c_3, \dots$  are the velocities possessed by the groups of  $n_1, n_2, n_3, \dots$  molecules of the gas, then average velocity is given by

$$\langle c \rangle = \frac{n_1 c_1 + n_2 c_2 + n_3 c_3 + \dots + n_n c_n}{n_1 + n_2 + n_3 + \dots + n_n}$$



Root mean square velocity defined as, <sup>square</sup> root of the mean of the squares of the different velocities possessed by molecules of a gas at a given temp. The root mean square velocity would be given by

$$\left\{ \langle c^2 \rangle^{1/2} = \left[ \frac{c_1^2 + c_2^2 + c_3^2 + \dots + c_n^2}{n} \right]^{1/2} \right\}$$

where  $c_1, c_2, c_3, \dots, c_n$  are the individual velocities of  $n$  molecules of the gas. Alternatively,

$$\langle c^2 \rangle^{1/2} = \left[ \frac{n_1 c_1^2 + n_2 c_2^2 + n_3 c_3^2 + \dots + n_n c_n^2}{n_1 + n_2 + n_3 + \dots + n_n} \right]^{1/2}$$

where  $c_1, c_2, c_3, \dots$  are velocities possessed by group of  $n_1, n_2, n_3, \dots$  molecules, respectively.

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

Using the Maxwell equation,

① The most probable velocity  $c_p$

$$c_p = (2kT/m)^{1/2} = (2RT/M)^{1/2} \quad \text{--- a}$$

② The average velocity  $\langle c \rangle$

$$\langle c \rangle = \left( \frac{8kT}{\pi m} \right)^{1/2} = \left( \frac{8RT}{\pi M} \right)^{1/2} \quad \text{--- b}$$

③ The root mean square velocity

$$\langle c^2 \rangle^{1/2} = \left( \frac{3kT}{m} \right)^{1/2} = \left( \frac{3RT}{M} \right)^{1/2} \quad \text{--- c}$$

It can be derived from equations (a), (b) and

④

$$\langle c^2 \rangle^{1/2} : \langle c \rangle : c_p = 1.00 : 0.92 : 0.82$$

## Derivation of Expression for $c_p$ , $\langle c \rangle$ and $\langle c^2 \rangle^{1/2}$

- ① Expression for  $c_p$ : - Differentiating with respect to  $c$  (using  $dN/N$  for  $p(c)dc$ ) and setting the result to zero, as required for a maximum.

$$\frac{d}{dc} \left( \frac{dN}{N} \right) = \left( \frac{m}{2\pi kT} \right)^{3/2} \exp\left(-\frac{mc^2}{2kT}\right) \left[ 8\pi c + 4\pi c^2 \left( -\frac{mc}{kT} \right) \right] = 0 \quad \text{--- ①}$$

The factor  $\left( \frac{m}{2\pi kT} \right)^{3/2}$  is a constant, different from zero.

Also, the factor  $\exp\left(-\frac{mc^2}{2kT}\right)$  is not equal to zero.

Hence, the third factor, viz

$$8\pi c + 4\pi c^2 \left( -\frac{mc}{kT} \right) = 0 \quad \text{--- ②}$$

$$c \equiv c_p = (2kT/m)^{1/2} = (2RT/M)^{1/2} \quad \text{--- ③}$$

- ② Expression for  $\langle c \rangle$ : The average velocity is given by expression.

$$\langle c \rangle = \int_0^{\infty} c p(c) dc \quad \text{--- ④}$$

Substituting the value of  $p(c)dc$  from we have

$$\langle c \rangle = 4\pi \left( \frac{m}{2\pi kT} \right)^{3/2} \int_0^{\infty} c^3 \exp\left(-\frac{mc^2}{2kT}\right) dc \quad \text{--- ⑤}$$

$$\frac{mc^2}{2kT} = x^2 \quad \text{so that} \quad c^2 = \frac{2kTx^2}{m} \quad \text{--- ⑥}$$

Differentiating both sides, we have

$$dc = 2kTx dx / mc \quad \text{--- ⑦}$$

$$\text{Also from} \quad c = \left( \frac{2kTx^2}{m} \right)^{1/2} = \left( \frac{2kT}{m} \right)^{1/2} x \quad \text{--- ⑧}$$



## Expansivity and compressibility :-

Gases expand on heating and are compressed on applying pressure. The variation of volume  $V$  with temperature  $T$ , keeping pressure  $P$  constant is called coefficient of thermal expansion, or expansivity,  $\alpha$ , of the gas.

$$\alpha = \frac{1}{V} \left( \frac{\partial V}{\partial T} \right)_P \quad \text{--- (1)}$$

The variation of  $V$  with  $P$ , keeping  $T$  constant is called the coefficient of isothermal compressibility or compressibility,  $\beta$ , of the gas. Thus

$$\beta = -\frac{1}{V} \left( \frac{\partial V}{\partial P} \right)_T \quad \text{--- (2)}$$

The volume of a gas decreases as pressure increases so that the quantity  $\left( \frac{\partial V}{\partial P} \right)_T$  is negative.

Q. Show that for an ideal gas  $\alpha = \frac{1}{T}$  and  $\beta = \frac{1}{P}$ .

For  $n$  moles of an ideal gas,  $PV = nRT$  or  $V = \frac{nRT}{P}$

On differentiating the equation with respect to  $T$  at constant  $P$

$$\left( \frac{\partial V}{\partial T} \right)_P = \frac{nR}{P} = \frac{V}{T}$$

$$\alpha = \frac{1}{V} \left( \frac{\partial V}{\partial T} \right)_P = \left( \frac{1}{V} \right) \left( \frac{V}{T} \right) = \frac{1}{T}$$

Again differentiating  $V = \frac{nRT}{P}$  with respect to  $P$  at constant  $T$ , we have

$$\left( \frac{\partial V}{\partial P} \right)_T = -\frac{nRT}{P^2} = \left( \frac{nRT}{P} \right) \left( -\frac{1}{P} \right) = \left( -\frac{V}{P} \right)$$

$$\beta = -\frac{1}{V} \left( \frac{\partial V}{\partial P} \right)_T = \left( -\frac{1}{V} \right) \left( -\frac{V}{P} \right) = \frac{1}{P}. \quad \text{Thus } \alpha = \frac{1}{T} \text{ and } \beta = \frac{1}{P}$$