(6) Degrees of freedom :-

The no. of independant coordinates necessary to specify the position and configuration of a dynamical system in space.

Or, the no. of independent quadratic variables by which the energy of a system is determined.

* Consider a material system consisting of N - Particles (x_1, y_1, z_1), (x_2, y_2, z_2), ... (x_N, y_N, z_N) and subject to m constraint equations.

If $m < 3N$, then the degrees of freedom of the system

$$f = 3N - m$$

(7) Equipartition of energy :-

If the molecules in their motion obey the laws of mechanics, the mean Kinetic energy of a system of molecules in thermal equilibrium at temperature T, is uniformly distributed among all the degrees of freedom and for each degrees of freedom it equals to $\frac{1}{2}KT$. K is Boltzman's Constant.

(8) Degrees of freedom and ratio of heat capacities:-

We consider a system consist of only free particles having f degrees of freedom.

According to equipartition theorem energy associated per each particle is $= \frac{1}{2}KTf$

$= \frac{1}{2}fKT$

∴ So, the energy per mole $E = \frac{1}{2}fKT \cdot N_A$

$= \frac{1}{2}fN_AKT$

$= \frac{1}{2}fRT \quad [\because N_AK = R]$

∴ Molar heat capacity at constant volume

$$C_v = \left(\frac{dE}{dT}\right)_v = \frac{d}{dT}\left(\frac{1}{2}fRT\right) = \frac{1}{2}fR \longrightarrow (i)$$

But for 1 mole of gas

$$C_p - C_v = R$$

or $C_p = \frac{1}{2}fR + R = R\left(1 + \frac{f}{2}\right) \longrightarrow (ii)$

$$\therefore \gamma = \frac{C_p}{C_v} = \frac{R\left(1+\frac{f}{2}\right)}{\frac{1}{2}fR} = 1 + \frac{2}{f}$$

$$\boxed{\therefore \gamma = 1 + \frac{2}{f}}$$

This is the required relation linking between γ and f.

* For monoatomic gas $f = 3$

$$\therefore \gamma = 1 + \frac{2}{f} = 1 + \frac{2}{3} = 1.67$$

** For diatomic gas $f = 3N - m = 3\times2 - 1 = 5$

Of these 3 are of translation and 2 of rotation.

$$\therefore \quad \gamma = 1 + \frac{2}{f} = 1 + \frac{2}{5} = 1.4$$

*** For linearly arranged triatomic gas molecule like CO_2 ($O=C=O$) ($m=2$)

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

$$\therefore \quad \gamma = 1 + \frac{2}{f} = 1 + \frac{2}{7} = 1.28$$

If the atoms are arranged at the vertices of a triangle then ($m=3$)

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

$$\therefore \quad \gamma = 1 + \frac{2}{f} = 1.33$$

(9) γ for a mixture of two ideal gases:—

Let a container consist of N_1 mole of one type of gas having f_1 degrees of freedom per molecule and another type of N_2 mole of gas having f_2 degrees of freedom per molecule.

$\therefore$ Total energy of the system

$$E = \frac{1}{2} KT \cdot f_1 \cdot N_1 N_A + \frac{1}{2} KT \cdot f_2 \cdot N_2 \cdot N_A$$

$$= \frac{1}{2} N_1 f_1 RT + \frac{1}{2} N_2 f_2 RT \quad [\because N_A K = R]$$

$$= \frac{1}{2} RT (N_1 f_1 + N_2 f_2)$$

$$\therefore C_V = \left(\frac{dE}{dT}\right)_V = \frac{1}{2} R (N_1 f_1 + N_2 f_2)$$

But, for (N_1+N_2) mole of gas

$$C_p - C_v = (N_1+N_2)R$$

$$\therefore C_p = C_v + (N_1+N_2)R$$

$$= \frac{1}{2}R(N_1f_1+N_2f_2) + (N_1+N_2)R$$

$$= \frac{R[(N_1f_1+N_2f_2) + (2N_1+2N_2)]}{2}$$

$$= \frac{R[N_1(2+f_1) + N_2(2+f_2)]}{2}$$

$$\therefore \gamma = \frac{C_p}{C_v} = \frac{\frac{R[N_1(2+f_1)+N_2(2+f_2)]}{2}}{\frac{1}{2}R(N_1f_1+N_2f_2)}$$

$$\boxed{\gamma = \frac{N_1(2+f_1)+N_2(2+f_2)}{N_1f_1+N_2f_2}}$$

This is the required relation.

*** For N_1, N_2, N_3 mole of gases the above equation can be modified as

$$\gamma = \frac{N_1(2+f_1)+N_2(2+f_2)+N_3(2+f_3)}{N_1f_1+N_2f_2+N_3f_3} \quad \text{(1)}$$

Where f_1, f_2, f_3 are the degrees of freedom of each type gases respectively.

(10) Dulong & Petit's law :-

If the temperature is not too low, the molar Sp. heat capacity of all pure substances in solid state are nearly equal to 6 Calorie.

Proof :-

Consider one gm atom of solid so there will be N_A of atoms. The atoms within the solid can vibrate only since they have fixed position. So, the no. of degrees of freedom (vibrational) $= 3N_A$. Now an atom can have both kinetic and potential energy. So, the average kinetic energy is equal to the average potential energy.

∴ Kinetic energy of the above solid $= \frac{1}{2}KT \times 3N_A$

∴ Total energy $U = 2 \times \frac{1}{2}KT \times 3N_A$

$= 3N_A KT$

∴ $C_V = \left(\frac{dU}{dT}\right)_V = 3N_A K$

$= 3R$

$= 3 \times 2 = 6$ Calorie.

[∵ $R \simeq 2$ Cal.]

(11) Mean free path :-

The path traversed by a molecule between two successive collisions is called a free path and the average distance traversed by this molecule between two successive collisions is called mean free path. Mean free path always be a straight line.

(12) Distribution of free path (Survival Equation) :-

To determine how the free paths are distributed among the molecules is equivalent to find the probability that molecule moving with a velocity c and ~~describe~~ traverse a distance x without suffering any collision. This is a function of x Say $f(x)$. Now, if the mean free path is λ, then the probability to suffer a collision in traversing a distance dx is dx/λ. So, the probability of no collision to traverse a distance dx is $(1 - dx/\lambda)$.

Now the probability of that molecule to traverse from these distance $x+dx$ with suffering no collision $f(x+dx)$ is the product of $f(x)$ and $(1 - \frac{dx}{\lambda})$

$$\therefore f(x+dx) = f(x)\left(1 - \frac{dx}{\lambda}\right) \longrightarrow (1)$$

Expanding with the help of Taylor series

$$f'(x)\,dx = -f(x)\frac{dx}{\lambda}$$

or $$\frac{f'(x)}{f(x)}\,dx = -\frac{dx}{\lambda}$$

Integrating we get

$$\ln f(x) = -\frac{x}{\lambda} + \ln A \quad (\text{const.})$$

$$f(x) = Ae^{-\frac{x}{\lambda}}$$

Now, when $x=0$, $f(x)=1$

$$\therefore A = 1$$

$$\therefore f(x) = e^{-x/\lambda}$$

This is the law of distribution of free paths.

The above eqn shows that the very long paths probability is very small.

P-T-O

Now, If N_0 molecules of velocity c are incident on the gas, then only $N_0 e^{-x/\lambda}$ will travel a distance x without suffering any collision, i.e

$$N = N_0 e^{-x/\lambda}$$

This is well known Survival Equation.

(13) Expression for mean free path (Elementary treatment)

Assume at any instant all molecules of a gas are at rest except one. This particular molecule moving with an average velocity $\bar{c}$. We also assume that the molecules are perfectly elastic sphere of diameter σ. So, the centre to centre distance during collision of the colliding molecules is σ. The centre to centre distance of the colliding molecules remain same if the radius of the moving molecule increase to σ and all the other molecules all shrunk to a geometrical mass point.

So, the effective cross sectional area of the moving molecule i.e Collision cross section ρ is $\rho = \pi \sigma^2$

After an interval 't' the moving molecule traverses a distance $\bar{c}t$ and sweeps out a cylindrical volume of cross section ρ and length $\bar{c}t$. Plainly the moving molecule collide with those molecule having their centre within this cylindrical volume.

in time t. If n be the number of molecule per unit volume. Then the no. of molecules within the cylindrical volume is $\rho \bar{c} t n$.

$\therefore$ So, the no. of Collision in time $t = \rho n \bar{c} t$

$\therefore$ Collision frequency (no. of collision per unit time)

$$= \rho n \bar{c}$$

$\therefore$ Mean free path $\lambda = \frac{\text{distance covered in time } t}{\text{no. of collision in } t}$

$$= \frac{\bar{c} t}{\rho n \bar{c} t} = \frac{1}{\rho n}$$

$$= \frac{1}{\pi \sigma^2 n} \quad [\because \rho = \pi \sigma^2]$$

This is the expression for mean free path when one molecule is moving and other assume to be in rest.

* But, For more complete calculation for mean free path must take into account the motion of all molecules of the gas, the fact that all molecules are not moving with the same speed and also other factors. After Consider the motion of all molecules the mean free path equation is

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