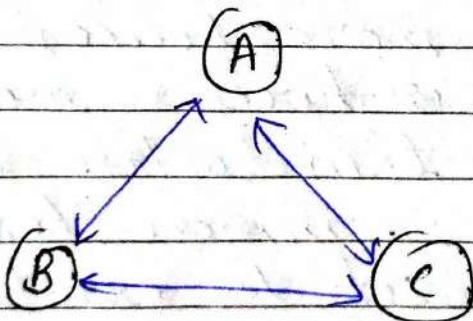


## Zeroth law of Thermodynamics

The zeroth law of thermodynamics frames an idea of temperature as an indicator of thermal thermal equilibrium.

zeroth law - When a body A is in thermal equilibrium with another body B and also separately in thermal equilibrium with a body C then, Body B and C will also be in thermal equilibrium with each other. This statement defines the zeroth law of thermodynamics. The law is based on the temperature measurement.



In other word this law can be stated as "Systems that are in thermal equilibrium exist as the same temperatures".

Zeroth law of thermodynamics takes into account that temperature is something worth measuring because it predicts whether it will

transfer between objects or not. This is true regardless of how the object interact even if the two object interact are not in physical contact, heat can still flow between them by means of radiation. On the other hand the zeroth law of thermodynamics states that if the system are in thermal equilibrium no heat flow will take place.

Thermal equilibrium :-

Temperature is the property that distinguishes thermodynamics from other science section. This property can distinguish between hot and cold. When two or more bodies are at different temperatures are brought into contact then after sometime they attempts common temperature and they are set to exist in thermal equilibrium. System are said to be thermal equilibrium. If there is no heat transfer even if they are in a position to transfer heat based in factors.

For eg:- If we put food in the refrigerator over night then the food is in thermal equilibrium with the air of the refrigerator. Heat no longer flows from

food to the air or from the air to the food and this state is known as thermal equilibrium.

This law is mostly used to compare the temperatures of different objects. If we want to measure the accurate temperature a reference body is required and the change in the characteristics of a body may be taken as the indication of a change in temperature.

The selected characteristic is known as thermodynamic property.

The most common application of zeroth law of thermodynamics can be seen in common thermometers having mercury in a tube. As the temperature increases, this mercury expands since the area of tube is constant. Due to this expansion the height is increased. Now the increase in height of the mercury level shows the changes in temperature basically helps us to measure it.

### Second law of thermodynamics

The first law of thermodynamics establishes an relation between heat and work. It follows

directly from this law that it is impossible to get work from any machine without giving it an equivalent amount of energy at any form. In other words this law is the generalization of the law of conservation of energy which include heat energy and states that the energy of the universe is constant. The first law of thermodynamics tell us that heat and mechanical work both are interconvertable. It does not tell us the limitation and condition for this conversion that is how much for this conversion that is how much heat is converted into work and whether the transformation itself can take place or not (The direction of energy transformation). The law specifying the condition of transformation of heat into work is called the second law of thermodynamics.

Kelvin statement of Second law  
It states that "It is impossible to get a continuous supply of work by cooling a body to a temperature lower than that

of the coldest of its surroundings"- or "A transformation whose only final result is to transform into work the heat extracted from a source which is at the same temperature through".

Clausius statement of the Second Law:-

It states that "It is impossible for any self-acting machine, an added by any external agency to transfer heat from one body to another at a higher temperature" or "It is impossible for any cyclic machine to produce no other effect than to convey heat continuously from one body to another at a higher temperature".

Both the statement of second law are equivalent. Violation of one automatic leads to violation of the other. They impart a direction for making the energy transformation possibilities. Let us take the following example of isolated isolation system.

1. Free expansion - The free expansion of an ideal gas from a region of high pressure to a region of low pressure takes

place spontaneously until a pressure become uniform.

(ii) Heat conduction - The passage of heat of from a region of high temperature to a region of low temperature takes place spontaneously until temperature become uniform.

(iii) Diffusion - The diffusion of a solute from a region of high temperature to a region of low temperature takes place spontaneously until temperatures become uniform.

Thus one can conclude that every system that is isolated changes continuously at slow or rapid rate in such a way as to approach a definite final state of equilibrium in such processes according to first law of thermodynamics. the total energy of a system involved remain constant before and after change. The important point to note in this process is the direction : e.g.: from high pressure to low pressure, from high

temperatures to low temp., from high concentration to low concentration.

There is thus a direction this allows the system to come to equilibrium. However if we imagine that after acquiring equilibrium the process is reversed then the system at its own will not move away to the state of equilibrium unless added by some external agency for example two bodies at the same temperature being in the state of thermal equilibrium will itself not create temperature difference between them provided one of them is not heated by some external source. "The principle which determines the direction from the process to take place is second law of thermodynamics." For first law it does not matter how the equilibrium has been attained because before and after the equilibrium state the equilibrium state, energy of a system remains the same. Therefore second law of thermodynamics can not be derived from first law. It requires another thermodynamical parameters for the description

and mathematical formulation.  
This parameter is entropy ( $S$ ).

## Unit - II

### Thermodynamic Potentials :-

The thermodynamic variables such as pressure ( $P$ ), temperatures ( $T$ ), volume ( $V$ ) and entropy ( $S$ ) define the state of a thermodynamical system. A relation between them exist because of the two thermodynamics law that is

$$dQ = dU + PdV$$

$$dQ = -TdS$$

which one combining give

$$TdS = dU + PdV$$

$$dU = TdS + PdV$$

Any of two these four variables are independent and then with the help of above relation the remaining variable can be determined for the full description of other phenomenon certain other relation among these variables are required. These relation terms as thermodynamic potential of their function

There exists four such potentials -

(1) Internal or Intrinsic energy

From the point of view of kinetic theory, matter is made up of molecules which are in a state of constant rapid motion, further they also possess inter-molecular attraction. Thus due to rapid motion they possess internal kinetic energy. And due and due to intermolecular attraction they possess internal potential energy.

The sum of these two energies is called total internal energy of system.

The internal energy is the independent on the path followed by the system in arriving at final state ( $f$ ) from the initial state

(i). It is the function of the two state only suppose  $dQ$  is the amount of heat absorbed by the system and  $dW$  is the work done by the system in arriving from initial state to final state then,

$$U_f - U_i = dU = dQ - dW$$

where  $U$  represent the change in internal energy of the system between the two states.

Putting  $dQ = Tds$  and  $dW = Pdv$  we get

$$dU = Tds - Pdv \quad \text{--- (1)}$$

Differentiating the internal energy partially w.r.t variable  $v$  and  $s$  we get

$$\cancel{\frac{\partial U}{\partial v}} \left( \frac{\partial U}{\partial v} \right)_S = -P \text{ and } \left( \frac{\partial U}{\partial s} \right)_v = T \quad \text{--- (2)}$$

As  $dU$  is a perfect differential we can write

$$\frac{\partial}{\partial s} \left( \frac{\partial U}{\partial v} \right) = \frac{\partial}{\partial v} \left( \frac{\partial U}{\partial s} \right)$$

putting for the b term from eq  $\cong$  (1) we get

$$\frac{\partial}{\partial s} (-P) = \frac{\partial}{\partial v} (T)$$

$$\left( \frac{\partial P}{\partial S} \right)_V = \left( \frac{\partial T}{\partial V} \right)_S \quad \text{--- (3)}$$

This equation establishes the relation among the four thermodynamical variables  $P, V, S$  and  $T$ . This is the first term relation.

(2) Helmholtz Function  $F$  :- One combining the first and second

law of thermodynamics, we have

$$dU = TdS - dW$$

suppose the temperature of the system remain constant, then

$$d(TS) = TdS$$

so that  $dU = d(TS) - dW$

$$\text{or } d(U - TS) = -dW$$

where the function  $F = U - TS$ . — (4)

is called Helmholtz function or Helmholz free energy. Therefore.

$$dF = -dW$$

which represents that in reversible isothermal process, the work done by the system is equal to the decrease in Helmholtz function  $F$ . On account of this fact  $F$  is also called as work function.

Differentiating equation (4) we get

$$dF = dU - TdS - SdT$$

Applying eq (1) we get

$$\begin{aligned} dF &= TdS + PdV - TdS - SdT \\ &= -PdV + SdT \end{aligned} \quad — (5)$$

Taking partial differentials of  $F$  with respect to independent variable  $T$  and  $V$ , we get

$$\left(\frac{\partial F}{\partial T}\right)_V = -S \text{ and } \left(\frac{\partial F}{\partial V}\right)_T = -P \quad — (6)$$

As  $dF$  is a perfect differential, we can write,

$$\frac{\partial}{\partial V} \left( \frac{\partial F}{\partial T} \right) = \frac{\partial}{\partial T} \left( \frac{\partial F}{\partial V} \right)$$

Using equation (6), we get

$$\left( \frac{\partial S}{\partial V} \right)_T = \left( \frac{\partial P}{\partial T} \right)_V \quad \text{--- (2)}$$

This equation establishes a relation among four thermodynamical variables  $P, V, S$  and  $T$ . This is second thermodynamical relation.

Physical significance :- from eq<sup>n</sup> (4), we find that  $TS$  is  $(U - F)$  and is called latent energy or bound energy of the system as it can not be used in useful form. Therefore.

$$U = F + TS$$

can be written in words as

Intrinsic energy = Helmholtz free energy  
+ latent energy

$$dU = dF + TdS$$

$$= dF + dQ$$

$$\text{or } dF = dU - dQ$$

$$- dF = dW$$

from first law of thermodynamics.  
 $dW$  is work done by the system in a reversible process and is therefore maximum.

This relation predicts that free energy  $F$  is such that decrease in it ( $-dF$ ) gives the maximum amount of work done ( $dW$ ) by the system during an isothermal change from its initial state to final state.

### (3) Enthalpy or Heat content $H$ :-

Thermodynamical phenomena at constant pressure are expressed in terms of another function called enthalpy or heat content of the system given by the relation.

$$H = U + PV \quad \text{--- (8)}$$

Differentiating we get

$$\begin{aligned} dH &= dU + PdV + VdP \\ &= T(ds - Pdv) + PdV + VdP \\ &= Tds + VdP \quad \text{--- (9)} \\ &= Tds, \end{aligned}$$

because process is carried out at constant pressure. Since  $Tds = dQ$  we find  $dH = dQ$  that is enthalpy represents the quantity of heat given to the system from an external source and hence the name heat content.

Let  $H_i$  and  $H_f$  be the initial and final enthalpies of the system, then

$$H_f - H_i = Q$$

Thus the change in enthalpy during an isobaric process equal to the heat transferred.

The enthalpy function  $H$  has an important property in porous plug experiment. In this experiment, a gas is made of pass under a constant pressure through insulated porous plug to a region of lower constant pressure. Let  $p_i$  and  $v_i$  be the initial pressure and volume respectively of a gas before passing the porous plug. Similarly, let  $p_f$  and  $v_f$  be the similar quantities of the gas after passing through the porous plug.

$$\text{External workdone by gas} = p_f v_f - p_i v_i$$

This workdone is at the cost of the initial internal energy of the gas, because no heat exchanges between gas and surroundings. Suppose  $U_i$  and  $U_f$  be the initial and final internal energies, then

$$U_i - U_f = p_f v_f - p_i v_i$$

$$\text{or } U_f + p_i v_i = U_i - p_f v_f$$

$$\text{or } H_i = H_f$$

Thus in a throttling process (such as porous plug experiments), the initial and final enthalpies remain the same.

Taking partial differential of  $H$  with respect to independent variable  $S$  and  $P$ , we get

$$\left(\frac{\partial H}{\partial P}\right)_S = V \text{ and } \left(\frac{\partial H}{\partial S}\right)_P = T \quad \text{--- (10)}$$

As  $dH$  is a perfect differential, we can write

$$\frac{\partial}{\partial S} \left( \frac{\partial H}{\partial P} \right) = \frac{\partial}{\partial P} \left( \frac{\partial H}{\partial S} \right)$$

using eq <sup>w</sup>(10), we get

$$\left(\frac{\partial V}{\partial S}\right)_P = \left(\frac{\partial T}{\partial P}\right)_S \quad \text{--- (11)}$$

This is relation among four thermodynamical variables and is third thermodynamical relation.

4. Gibbs Potential  $G$  :-

Suppose the thermodynamic process is isothermal and isobaric ( $dP = 0$ ), then from eq <sup>w</sup>(9), we get

$$dH = T(dS) + d(TS)$$

$$\text{or } d(H - TS) = 0$$

$$G = H - TS$$

$$= U + PV + TS \quad \text{--- (12)}$$

is called Gibbs function or Gibbs free energy.

Differentiating equation (12), we get

$$\begin{aligned} d(G_i) &= dU + PdV + VdP + TdS = SdT \\ &= (TdS - PdV) + PdV + VdP - TdS = SdT \\ &= VdP - SdT \end{aligned} \quad (3)$$

Taking the partial derivatives of  $G_i$  with respect to independent variables  $P$  and  $T$  we get

$$\left(\frac{\partial G_i}{\partial P}\right)_T = V \text{ and } \left(\frac{\partial G_i}{\partial T}\right)_P = -S$$

As  $dG_i$  is a perfect differential, we can write

$$\frac{\partial}{\partial T} \left( \frac{\partial G_i}{\partial P} \right)_T = V \text{ and } \left( \frac{\partial^2 G_i}{\partial T \partial P} \right)_P = -S \quad (4)$$

As  $dG_i$  is a perfect differential

Using equation (4) we get

$$\left(\frac{\partial V}{\partial T}\right)_P = \left(\frac{\partial S}{\partial P}\right)_T \quad (5)$$

This is fourth thermodynamical relation.

Physical significance:- Equation (12) can be written as

$$H = G_i + TS$$

In this equation term  $TS$  can be written as

$$U - F = TS \quad (\text{From eq } (4))$$

where  $(U - F)$  is called latent energy or bound energy of the system as it

can not be used in useful form. Therefore we can write the above expression of  $H$  as

enthalpy = Gibbs free energy + latent energy

$$G = U - TS + PV$$

$$\begin{aligned} dG &= dU - TdS - SdT + PdV + VdP \\ &= dW - SdT + PdV + VdP \end{aligned} \quad (1)$$

If the process is isothermal ( $dT = 0$ ) and isobaric ( $dP = 0$ ) then

$$\begin{aligned} dG &= -dW + PdV \\ -dG &= (dW - PdV) \end{aligned}$$

which predicts that  $-dG$  gives the maximum work which can be obtained from the system other than that due to change of volume ( $PdV$ ) at constant temperature and pressure. The work other than that due to change of volume is called net work. Hence net work  $= PdV$ .

Date- 15/07

Maxwell's distribution law of velocity:-

The molecule of a gas do not at all move with the same speed. Due frequent mutual collision and so their velocities vary. The manner in which the molecule of gas is are distributed over the possible velocity from zero to very high value was first worked out by Maxwell.

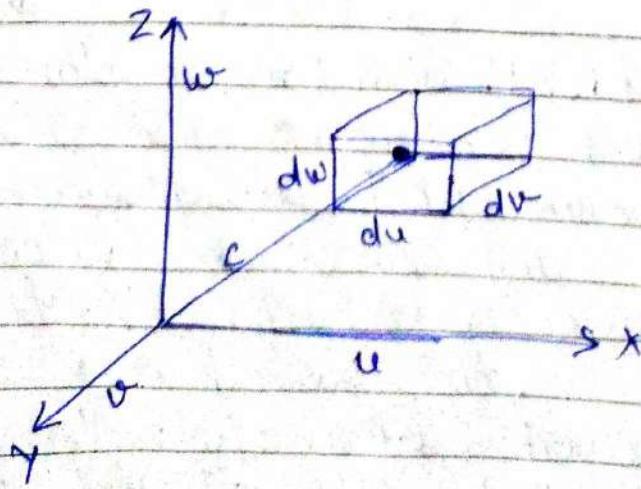
using the theory of probability: This law is known as Maxwell's distribution law. In deriving this law certain assumptions are made which are as follows -

(1) The gas in an enclosed maintain as a constant temperature assumption a steady state in which it is in thermal equilibrium with its surrounding.

In the steady state the density of a gas remains uniform on an average throughout the gas.

(2) The velocity along the three co-ordinate axes are independent of each other, i.e. the probability of a molecule along any axis will depend on the velocity along that axis only and not on the other two.

The probability of the velocity of a molecule lying between certain limits is the function of velocity and of the limit considered.



Let  $u, v, w$  be the component velocities of a molecule along  $x, y, z$  axis respectively as shown in the fig. The number of molecules per cubic centimeter ( $\text{cc}$ ) having the velocity lying between  $u$  and  $u+du$  can be denoted by  $n(u)$ .  $n(u)$  must be sum function of  $U$ , i.e.  $n(f(u))$ . Where  $n$  is the number of molecule per  $\text{cc}$  and  $f(u)$  is function of  $u$  to be determine. The probability that will have velocities lying between  $u$  and  $u+du$  is  $f(u)du$ . Hence the probability that a molecule may have its velocity simultaneously between  $u$  and  $u+du$ ,  $v$  and  $v+dv$ , and  $w$  and  $w+dw$  is

$$f(u)f(v)f(w) du dv dw \quad (1)$$

All the molecules whose velocity component lying in the range  $u$  and  $(u+du)$ ,  $v$  and  $(v+dv)$ , and  $w$  and  $(w+dw)$  will be contain in the element of volume. The chance that a single velocity of value  $c$  is in this volume element  $du dv dw$  is given by the assumption number 3 as  $\Phi F(c) du dv dw$  because  $du dv dw$  is the limit and  $F(c)$  represented is the function of velocity  $c$  for convenience we write the function  $\Phi(c)^2$

$$\therefore f(u)f(v)f(w) du dv dw = \Phi(c)^2 du dv dw$$

$$\text{or } f(u)f(v)f(w) = \phi(c)^2$$

$$f(u)f(v)f(w) = \phi(u^2+v^2+w^2)$$

where  $c^2 = u^2 + v^2 + w^2$  ————— (2)

The eq (2) determines the nature of distribution law. Differentiating eq (2) we get,

$$d[f(u)f(v)f(w)] = d[\phi(c)^2] = 0$$

because the for a particular value of  $c = \phi(c)^2$  is constant and its differential will be 0.

$$f'(u)f(v)f(w)du + f(u)f'(v)f(w)dv + f(u)f(v)f'(w)dw = 0$$

dividing by  $f(u)f(v)f(w)$ , we get

$$\frac{f'(u)f(v)f(w)}{f(u)f(v)f(w)} du + \frac{f(u)f'(v)f(w)}{f(u)f(v)f(w)} dv + \frac{f(u)f(v)f'(w)}{f(u)f(v)f(w)} dw = 0$$

$$\frac{f'(u)}{f(u)} du + \frac{f'(v)}{f(v)} dv + \frac{f'(w)}{f(w)} dw = 0$$

————— (3)

again  $c^2 = u^2 + v^2 + w^2$  on differentiation gives

$$d(c^2) = d[u^2 + v^2 + w^2]$$

$$0 = d(u^2) + d(v^2) + d(w^2)$$

$$0 = 2u du + 2v dv + 2w dw$$

Let the constant quantity will be 1 which is an arbitrary constant.

$$0 = \lambda u du + \lambda v dv + \lambda w dw \quad \text{--- (4)}$$

adding eq.(3) and (4), we get

$$\left( \frac{f'(w) + \lambda w}{f(w)} \right) du + \left( \frac{f'(v) + \lambda v}{f(v)} \right) dv + \left( \frac{f'(u) + \lambda u}{f(u)} \right) dw = 0 \quad \text{--- (5)}$$

According to assumption number (2) the velocity components are independent to each other. Hence eq. (5) can only be satisfied when each of the term is separately equal to zero.

$$\left( \frac{f'(u) + \lambda u}{f(u)} \right) du = 0 \quad \text{--- 6(a)}$$

$$\left( \frac{f'(v) + \lambda v}{f(v)} \right) dv = 0 \quad \text{--- 6(b)}$$

$$\left( \frac{f'(w) + \lambda w}{f(w)} \right) dw = 0 \quad \text{--- 6(c)}$$

Now Integrating eq. 6(a) we have

$$\int \left\{ \frac{f'(u) + \lambda u}{f(u)} \right\} du$$

$$+ \frac{f'(u) du - \int \lambda u du}{f(u)}$$

$$= \log_e f(u) = -\lambda \frac{u^2}{2} + \log_e A$$

$A = \text{constant}$   
of integration

thus

$$\log_e f(u) - \log_e A = \lambda \frac{u^2}{2}$$

$$\log \frac{f(u)}{A} = -\frac{\lambda u^2}{2}$$

$$f(u) = A e^{-\lambda u^2}$$

$$f(u) = A e^{-\frac{\lambda u^2}{2}}$$

Let  $\frac{\lambda}{2} = \frac{1}{\alpha^2}$  therefore the eq will

become

$$f(u) = A e^{-u^2/\alpha^2} \quad (7)$$

Similarly writing for other two component

$$f(v) = A e^{-v^2/\alpha^2} \quad (8)$$

$$f(w) = A e^{-w^2/\alpha^2} \quad (9)$$

From eqn (7), (8) and (9) we have

$$f(u)f(v)f(w) = A^3 e^{-(\frac{u^2+v^2+w^2}{\alpha^2})} \quad (10)$$

Thus the probability that molecule have the velocity between  $u$  and  $(u+du)$  is given by

$$f(u)du = A e^{-u^2/\alpha^2} du \quad (11)$$

Evaluation of constant  $A$  and  $\alpha$ .  
 The only problem remains to evaluate the value of the constant  $A$  and  $\alpha$  in terms of known quantities.

Let  $n$  be the number of molecules per c.c. the gas with all possible velocities from  $-\infty$  to  $+\infty$ . Then the number of molecules per cc. with velocity components between  $u$  and  $u+du$ ,  $v$  and  $v+dv$  and  $w$  and  $w+dw$  is  $n f(u) f(v) f(w) du dv dw$ . Hence

$$\iiint_{-\infty}^{+\infty} n (f(u) f(v) f(w)) du dv dw = n$$

$$\text{or, } \iiint_{-\infty}^{+\infty} A^3 e^{-(u^2 + v^2 + w^2)/\alpha^2} du dv dw = 1 \quad (1)$$

The value of the definite integral  $\int_{-\infty}^{+\infty} e^{-u^2/\alpha^2} du = \sqrt{\pi} \cdot \alpha$

$$\int_{-\infty}^{+\infty} e^{-u^2/\alpha^2} du = \sqrt{\pi} \cdot \alpha$$

$$\therefore A^3 (\sqrt{\pi})^3 \alpha^3 = 1$$

$$A = \frac{1}{\alpha \sqrt{\pi}}$$

In order to consider the value of  $\alpha$ , we calculate the pressure exerted by the gas on the walls of the enclosure. Let consider the case of a molecule moving along  $x$  axis with velocity  $u$ . The molecule will

collide with the surface of the enclosure which is perpendicular in X axis and will be reflected back with velocity  $-u$ . The change in momentum of the molecule will be  $2mu$ . The components v and w do not contribute anything to the pressure for this surface. We know that the pressure is equal to the change in momentum suffered by the molecules striking per unit area of the wall per second. If  $n_u$  be the number of molecules per unit volume having velocity  $u$ , then the number of impacts on an area  $\Delta A$  in time  $\Delta t$  will be  $n_u u \Delta A \Delta t$ . Now the pressure  $P$  on the wall averaged through the time interval  $\Delta t$  given by.

$$P \Delta A \Delta t = \sum_{u=0}^{\infty} 2mu \times n_u u \Delta A \Delta t$$

$$P = 2m \sum_{0}^{\infty} n_u u^2 \quad \text{--- (13)}$$

The number of molecules per cc having velocity component lying between  $u$  and  $u+du$  is given in accordance with eq. (11) by

$$n_u = n f(u) = n A e^{-u^2/\alpha^2}$$

$$= n \frac{1}{\alpha \sqrt{\pi}} e^{-u^2/\alpha^2} \quad \text{--- (14)}$$

Substituting the value of  $n_u$  from eq. (14) in eq. (13), we have

$$P = 2m \sum_{n=0}^{\infty} n \frac{1}{\alpha \sqrt{\pi}} e^{-u^2/\alpha^2} u^2$$

Replacing the sign of summation by integration we have

$$P = 2m \int_0^{\infty} n \frac{1}{\alpha \sqrt{\pi}} e^{-u^2/\alpha^2} u^2 du$$

$$= 2mn \cdot \frac{1}{2\sqrt{\pi}} \int_0^{\infty} e^{-u^2/\alpha^2} u^2 du$$

$$= 2mn \cdot \frac{1}{2\sqrt{\pi}} \cdot \frac{1}{4} \cdot \sqrt{\pi} \cdot \sqrt{2\alpha}$$

$$= \frac{mn}{2} \alpha^2$$

$$\text{because } \int_0^{\infty} e^{-u^2/\alpha^2} u^2 du = \frac{1}{4} \sqrt{\pi} \alpha^2$$

We also known that

$$P = nkT$$

$$nkT = \frac{mn}{2} \alpha^2$$

$$\frac{1}{\alpha^2} = \left( \frac{m}{2kT} \right) \quad (15)$$

$$A = \frac{1}{2\sqrt{\pi}} = \sqrt{\left( \frac{m}{2\pi kT} \right)} \quad (16)$$

Now the number of molecules dn having velocity components lying b/w u and u+du v and dv, w and w+dw is given by

$$dn = n f(u) f(v) f(w) du dv dw$$

$$= n A^3 e^{-\frac{(u^2+v^2+w^2)}{2}} du dv dw$$

$$= \frac{n}{m} \left( \frac{m}{2\pi kT} \right)^{3/2} \exp \left[ -\frac{m(u^2+v^2+w^2)}{2kT} \right] du dv dw$$

— (7)

This is known as Maxwell distribution law of velocity.

### K-3 Viscosity

According to Maxwell's law of distribution of velocities, most of the molecules of a gas are moving with most probable speed but individual molecule deviates from the standard value. Consider the case of a gas moving in parallel layers along the XY plane. The velocity of a layer in contact with XY plane is zero and increases towards the Z-axis. The tendency of the molecules in the upper layer is to accelerate the motion of the molecules in the lower layer while the tendency of the molecules in the lower layer is to retard the motion of the molecules in the upper layer. Thus a velocity gradient is established. Due to this velocity gradient, a viscous drag exists between the two layers or different layers of the gas tend to destroy the relative motion between

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them. This property of gas is called viscosity. If  $F$  be the viscous force acting between two layers, and  $A$  be the area of cross-section of the layer, then

$$F \propto A \frac{dv}{dz}$$

where  $(dv/dz)$  is velocity gradient along the  $z$ -direction, i.e. rate of change in velocity per unit length along  $z$ -axis. Then

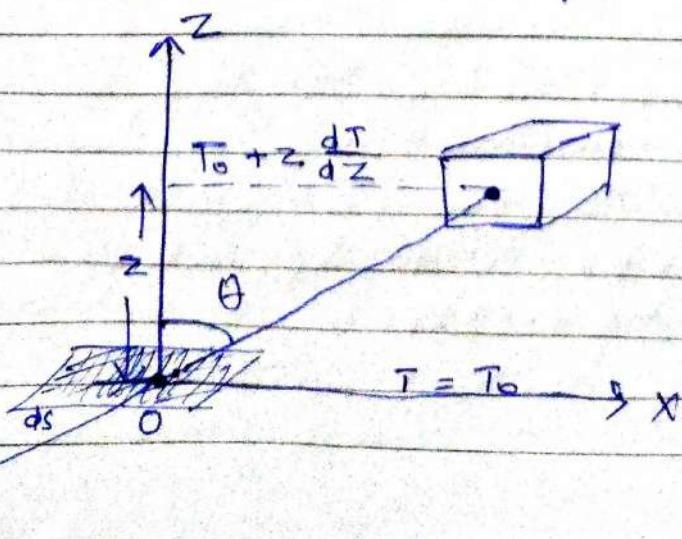
$$F = -\eta A \frac{dv}{dz}$$

where  $\eta$  is constant, known as coefficient of viscosity.

## Heat conduction

The conduction of heat through a gas is a molecular process. The gas molecules in a hotter region have greater average kinetic energies in comparison to those which are in the hotter region. When the hotter molecules collide with colder molecules they impart their excess energy. The thermal conductivity is the transport of energy resulting from molecular motion.

The problem of heat conduction may be treated in a similar way as that viscosity. The only difference is that in the heat the molecules are considered as the carrier of heat energy instead of momentum, assume the static thermal state of a gas. Let there exist an temperature gradient let  $T_0$  is its temperature. The temperature at a distance  $z$  above  $T_0$  and below the XY plane.



$$T_z = \left[ T_0 + z \frac{dT}{dz} \right]$$

Let  $n$  be the no. of molecule per cc,  
 $\lambda$  the mean free path and  $\vec{v}$  avg  
velocity. In order to consider no.  
of molecule striking the elementary  
surface area  $ds$  of the XY plane in  
time  $dt$ . We assume a volume element  
 $dV$  at a distance  $r$  from  $ds$  making  
an angle  $\theta$  with  $z$  axis. Now the  
no. of molecules present in this volume  
 $dV$  having velocities lying between  $v$   
and  $v+dv$  is given by

$$n dv \frac{4v^2}{\lambda^3 \sqrt{\pi}} e^{-v^2/\lambda^2} dv$$

where

$$\frac{1}{\lambda^2} = \frac{1}{2}$$

The no. of molecules coming out from  
the volume  $dV$  towards the area  
 $ds$  without any collision in this  
way is expressed as

$$n dv \frac{4v^2}{\lambda^3 \sqrt{\pi}} e^{-v^2/\lambda^2} dv \left( \frac{v^2}{\lambda} \right) \left( \frac{ds \cos \theta}{4\pi r^2} \right) \left( \frac{-r}{\lambda} \right)$$

~~dt~~ The total energy by these molecules

$$= mcv \left[ T_0 + 2 \frac{dT}{dz} \right] \times n dV \cdot \frac{4v^2}{\alpha^3 \sqrt{\pi}} e^{-v^2/\alpha^2} dv \left( \frac{\vec{v}}{\lambda} \right) \times \\ \left( \frac{ds \cos \theta}{4 \pi \alpha^2} \right) e^{-(r/\lambda)}$$

The energy carried by the molecules coming towards  $ds$  from volume element  $dV$  below the X-Y plane is given by

$$= mcv \left[ T_0 - 2 \frac{dT}{dz} \right] \times n dV \cdot \frac{4v^2}{\alpha^3 \sqrt{\pi}} e^{-v^2/\alpha^2} dv \left( \frac{\vec{v}}{\lambda} \right) \times \\ \left( \frac{ds \cos \theta}{4 \pi \alpha^2} \right) e^{-(r/\lambda)}$$

The net transfer of energy across  $ds$  in time  $dt$  can be obtained by subtracting the above expressions.

$$\therefore d(a\theta) = 2m cv 2 \left( \frac{dT}{dz} \right) \times n dV \cdot \frac{4v^2}{\alpha^3 \sqrt{\pi}} e^{-v^2/\alpha^2}$$

$$dv \left( \frac{\vec{v}}{\lambda} \right) \times \left( \frac{ds \cos \theta}{4 \pi \alpha^2} \right) e^{(-r/\lambda)} dt$$

$$\text{or } d\left(\frac{d\theta}{dt}\right) = 2m cv 2 \left( \frac{dT}{dz} \right) \times n dV \frac{4v^2}{\alpha^3 \sqrt{\pi}} e^{-v^2/\alpha^2}$$

$$dv \left( \frac{\vec{v}}{\lambda} \right) \times \left( \frac{ds \cos \theta}{4 \pi \alpha^2} \right) e^{(-r/\lambda)}$$

Substituting  $dV = r^2 dr \sin\theta d\theta d\phi$  and  $Z = r \cos\theta$  and integrating.

$$\int \frac{d(\theta)}{dt} = \frac{2m(vn\bar{v}ds)}{\alpha^3 \pi^{3/2} \lambda} \left( \frac{dT}{dz} \right) \int_0^\infty v^2 e^{-v^2/\alpha^2} dv$$

$$\int_0^{\pi} r e^{(-r/\alpha)} dr \int_0^{\pi} \sin\theta \cos^2\theta d\theta \int_0^{2\pi} d\phi$$

$$\text{or } \frac{d\theta}{dt} = \frac{2m(vn\bar{v}ds)}{\alpha^3 \pi^{3/2} \lambda} \left( \frac{dT}{dz} \right) \int_0^\infty v^2 e^{-v^2/\alpha^2} dv$$

$$\int_0^{\pi} \sin\theta \cos^2\theta d\theta \int_0^{2\pi} d\phi$$

$$\text{or } \frac{d\theta}{dt} = \frac{2m(vn\bar{v}ds)}{\alpha^3 \pi^{3/2} \lambda} \left( \frac{dT}{dz} \right) \left[ \frac{\alpha^3 \sqrt{\pi}}{4} \int(A)^2 \left( \frac{1}{3} \right) \right]_{(2\pi)}$$

$$\text{or } \frac{d\theta}{dt} = \frac{1}{3} \cdot mn \bar{v}^2 \lambda C_V \frac{dT}{dz}$$

But according to the definition of the coefficient of thermal conductivity we know that

$$\frac{d\theta}{dt} = k \cdot ds \frac{dT}{dz}$$

Comparing equations (1) and (2) we get

$$k = \frac{1}{3} \rho mn \bar{v}^2 \lambda C_V$$

$$= \frac{1}{3} \rho \bar{v}^2 \lambda C_V$$

$$= \eta C_V$$

(where  $\rho = mn =$   
density of gas)

where  $\eta = \frac{1}{3} p\vec{v} \cdot \vec{\lambda}$ .

This relation does not agree with the experiment data. According to the theoretical considerations,  $K/nC_V$  must be unity but it is found ~~per~~ practically equal to  $\epsilon$  which varies from 1 to 2.5. In case of monoatomic gases, Chapman obtained the following relation.

$$K = 2.5\eta C_V.$$

The value of  $\epsilon = 2.5$  is found fairly accurate in all monoatomic gases.

The evaluation of  $\epsilon$  in case of polyatomic molecules have internal motion in addition to translational  $\rightarrow$  is due to the fact that the polyatomic molecules have internal motion in addition to translational motion. For simplicity let us assume that the polyatomic molecules possess energy (other than translational) which is  $\beta$  times the average translational energy. Thus the average energy  $E$  is given by

$$\bar{E} = \frac{3}{2} RT + \beta \frac{3}{2} RT$$

$$= \frac{3}{2} RT (1 + \beta)$$

Now  $C_v$  measured in heat units is given by

$$C_v = \frac{1}{mJ} \cdot \frac{dE}{dT} = \frac{3R(1+\beta)}{2mJ} \quad (6)$$

we also know that

$$C_p - C_v = \frac{R}{mJ}$$

$$C_p = C_v + \frac{R}{mJ}$$

$$C_p = \frac{3R(1+\beta)}{2mJ} + \frac{R(2+3(1+\beta))}{2mJ} \quad (7)$$

$$\frac{C_p}{C_v} = \gamma = \frac{R[2+3(1+\beta)]}{3R(1+\beta)}$$

$$= 1 + \frac{2}{3(1+\beta)}$$

$$(1+\beta) = \frac{2}{3(\gamma-1)} \quad (8)$$

Substituting the value of  $C_v$  from equation (6) in equation (3), we have

$$K = \frac{3R(1+\beta)}{2mJ} \cdot n$$

When the energy is wholly translational ( $\beta = 0$ ) and the value of  $K$  should be multiplied by  $5/2$ . Combining these

two contributions to transport of energy we get.

$$K = \frac{3R}{2mJ} \eta (5/2 + \beta) = Cv$$

$$= \frac{Cv}{1+\beta} \cdot \eta (5/2 + \beta)$$

$$= \eta Cv \frac{(5/2 + \beta)}{(2 + \beta)} \quad \text{--- (7)}$$

Substituting the value of  $\beta$  and  $(1+\beta)$  from eq.  $\approx 8$  in eq.  $\approx 7$ , we get

$$K = \eta \cdot Cv \cdot \frac{3}{4} (9\gamma - 5)$$

$$\frac{K}{\eta Cv} - \varepsilon = \frac{(9\gamma - 5)}{4} \quad \text{--- (8)}$$

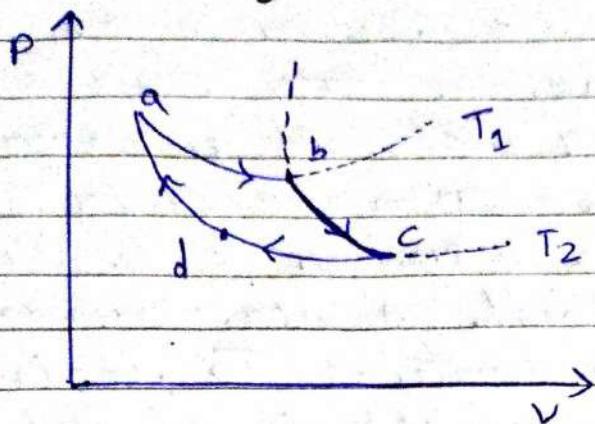
$\gamma = 1.66$  in case of monatomic gases,  
hence  $\varepsilon = 2.5$ .

$\gamma = 1.4$  in case of diatomic gases  
hence  $\varepsilon = 1.9$

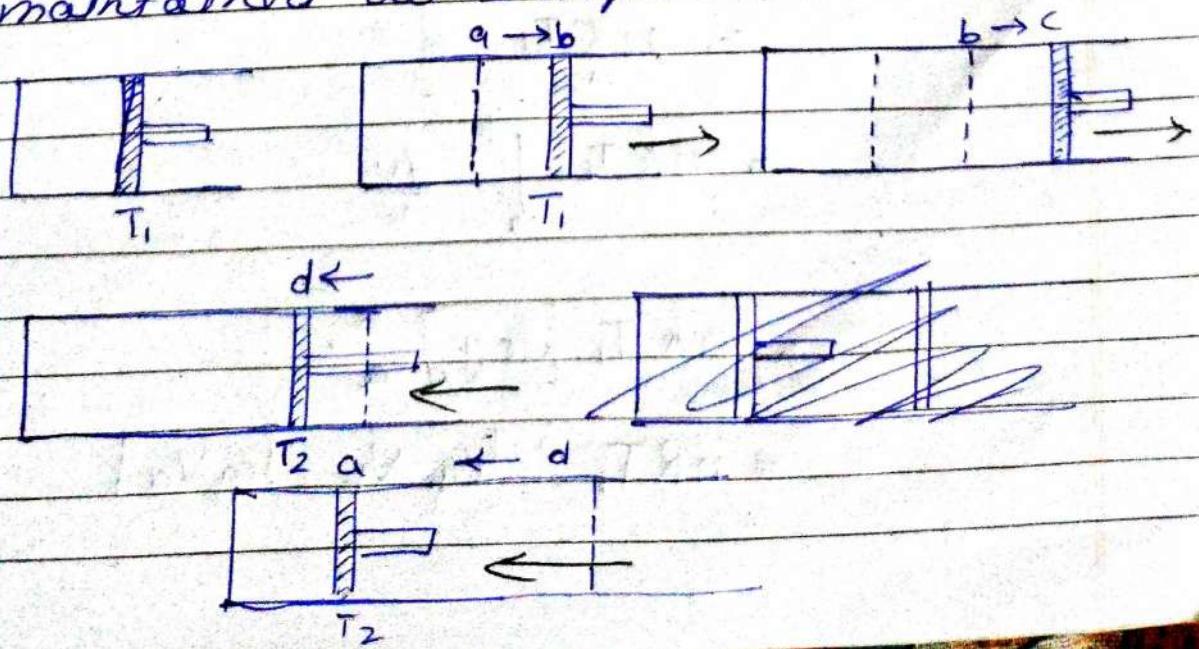
$\gamma = 1.3$  in case of triatomic gases,  
hence  $\varepsilon = 1.75$

The value of  $\varepsilon$  is still smaller in the case of polyatomic molecules. These values agree well with the experimental values.

## Carnot Cycle



Consider the closed cyclic path as shown above. The path  $a \rightarrow b$  is an isothermal expansion process,  $b \rightarrow c$  is an adiabatic expansion process,  $c \rightarrow d$  is an isothermal compression and  $d \rightarrow a$  is adiabatic process. Such a cycle bounded by two isothermals and two adiabatics is called a Carnot cycle. All processes are assumed to be reversible for correctness. Imagine a cylinder filled with a gas maintained at temperature  $T_1$ .



Let it undergo reversible isothermal expansion at  $T_1$  from  $a \rightarrow b$  in the indicator diagram - the cylinder insulated and let it undergo reversible adiabatic expansion to state  $c$ . which have the system at  $T_2$ , by placing in contact with a heat ~~reservoir~~ reservoirs at temperatures  $T_2$  it is made to undergo reversible insulated and made to undergo adiabatic contraction till the initial state  $a$  is reached during the process  $a \rightarrow b$  heat  $q_1$  is absorbed by the system and during the process  $c \rightarrow a$  heat  $q_2$  is released by the system. Assuming an ideal gas as a working substance  $q_1$ .

$$[Q] = \int P dV$$

(as  $\int du = u$  as the temperature is constant).

$$\begin{aligned}
 &= nRT_1 \int_a^b \frac{dV}{V} \\
 &= nRT_1 \int_a^b \frac{dV}{V}
 \end{aligned}$$

$$= nRT_1 \left[ \log V \right]_a^b$$

$$= nRT_1 (\log V_b - \log V_a)$$

$$= nRT_1 \log \left( \frac{V_b}{V_a} \right) \quad (1)$$

$$[Q_2] = \int P dV$$

$$= \frac{nRT_2}{V} dV$$

$$= nRT_2 \int_c^d \frac{dV}{V}$$

$$= nRT_2 \left[ \log V \right]_c^d$$

$$= nRT_2 (\log V_d - \log V_c)$$

$$= nRT_2 \log \left( \frac{V_d}{V_c} \right) \quad (2)$$

Now point b and c lie on an adiabatic. hence

$$T_1 = T_2 V_b^{\frac{1}{\gamma-1}} = T_2 V_c^{\frac{1}{\gamma-1}} \quad (3)$$

~~eliminating  $T_1$  and  $T_2$  we get,  
multiplying eq  $\cong (3)$~~

And b and c lie on an adiabatic  
hence

$$T_2 = V_d^{\frac{1}{\gamma-1}} = T_2 V_a^{\frac{1}{\gamma-1}} \quad (4)$$

~~eliminating  $T_1$  and  $T_2$  we get  
multiplying eq  $(3)$  and  $(4)$~~

$$V_b V_d = V_c V_a$$

$$\frac{V_b}{V_a} = \frac{V_c}{V_d} \quad \text{--- (5)}$$

$$\text{So efficiency } \eta = 1 - \left| \frac{\theta_2}{\theta_1} \right| \quad \text{--- (6)}$$

$$= 1 - \frac{T_2}{T_1} \cdot \frac{\log\left(\frac{V_d}{V_c}\right)}{\log\left(\frac{V_b}{V_a}\right)} \quad (\theta_2 \approx 5)$$

$$\boxed{\eta = 1 - \frac{T_2}{T_1}} \quad \text{--- (7)}$$

Thus the efficiency of carnot engine depends only on the temperature of two reservoirs. The nature of the working substance place no roll in efficiency.

Bose-Einstein Distribution law :- Let us consider a system having  $n$  indistinguishable particles. Let these particles be divided into quantum groups or levels such that there are  $n_1, n_2, \dots, n_i, \dots$  no. of particles in groups whose approximate constant energies  $\epsilon_1, \epsilon_2, \dots, \epsilon_i, \dots$  respectively. Let  $g_i$  be the number of eigen state of the  $i^{\text{th}}$  level.

In B-E statistics the conditions are :-

- i) The particles are indistinguishable from each other so that there is no distinction between the different way in which  $n_i$  particles can be chosen.
- ii) Each eigen state i.e. sub-level or call of  $i^{\text{th}}$  quantum state may contain 0, 1, 2 ... upto  $n_i$  identical particles.
- iii) The sum of energies of all the particles in the different quantum groups taken together constitutes the total energy of the system.

and  $n_i$  indistinguishable particles are to be distributed among these section.

The particles satisfying these conditions are called Bosons. Their spin is zero or 1. e.g. Meson, helium nuclei, phonons and photons.

for this distribution let us imagine a box divided among these section. The

that which of the compartment will have the sequencer, can be made in  $g_i$  ways. Once this have been done, the remaining  $(g_i - 1)$  compartments and  $n_i$  particles i.e total particles.

$(n_i + g_i - 1)$  can be arrange in any order i.e no. of ways doing this will be equal to  $(n_i + g_i - 1)!$ . This the total no. of ways realising the distribution will be  $g_i (n_i + g_i - 1)!$  . . . . . (1)

The particles are indistinguishable and therefore rearrangement of particles will not give rise to permutations which correspond to the same configuration, hence eq  $\cong$  (1) should be divided by  $n_i!$

Secondly the distribution which can be derived from one another by mere permutation of the cells among themselves, do not produce different states, the eq  $\cong$  (1) should also be divided by  $g_i!$  we thus obtain the required no. of ways as

$$g_i (n_i + g_i - 1)!$$

$$g_i! n_i!$$

$$\text{or } (n_i + g_i - 1)!$$

$$n_i! (g_i - 1)!$$

Similar expression will be for other quantum state so if there are  $n_1$  particles in energy level  $\epsilon_1$  of statistical weight  $g_1$ ,  $n_2$  particles in energy level  $\epsilon_2$  of statistical weight  $g_2$ , ..., then the total no. of distinguishable arrangements is

$$G_i = \frac{(n_1 + g_1 - 1)!}{n_1! (g_1 - 1)!} \cdot \frac{(n_2 + g_2 - 1)!}{n_2! (g_2 - 1)!} \cdots \frac{(n_i + g_i - 1)!}{n_i! (g_i - 1)!}$$

$$\text{or } G_i = \prod_i \frac{(n_i + g_i - 1)!}{n_i! (g_i - 1)!} \quad (2a)$$

As  $n_i$ 's and  $g_i$ 's are large no.s we may neglect 1 in the above exp.  $\approx$  so

$$G_i = \prod_i \frac{(n_i + g_i)!}{n_i! g_i!} \quad (2b)$$

In accordance with the postulate of equal a probability of state, the probability  $\omega$  of the system for occurring with the specified distribution is proportional to the total no. of eigen state i.e.

$$\omega = \prod_i \frac{(n_i + g_i)!}{n_i! g_i!} \times \text{constant.} \quad (3)$$

Taking log of eq  $\approx$ , we have

$$\log \omega = \log \left[ \prod_i \frac{(n_i + g_i)!}{n_i! g_i!} \times \text{const} \right]$$

$$\begin{aligned}
 &= \sum_i [ \log(n_i + g_i)! - \log n_i! - \log g_i!] + \text{cons.} \\
 &- \sum_i [(n_i + g_i) \log n_i] \\
 &= \sum_i [\log(n_i + g_i)! - \log n_i! - \log g_i!] + \text{cons.} \quad (4)
 \end{aligned}$$

On using stirling approximation,

$$\log n! = n \log n - n$$

so we get,

$$\log P = \sum_i [(n_i + g_i) \log(n_i + g_i) - n_i \log n_i - g_i \log g_i] + \text{cons.} \quad (5)$$

(Remembering that  $g_i$  is not subject to variation and  $n_i$  varies continuously)

On differentiating both sides

$$\begin{aligned}
 S(\log P) &= \sum_i [(n_i + g_i) \frac{\partial}{\partial (n_i + g_i)} \{ n_i + \log(n_i + g_i) \} \\
 &\quad - n_i \frac{\partial}{\partial n_i} \{ n_i - \log n_i \}] \\
 &= \sum_i [\log(n_i + g_i) - \log n_i] \delta n_i \\
 &= - \sum_i \left\{ \log \frac{n_i}{n_i + g_i} \right\} \delta n_i.
 \end{aligned}$$

for most probable distribution  $P_{\max}$ , we have  $S(\log P_{\max})$ . Thus the condition of most probability distribution given

$$S(\log \Omega_{\max}) = 0$$

$$\sum_i \left\{ \log \frac{n_i}{n_i + g_i} \right\} S n_i = 0 \quad (6)$$

The two subsidiary condition are -

- (i) Total no. of particles of the system is const.  
i.e.

$$n = \sum n_i = \text{const} \quad (7)$$

i.e.  $\delta n = \sum \delta n_i = 0$

- (ii) Total energy of the system is constant i.e.

$$E = \sum_i n_i E_i = \text{const.}$$

i.e.  $\delta E = \sum E_i \delta n_i = 0 \quad (8)$

on multiplying  $\delta g_i \approx (7)$  by  $\alpha$  and  $(8)$  by  $\beta$  and adding with  $\delta g_i \approx (6)$  where  $\alpha & \beta$  are largestes under minimum multiplier.

As the variations  $S n_i$  are independent of each other, we get

$$\log \left( \frac{n_i}{n_i + g_i} \right) + \alpha + \beta E_i = 0$$

$$\text{or } \frac{n_i}{n_i + g_i} = e^{-(\alpha + \beta E_i)}$$

$$\text{or } \frac{n_i + g_i}{n_i} = e^{\alpha + \beta E_i}$$

$$\text{or } 1 + \frac{g_i}{n_i} = e^{\alpha + \beta E_i}$$

$$\text{or } \frac{g_i}{n_i} = e^{\alpha + \beta E_i} - 1$$

$$\text{or } n_i = \frac{g_i}{e^{\alpha + \beta E_i} - 1}$$

Fermi-Dirac Distribution law, Degenerate electron gas, specific heat of degenerate electron gas -

F.D. statistics is obeyed by indistinguishable particles of half-integral spin that have anti-symmetrical wave function  $\psi_n$  and obey Pauli exclusion principle.

The particles satisfying these conditions are known as Fermions. e.g. - electrons, proton and neutrons. The fermions cannot be in the same single particle state.

In F.D. statistics the conditions are -

- (i) The particles are indistinguishable from each other so that there is no distinction between the different ways in which  $n_i$  principle particles are chosen.
- (ii) The principles obey Pauli's exclusion principle according to which each sub-level or cell may contain 0 or 1 particles. Then obviously  $g_i$  (degeneracy

or statistical weight or no. of sublevels) must be greater than or equal to  $n_i$ .

(iii) The sum of energies of all the particles in the different quantum groups taken together constitutes the total energy of the system.

Since due to Pauli's principle no cell can occupy more than one particle, so among  $g_i$  cells only  $n_i$  cells are occupied by are empty. The cells can be arranged in  $g_i!$  ways. But as the particles are indistinguishable all the occupied cells give rise to indistinguishable arrangements of  $n_i$  particles in  $g_i$  cells is

$$\frac{g_i!}{n_i!(g_i - n_i)!} \quad \textcircled{1}$$

Hence the total no. of eigen states for the whole system is given by

$$G_i = \prod_i \frac{g_i!}{n_i!(g_i - n_i)!} \quad \textcircled{2}$$

The probability  $\Omega$  of the system for occurring with the specified distribution is proportional to the total no. of eigen states i.e.

$$\Omega = \prod_i \frac{g_i!}{n_i!(g_i - n_i)!} \times \text{constant} \quad \textcircled{3}$$

on taking log on both sides

$$\log \Omega = \log \left\{ \pi_i \frac{g_i!}{n_i!(g_i - n_i)!} \right\}$$

$$= \sum_i \log g_i! - \log n_i! - \log (g_i - n_i)! + \text{const} \quad (4)$$

As  $n_i$  and  $g_i$  are large numbers, so using Stirling approximation, (4) reduces to

$$\begin{aligned} \log \Omega &= \sum_i [g_i + g_i \log g_i - n_i \log n_i + n_i - (g_i - n_i)] \\ &\quad + (g_i - n_i) + (g_i - n_i) + \text{const.} \end{aligned}$$

$$= \sum_i (n_i - g_i) \log (g_i - n_i) + g_i \log g_i - n_i \log n_i + \text{const} \quad (5)$$

on differentiating both sides ( $g_i = \text{const.}$ )

$$\begin{aligned} S(\log \Omega) &= \sum [ \log (g_i - n_i) - \log n_i ] S_{ni} \\ &= - \sum \left\{ \log \frac{n_i}{g_i - n_i} \right\} S_{ni} \quad (6) \end{aligned}$$

for most probable distribution  $\Omega = \Omega_{\text{max}}$   
so  $S(\log \Omega_{\text{max}}) = 0$ . Thus the conditions  
of most probable distribution gas

$$\sum_i \left\{ \log \frac{n_i}{g_i - n_i} \right\} S_{ni} = 0 \quad (7)$$

The two subsidiary conditions are:

(i) The total no. of particle of the system is constant

$$\text{i.e. } n = \sum n_i = \text{const.}$$

$$\text{i.e. } \delta n = \sum \delta n_i = 0 \quad \text{--- (8)}$$

(ii) Total energy of the system is constant

$$E = \sum_i n_i E_i = \text{const.}$$

$$\begin{aligned} \text{i.e. } \delta E &= \sum_i E_i \delta n_i \\ &= 0 \quad \text{--- (9)} \end{aligned}$$

on multiplying eq  $\cong$  (8) by  $\alpha$  and eq  $\cong$  (9) by  $\beta$  and adding with eq  $\cong$  (7) ( $\alpha$  &  $\beta$  are Lagrangian undetermined multiplier)

$$\sum_i \left\{ \log \frac{n_i}{g_i - n_i} + \alpha + \beta E_i \right\} \delta n_i = 0$$

As the variation  $\delta n_i$  are independent of each other. i.e.  $\delta n_i \neq 0$ . we get,

$$\log \left( \frac{n_i}{g_i - n_i} \right) + \alpha + \beta E_i = 0$$

$$-\alpha - \beta E_i$$

$$\text{or } \frac{n_i}{g_i - n_i} = e^{-\alpha - \beta E_i}$$

$$\text{or } \frac{g_i - n_i}{n_i} = e^{\alpha + \beta E_i}$$

$$\text{or } \frac{g_i}{n_i} - 1 = e^{\alpha + \beta E_i}$$

$$\text{or } \frac{g_i}{n_i} = e^{\alpha + \beta E_i} + 1$$

$$\text{or } n_i = \frac{g_i}{e^{\alpha + \beta E_i} + 1}$$

where  $\beta = \frac{1}{kT}$  &  $\alpha = -\frac{E_F}{RT}$ ,  $E_F$  = Fermi-energy

This is F.D distribution law which represents the most probable distribution of the particles among various energy levels for a system.

Degeneracy of a gas :- A gas is said to be degenerate if its behaviour (degenerate means deviation from standard behaviour.) contribution to the specific heat of metals at low temp is given by

$$c_V = \left( \frac{\partial E}{\partial T} \right)_V$$

$$= \frac{2}{\pi T} \left[ \frac{3}{5} N E_F(0) \left\{ 1 + \frac{5}{12} \left( \frac{\pi R T}{E_F(0)} \right)^2 \right\} \right]$$

$$= \frac{1}{2} \left( \frac{N \pi^2 R^2}{E_F(0)} \right) T$$

$$\text{or } C_V = \lambda T \text{ where } \lambda = \frac{N \pi^2 R^2}{2 E_F(0)} = \text{const.}$$

$$\therefore C_V \propto T$$

Thus the sp. heat of electron gas at constant volume is proportional to the absolute temp and vanishes at the absolute zero.

state-

Planck's law :-

Planck assumed that the walls of cavity to contain diebrical oscillators of all frequencies and assumed that they emit radiations into the cavity and also absorb radiations from it only in multiples of a certain minimum energy ( $E$ ) proportional to the frequency ( $\nu$ ) of the oscillator. Hence  $E = h\nu$  where  $h$  is the Planck's constant.

In the state of equilibrium the average rate of emission of energy by the oscillator is equal to the average rate of absorption of energy from the radiation field in the cavity. According to the law of electrodynamics, the average rate of emission of energy by oscillators of cyclic frequency  $\omega$  and of average energy

$$E = \frac{2e^2\omega^2}{3mc^3} \cdot E \quad \text{where } \omega = 2\pi\nu$$

$e$  = charge of each mass of oscillators  
 and  $m$  = mass of the oscillator.

According to the law of electrodynamics  
 the average rate of absorption of  
 energy by oscillators from radiation  
 field of energy density  $u_V = \frac{\pi e^2 u_V}{3m}$

for equilibrium,

$$\frac{2e^2\omega^2}{3mc^3} \cdot E = \frac{\pi e^2 u_V}{3m}$$

$$\text{or } u_V = \frac{8\pi\nu^2}{c^3} \cdot E \quad \dots \quad (1)$$

$$\therefore \omega = 2\pi\nu$$

To calculate the average energy of the  
 oscillators in thermal equilibrium  
 at temp T. let us assume that there  
 are  $n_0, n_1, n_2, n_3, \dots, n_x, \dots$  oscillators  
 of energy  $0, E, 2E, 3E, \dots, xE, \dots$ . Then  
 $\therefore N$  (total no. of oscillators) =  $\sum_{x=0}^{\infty} n_x$

$$\therefore E \text{ (total energy of the system)} = \sum_{x=0}^{\infty} n_x xE$$

According to Boltzmann distribution law

$$n_x = A e^{-\frac{xE}{RT}}$$

$$\text{where } x = 0, n_0 = n_0 \text{ and so } n_0 = A$$

$$\therefore N_r = n_0 e^{-\frac{\gamma E}{RT}}$$

$$\therefore \bar{E} = \frac{E}{N}$$

$$= \frac{\sum_{\gamma=0}^{\infty} n_0 e^{-\frac{\gamma E}{RT}} \gamma E}{\sum_{\gamma=0}^{\infty} n_0 e^{-\frac{\gamma E}{RT}}}$$

$$\bar{E} = \frac{e \sum_{\gamma=0}^{\infty} \gamma e^{-\frac{\gamma E}{RT}}}{\sum_{\gamma=0}^{\infty} e^{-\frac{\gamma E}{RT}}}$$

$$\text{Let } \omega = \frac{E}{RT} = \frac{h\nu}{RT}$$

(memorized)

$$\text{Then let } S = \sum_{\gamma=0}^{\infty} \gamma e^{-\gamma \omega} \quad (\text{assuming the } n$$

$$\text{or } S = e^{-\omega} + 2e^{-2\omega} + 3e^{-3\omega} + \dots + \gamma e^{-\gamma \omega} + \dots$$

$$\therefore S e^{-\omega} = e^{-2\omega} + 2e^{-3\omega} + \dots + (\gamma - 1)e^{-\gamma \omega} + \dots$$

or subtracting

$$S(1 - e^{-\omega}) = e^{-\omega} + e^{-2\omega} + e^{-3\omega} + e^{-\gamma \omega} + \dots$$

$$\text{or } S(1 - e^{-\omega}) = e^{-\omega} (1 + e^{-\omega} + e^{-2\omega} + e^{-3\omega} + \dots)$$

$\because$  bracketed term  $(1 - e^{-\omega})^{-1}$

$$\text{or } S(1 - e^{-\omega}) = \frac{e^{-\omega}}{1 - e^{-\omega}}$$

$$\text{or } S = \frac{e^{-\omega}}{(1 - e^{-\omega})^2}$$

$$\text{Let } S' = \sum_{\gamma=0}^{\infty} e^{-\gamma \omega}$$

$$\text{or } S' = 1 + e^{-x} + e^{-2x} + \dots + e^{-nx}$$

$$\text{or } S' = (1 - e^{-x})^{-1}$$

$$S' = \frac{1}{1 - e^{-x}}$$

$$\bar{E} = \frac{\frac{e^{-x}}{(1 - e^{-x})^2} \cdot e}{\frac{1}{1 - e^{-x}}}$$

$$\text{or } \bar{E} = \frac{e e^{-x}}{1 - e^{-x}}$$

$$\text{or } \bar{E} = \frac{e}{e^x - 1} = \frac{h\nu}{e^{h\nu/RT} - 1}$$

on putting in ①

$$\therefore U_V = \frac{8\pi V^2}{c^3} \cdot \frac{h\nu}{e^{h\nu/RT} - 1}$$

$$\text{or } U_V = \frac{8\pi h V^3}{c^3} \cdot \frac{1}{e^{h\nu/RT} - 1} \quad \textcircled{2}$$

To find  $U_\lambda$  we have to use the  
relations  $V\lambda = c$  and  $U_\lambda d\lambda = U_V dV$   
 $\therefore$  increase in frequency corresponds to  
a decrease in wavelength

$$\therefore -U_\lambda d\lambda = \frac{8\pi h}{c^3} \cdot \frac{1}{e^{h\nu/RT} - 1} \cdot d(\nu)$$

$$\text{or } -U_{\lambda} \Delta \lambda = -\frac{8\pi h c}{\lambda^5} \cdot \frac{\Delta \lambda}{e^{h\epsilon/kT} - 1}$$

The -ve sign shown that with increase in  $\lambda$ ,  $U_{\lambda}$  decreases.

$$\therefore U_{\lambda} = \frac{8\pi h c}{\lambda^5} \cdot \frac{1}{e^{h\epsilon/kT} - 1} \quad \text{--- (3)}$$

$$\therefore E_{\lambda} = \frac{e}{4\pi} U_{\lambda}$$

$$\therefore E_{\lambda} = \frac{2h\epsilon^2}{\lambda^5} \cdot \frac{1}{e^{h\epsilon/kT} - 1} \quad \text{--- (4)}$$

Any of the above (2), (3) & (4) is known as Planck's law

\* Deduction of Wien's law :-  
for shorter wavelength i.e.  $\lambda$  is small  
then  $e^{h\epsilon/kT} > 1$ , then Planck's  
law reduces to

$$U_{\lambda} = \frac{8\pi h c}{\lambda^5} \cdot \frac{1}{e^{h\epsilon/kT}}$$

$$\text{i.e. } \frac{h\epsilon}{\lambda_{m\text{RF}}} = 4.965$$

$$\text{or } \lambda_{m\text{RF}} = \frac{h\epsilon}{4955k}$$

$$\text{or } \Delta mT = \frac{6.62 \times 10^{-34} \times 3 \times 10^8}{4.965 \times 1.38 \times 10^{23}} \text{ mK} \quad \text{where } \kappa = 1.38 \times 10^{-23}$$

$$= 0.02899 \text{ mK}$$

$$\Delta mT = b$$

where  $b$  is known as Wein's displacement constant and this is Wein's displacement law.

2. Deduction of Stefan's - Boltzmann Law from Planck Constant Law

It state that the total amount of energy radiated per second per unit area of a perfectly black body is directly proportional to fourth power of the ~~absot~~ absolute temperature of the surface of the body i.e

$$E \propto T^4$$

$$\text{or } E = \sigma T^4 \quad \text{where } \sigma \text{ is called Stefan's constant and its value is } 5.67 \times 10^{-8} \text{ JS}^{-1} \text{ m}^{-2} \text{ K}^{-4}$$

It was theoretically explained by Boltzmann, so this law is also known as Stefan's - Boltzmann Law. The total energy inside the hollow shell enclosures having end all possible wavelength is given by

$$E = \int_0^{\infty} E(\lambda) d\lambda \quad \text{--- (1)}$$

But from Planck's Law

$$E(\lambda) d\lambda = \frac{8\pi h c}{\lambda^5} \frac{1}{e^{\frac{hc}{\lambda RT}} - 1} d\lambda$$

Then eqn (0) becomes

$$E = \int_0^\infty 8\pi h c \frac{\lambda^{-5}}{e^{\frac{hc}{\lambda RT}} - 1} d\lambda$$

This can also be expressed in form of all frequencies i.e. from  $\nu = 0$  to  $\nu = \infty$

Then

$$E = \frac{8\pi h}{c^3} \int_0^\infty \nu^3 \frac{d\nu}{e^{\frac{h\nu}{RT}} - 1}$$

on putting  $d\nu = \frac{RT}{h} dx$  we have  $d\nu = \frac{RT}{h} dx$

$$\therefore E = \frac{8\pi h}{c^3} \left( \frac{RT}{h} \right)^4 \int_0^\infty \frac{x^3}{e^x - 1} dx$$

$$= \frac{8\pi h}{c^3} \left( \frac{RT}{h} \right)^4 \int_0^\infty \frac{x^3 e^x}{e^{2x} (1 - e^{-x})} dx$$

$$= \frac{8\pi h}{c^3} \left( \frac{RT}{h} \right)^4 \int_0^\infty x^3 e^{-x} (1 - e^{-x})^{-1} dx \quad (2)$$

Since  $F(\nu) d\nu$  is always a +ve quantity

$$\therefore e^{\frac{h\nu}{RT}} > 1 \text{ or } e^x > 1$$

$$\text{Hence } e^{-x} < 1$$

Hence by using binomial theorem, we

get

$$(1 - 2e^{-2x})^{-1} = 1 + e^{-2x} + e^{-4x} + \dots$$

∴ Eq ② becomes

$$E = \frac{8\pi R^4 T^4}{C^3 h^3} \int_0^\infty 2e^{3x} e^{-2x} (1 + e^{-2x} + e^{-4x} + \dots) dx$$

$$\text{or } E = \frac{8\pi R^4 T^4}{C^3 h^3} \int_0^\infty 2e^{3x} \sum_{m=1}^\infty e^{-mx} dx \quad \text{--- ③}$$

Now using standard integral

$$\int_0^\infty \sum_{m=1}^\infty x^3 e^{-mx} dx = \sum_{m=1}^\infty \frac{6}{m^4} \text{ where } m \text{ is an integer}$$

and  $\sum_{m=1}^\infty \frac{1}{m^4} = \frac{\pi^4}{90}$  standard mathematical result

∴ eq ③ becomes

$$E = \frac{8\pi R^4 T^4}{C^3 h^3} 6 \sum_{m=1}^\infty \frac{1}{m^4}$$

$$\text{or } E = \frac{8\pi R^4 T^4}{C^3 h^3} 6 \cdot \frac{\pi^4}{90}$$

$$\text{or } E = \left( \frac{8\pi^5 R^4}{15 C^3 h^3} \right) \cdot T^4$$

$$\Rightarrow E = \sigma T^4$$

$$\text{where } \sigma = \frac{8\pi^5 R^4}{15 C^3 h^3}$$

This is Stefan's - Boltzmann Law

③ Deduction of Wien's Distribution Law :-  
According to Planck's law, we have

$$E \lambda d\lambda = \frac{8\pi hc}{\lambda^5} \frac{1}{e^{\frac{hc}{\lambda RT}} - 1} d\lambda$$

If  $\lambda$  is small then  $\frac{hc}{\lambda RT}$  is large and hence  
 $e^{\frac{hc}{\lambda RT}} \gg 1$

$$\therefore E \lambda d\lambda = \frac{8\pi hc}{\lambda^5} \frac{1}{e^{\frac{hc}{\lambda RT}}} d\lambda$$

$$\begin{aligned}\therefore E \lambda d\lambda &= \frac{8\pi hc}{\lambda^5} \frac{d\lambda}{e^{\frac{hc}{\lambda RT}}} \\ &= \frac{8\pi hc}{\lambda^5} e^{-\frac{hc}{\lambda RT}} d\lambda\end{aligned}$$

$$E \lambda d\lambda = A \frac{f(\lambda T)}{\lambda^5} d\lambda$$

where  $A = 8\pi hc$   
 $f(\lambda T) = e^{-\frac{hc}{\lambda RT}}$  function of  $\lambda$  &  $T$

This is the Wien's distribution law