If an amount of heat dQ is supplied to a system. This is used in the following three parts.

i) A part is used in raising the temperature of the system which is equivalent of increasing its kinetic energy (dU_K)

2) A part is used in doing internal work against molecular attraction which is equivalent of increasing the potential energy of the system (dU_P)

③ The rest part is used for doing external work (dW)

$$dQ = dU_K + dU_P + dW$$
$$dQ = dU + dW$$

Thus, i) The heat is a form of energy in transit

ii) energy is conserved in Thermodynamic System

iii) every thermodynamic system possess internal energy.

Heat Content (ENTHALPY) H.

Enthalpy (H) is a property of the system, which is mathematically defined as

$$H = U + PV$$

U – Total internal energy of the system and

PV : is the work energy.

differentiate th above equation

$$dH = dU + d(PV) = dU + PdV + VdP.$$

if this process occurs at constant pressure then $dP = 0$ then.

$$dH = dU + PdV.$$

but $PdV = dW$ work done.

$$\therefore \quad dH = dU + dW. \longrightarrow ①$$

But th the first law of thermodynamics is

$$dQ = dU + dW \longrightarrow ②$$

Comparing $dH = dQ$

This explain the name of heat content (Enthalpy)

Heat Capacity

The heat capacity (C) of the system is defined as the ratio of the ~~[illegible]~~ heat energy absorbed by the system from the surroundings to increase the temperature of th system.

$$C = \frac{dQ}{dT}$$

The heat capacities can be measured at constant volume (C_v) and at constant pressure (C_p)

While the system remains at constant volume

$$C_v = \cancel{\frac{dQ}{dT}} \qquad C_v = \left(\frac{dQ}{dT}\right)_v$$

while the system remains at Constant pressure.

$$c_p = \left(\frac{dQ}{dT}\right)_p$$

Relation between c_p and c_v

If v and T are chosen as the independent variables

$$U = f(v, T)$$

differentiate it $du = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial v}\right)_T dv \longrightarrow ①$

According to first law of thermodynamics.

$dQ = du + p\,dv \longrightarrow ②$ $(dw = p\,dv)$

equ ① apply in equ ②

$$dQ = \left(\frac{\partial U}{\partial T}\right)_v dT + \left(\frac{\partial U}{\partial V}\right)_T dv + p\,dv.$$

divide by dT in both side.

$$\left(\frac{dQ}{dT}\right) = \left(\frac{\partial U}{\partial T}\right)_v \frac{\cancel{dT}}{\cancel{dT}} + \left(\frac{\partial U}{\partial V}\right)_T \frac{dv}{dT} + p\frac{dv}{dT}$$

$$\left(\frac{dQ}{dT}\right) = \left(\frac{\partial U}{\partial T}\right)_v + \left[p + \left(\frac{\partial U}{\partial V}\right)_T\right]\frac{dv}{dT} \longrightarrow ③$$

i) when the gas is heated at Constant Volume.

$$\left(\frac{dQ}{dT}\right)_v = c_v. \quad \text{and} \quad \frac{dv}{dT} = 0.$$

∴ eqn ③ will be

$$c_v = \left(\frac{\partial U}{\partial T}\right)_v$$

ii) when the gas is heated at Constant pressure

$$\left(\frac{dQ}{dT}\right)_P = C_P$$

from equ ③

$$C_P = C_V + \left[P + \left(\frac{\partial u}{\partial v}\right)_T\right]\left(\frac{\partial v}{dT}\right)_P$$

$$C_P - C_V = \left[P + \left(\frac{\partial u}{\partial v}\right)_T\right]\left(\frac{dv}{dT}\right)_P$$

For perfect gas $\left(\frac{\partial u}{\partial v}\right) = 0$

$$\therefore \boxed{C_P - C_V = P\left(\frac{dv}{dT}\right)}$$

ENTROPY and Second law of thermodynamics

The Concept of entropy is transformation.

Some example of ~~spontaneously at a~~ changes are following

1. The expansion of an ideal gas from a region of high pressure to one of low pressure takes places spontaneously until pressure become uniform.
2. Similarly, the diffusion of solute from a region of high concentration - low concentration until become uniform.
3. Inly the passage of heat from high temperature to low temperature until become uniform.

In each of above processes, according to first law of thermodynamics, the total energy of the system is remains Constant.

- Reverse process ? we need external energy.
- If internal energy of the two system is same.....
  what happen, How can explain the direction of the transformation. To explain these things a desired property in necessary.

The physical quantity entropy is a measurable property and describes the ability of the system to do work.

The more usual forms of the Second law of Thermodynamics are as follows.

i. It is impossible the sole effect of extracting heat from a single reservoir and performing an equivalent amount of work.

ii. It is impossible to heat to flow from a cooler body to another hotter body without any external work.

This is known as Kelvin-Planck statment and latter known as clausius statement.

If dQ is the quantity of heat absorped or rejected at a temperature T is going from state A to state B then the change in entropy ds is given by

$$ds = \frac{dQ}{T} \rightarrow dQ = T \cdot ds.$$

This is second law of thermodynamics in mathematical form.

Calculations of Entropy

1. Entropy of an ideal gas:-

Let us consider n gram of molecules of an ideal gas occupying a volum V at a pressure P and temperature T. Let quantity of heat dQ be given to the gas, then the first law of Thermodynamics

$$dQ = dU + dw$$

If C_v is the heat capacity of the gas at Constant volume, dT the rise in temperature and dv change in volume then

$$du = C_v dT \qquad \text{and} \qquad dw = P\cdot dv.$$

$$\therefore \; dQ = C_v dT + P\cdot dv.$$

Hence The change in entropy, by 2nd law

$$ds = \frac{dQ}{T} = \frac{C_v dT}{T} + \frac{P dV}{T} \longrightarrow ①$$

If we select arbitrary reference state 1 at temp T_0, pressure P_0 and volume V_0 entropy is S_0. Then the entropy of the gas in the state 2 at temp T, pressure P and volume V is given by

$$S = S_0 + \int_1^2 \frac{C_v dT}{T} + \int_1^2 \frac{P dv}{T} \longrightarrow ②$$

Ⓐ value of S in terms of temperature & volume:-

we know ~~from~~ $PV = nRT \longrightarrow P = \frac{nRT}{V}$

apply in equ ②.

$$S = S_0 + \int_1^2 C_v \frac{dT}{T} + nR\int_1^2 \frac{dV}{V}$$

If C_v is constant then

~~$S = S_0 + \int_1^2 C_v \frac{dT}{T} + n$~~

$$S = S_0 + C_v \log\frac{T}{T_0} + nR \log\frac{V}{V_0}.$$

For the case of Isothermal expansion, $T = T_0$ Then

$$S = S_0 + nR \log_e \frac{V}{V_0}$$

Ⓑ Value of S in terms of temperature & pressure

$$PV = nRT \rightarrow V = \frac{nRT}{P}$$

differentiate pressure

$$Pdv + vdp = nRdT$$

$$Pdv = nRdT - vdp$$

$$Pdv = nRdT - nRT\frac{dp}{P}$$

Apply in equ ②

$$S = S_0 + \int_1^2 C_v \frac{dT}{T} + \int_1^2 \left(nR\,dT - nRT\frac{dP}{P}\right)\frac{\ }{T}$$

$$= S_0 + \int_1^2 C_v \frac{dT}{T} + nR\int_1^2 \left(\frac{dT}{T} - \frac{dP}{P}\right)$$

remove the integration.

$$S = S_0 + C_v \log_e \frac{T}{T_0} + nR\left(\log_e \frac{T}{T_0} - \log_e \frac{P}{P_0}\right)$$

$$S = S_0 + \underset{0}{C_v \log_e \frac{T}{T_0}} + (C_p - C_v)\left(\underset{0}{\log_e \frac{T}{T_0}} - \log_e \frac{P}{P_0}\right)$$

For Isothermal expansion $T = T_0$. Then

$$S = S_0 - (C_p - C_v)\log \frac{P}{P_0}$$

Ⓒ Value of S in terms of pressure and volume.

$$PV = nRT$$

$$T = \frac{PV}{nR} \rightarrow dT = \frac{Pdv + Vdp}{nR}$$

Apply in equ ②

$$S = S_0 + \int_1^2 c_v \frac{pdv + vdp}{\cancel{nR}} \frac{\cancel{nR}}{pv} + \int_1^2 p dv \frac{nR}{pv}$$

$$S = S_0 + \int_1^2 c_v \left(\frac{\cancel{p}dv}{\cancel{p}v} + \frac{\cancel{v}dp}{p\cancel{v}} \right) + nR \int_1^2 \left(\frac{dv}{v} \right)$$

$$= S_0 + \int_1^2 c_v \left(\frac{dv}{v} + \frac{dp}{p} \right) + nR \int_1^2 \frac{dv}{v}$$

$$= S_0 + \int_1^2 c_v \left(\frac{dv}{v} + \frac{dp}{p} \right) + (c_p - c_v) \int_1^2 \frac{dv}{v}$$

$$= S_0 + \cancel{\int_1^2 c_v \frac{dv}{v}} + \int_1^2 c_v \frac{dp}{p} + \int_1^2 c_p \frac{dv}{v} - \cancel{\int_1^2 c_v \frac{dv}{v}}$$

$$S = S_0 + \int_1^2 c_v \frac{dp}{p} + \int_1^2 c_p \frac{dv}{v}$$

$$S = S_0 + c_v \log \frac{p}{p_0} + c_p \log \frac{v}{v_0}$$

2. Entropy of Steam.

Let us consider m gm of ice at absolute temp T_1, now we need find the total gain in entropy when the change in temperature T_2.

If a small amount of heat dq is given to substance the change in entropy is

$$ds = \frac{dq}{T}$$

To convert m gm of ice at T_1 K into water at the same temp. the amount of heat required mL_i where L_i latent heat of ic.

Hence change in entropy in this process

$$\frac{mL_i}{T_1}$$

Again when m gm of water at T_1 K is heated. to T_2 K, Then the change in entropy.

$$ds = \int_{T_1}^{T_2} \frac{dQ}{T} = \int_{T_1}^{T_2} \frac{mC\,dT}{T} \qquad \left(dq = \overset{\text{molag heat}}{m}\underset{\text{specific heat}}{C}\,dT\right.$$

$$ds = mC \log_e \frac{T_2}{T_1}$$

Now to convert m gm of water at T_2 K into Steam at the Same temper. the amount of heat required mL_s, where L_s Latent heat of Steam.

The chang in during this process $= \frac{mL_s}{T_2}$.

The Total gain in entropy ~~of~~ ~~at +~~ Steam at T_2 K

$$ds = \frac{mL_i}{T_1} + mC \log \frac{T_2}{T_1} + \frac{mL_s}{T_2}.$$

Thermodynamic potentials and reciprocity relations.

The first and Second law of thermodynamics provide the following functions.

$$dq = du + p\,dv \quad \text{and}$$

$$dQ = T.ds$$

Combining these.

$$T.ds = dU + p.dv$$

$$dU = T.ds - p.dv$$

For a Complete Knowledge of a homogeneous System, certain other relations are required that is thermodynamic potentials. There are four principal thermodynamic potentials.

① Internal Energy.

When a System apparently shows no mechanical energy, but is still capable of doing work. It is said to possess internal or Intrinsic energy.

The total kinetic energy of the molecules is called internal kinetic energy while the potential energy arising due to inter molecular attractions is called internal potential energy.

"When a System passes from one State to the other System, the change in the internal energy is independent of path followed between two states, but depends only on initial and final states."

From the first and Second law of thermodynamics

$$dU = T \cdot ds - p\,dv.$$

Differentiate this internal energy partially with respect to variables S and V. we get

$$\frac{\partial U}{\partial S} = T \quad \text{and} \quad \frac{\partial U}{\partial V} = -P.$$

These are relations Connecting the internal energy U with thermodynamic variables S, V, T, and P.

As dU is perfect differential then we have

$$\frac{\partial}{\partial V}\left(\frac{\partial U}{\partial S}\right) = \frac{\partial}{\partial S}\left(\frac{\partial U}{\partial V}\right)$$

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

This is first thermodynamical relations

② Helmholtz free energy

we know $\quad dU = TdS - dW \longrightarrow ①$

If we consider the system exchanges heat with the surroundings and maintained at constant temperature, then we may write

$$TdS = d(TS) \longrightarrow ②$$

equ ② in ①

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

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

$$d(U-TS) = -dW$$

or $\quad F = U - TS$

where this function is called Helmholtz free energy.

Differentiating this function then.

$$dF = dU - d(TS)$$

$$= dU - TdS - SdT$$

from equ ① $\quad dF = TdS - PdV \longrightarrow ③ \quad (dW = PdV)$

~~taking~~

Taking partial differential we get

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

As dF is a perfect differential.

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

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

$$\boxed{\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V}$$

This is second thermodynamical relation.

③ Enthalpy or Heat Content

Enthalpy (H) is a property of the system, it is mathematically write as

$$H = U + PV$$

differential $dH = dU + d(PV)$

$$= (T\,dS - P\,dV) + \cancel{P\,dV} + V\,dP$$

$$dH = T \cdot dS + V\,dP.$$

As S and P are independent variables, taking partial differentials of H

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

Since dH is a perfect differentials

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

thus

$$\boxed{\left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P}$$

This is third thermodynamical relation.

④ Gibb's potential (G)

from the definition of enthalpy

$$H = U + PV$$

differentiate

$$dH = dU + d(PV)$$

~~$= Tds - pdv + pdv + vdp$~~

$$= (Tds - \cancel{pdv}) + \cancel{pdv} + vdp$$

$$dH = Tds + v\,dp.$$

If the process is isothermal $[Tds = d(TS)]$ as well as isobaric $dp = 0$ then above equation

$$dH = d(TS)$$

$$dH - d(TS) = 0.$$

$$d(H - TS) = 0 \qquad dG = 0$$

$$\therefore G = H - TS.$$

This is thermodynamical potential at constant pressure. (or) Gibb's function.

$$G = U + PV - TS$$

$$dG = dU - TS + PV.$$

$$dG = dU - Tds - sdT + pdv + vdp.$$

But we know $dU = Tds - pdv.$ apply it

$$dG = \cancel{T\,ds} - \cancel{p\,dv} - \cancel{T\,ds} - s\,dT + \cancel{p\,dv} + v\,dp$$

$$dG = v\,dp - s\,dT$$

Taking partial differential.

$$\left(\frac{\partial G}{\partial P}\right)_T = V \quad \text{and} \quad \frac{\partial G}{\partial T} = -S.$$

As dG is a perfect differential.

$$\frac{\partial}{\partial T}\left(\frac{\partial G}{\partial P}\right) = \frac{\partial}{\partial p}\left(\frac{\partial G}{\partial T}\right)$$

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

This is fourth thermodynamical relations.

Thus we have four thermodynamical

Potentials Internal energy $U\,(S, V)$
Helmholtz free energy $F\,(T, V)$
Enthalpy $H\,(S, P)$
Gibb's potential $G\,(T, P)$.

These relation are known as
Maxwell's relations.

Deductions from Thermodynamical relations

1. Clausius Clapeyron's equations.

From Maxwell's Second law of thermodynamic relation.

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$$ multiply both by T

But $(T \cdot ds = \partial Q)$.

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

$$\left(\frac{\partial Q}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V \xrightarrow{} ①$$

Here $\left.\frac{\partial Q}{\partial V}\right)_T$ represents the quantity of heat absorbed or liberated per unit change in volume at Constant temperature.

Therefore this amount of heat absorbed or Liberated at Constant temp must be Latent heat.

Let L be the Latent heat when Substance changes in volume from V_1 to V_2 at Constant temperature then

$$\partial Q = L \quad \text{and} \quad \partial V = V_2 - V_1$$

Apply in equ ①

$$\left(\frac{L}{V_2 - V_1}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V \Rightarrow$$

$$\frac{\partial P}{\partial T} = \frac{L}{T(V_2 - V_1)}.$$

This equation is called clausius-clapeyron Latent heat equation.

② Ratio of isothermal and adiabatic elasticities.

The Coefficient of Volume elasticity is defined as.

$$E = -\frac{\text{Stress}}{\text{Volume strain}} = -\frac{\partial P}{\partial V/V} = -V\frac{\partial P}{\partial V}.$$

Therefore the adiabatic elasticity E_S (Entropy Constant) and isothermal elasticity E_T (Temp constant) are given

$$E_S = -V\left(\frac{\partial P}{\partial V}\right)_S \quad \text{and} \quad E_T = -V\left(\frac{\partial P}{\partial V}\right)_T$$

Hence the ratio $E = \frac{E_S}{E_T} = \frac{\left(\frac{\partial P}{\partial V}\right)_S}{\left(\frac{\partial P}{\partial V}\right)_T} = \frac{\left(\frac{\partial P}{\partial T}\cdot\frac{\partial T}{\partial V}\right)_S}{\left(\frac{\partial P}{\partial S}\frac{\partial S}{\partial V}\right)_T}$

from thermodynamical relations.

$$E = \frac{E_S}{E_T} = \frac{\cancel{-}\left(\frac{\partial S}{\partial V}\right)_P\left(\frac{\partial P}{\partial S}\right)_V}{\cancel{-}\left(\frac{\partial T}{\partial V}\right)_P\left(\frac{\partial P}{\partial T}\right)_V} = \left(\frac{\partial S}{\cancel{\partial V}}\cdot\frac{\cancel{\partial V}}{\partial T}\right)_P\left(\frac{\cancel{\partial P}}{\partial S}\,\frac{\partial T}{\cancel{\partial P}}\right)_V$$

$$= \left(\frac{\partial S}{\partial T}\right)_P\left(\frac{\partial T}{\partial S}\right)_V. = \frac{\left(\frac{\partial S}{\partial T}\right)_P}{\left(\frac{\partial S}{\partial T}\right)_V}$$

multiply and divided by T

$(T\partial S = \partial Q.$

$$E = \frac{T\left(\frac{\partial S}{\partial T}\right)_P}{T\left(\frac{\partial S}{\partial T}\right)_V} = \frac{\left(\frac{\partial Q}{\partial T}\right)_P}{\left(\frac{\partial Q}{\partial T}\right)_V} = \frac{C_P}{C_V}.$$

Thus the ratio of isothermal and adiabatic elasticity of any substance is equal to ratio of specific heat capacities of substances at constant pressure and constant volume.

Properties of thermodynamic relations.

① **Internal energy (U)**

This concepts depends on the first law of thermodynamics $U(S,V)$

$$dU = dQ - dW \longrightarrow ①$$

The internal energy depends only on state of the system and is function of independent variables $\underline{S \,\&\, V}$

For adiabatic ~~process~~ $dQ = 0$ therefore equ ① will be

$$dU = -dW \longrightarrow ②$$

Thus the change in the internal energy when the system goes adiabatically from one state to another is equal to external work done on the system.

② **Enthalpy (H)** $H(S,P)$

The enthalpy is defined by

$$H = U + PV \longrightarrow ③$$

This function is often called heat content, but namely enthalpy.

differentiate equ ③.

$$dH = dU + pdv + vdp = Tds - \cancel{pdv} + \cancel{pdv} + vdp$$

$$dH = Tds + vdp$$

Obviously the enthalpy is a function of independent variables $\underline{S \,\&\, P}$.

If any process Isobaric process carried out at constant pressure, then $dp = 0$ then

$$dH = Tds = dQ$$

Thus ~~the H heat~~ if th heat is supplied to any system at constant pressure ($dp=0$), then the change in enthalpy is equal to the heat supplied.

③ Helmholtz free energy (F)

This is also called thermodynamic potential at constant volume or available energy is defined as

$$F = U - TS \qquad F(T,V)$$

Differentiate $dF = dU - d(TS)$

$$= T\cancel{dS} - pdV - T\cancel{dS} - SdT$$

$$dF = -SdT - pdV.$$

The Helmholtz function is the function of independent variables T & V. For reversible isothermal change ($dT=0$) Then:

$$dF = -pdV = -dW.$$

$$dF + dW = 0$$

This means that in reversible isothermal changes, the external work is done wholly at cost of the system. of Helmholtz free energy.

④ Gibb's ~~free~~ potential (G) $G(T,P)$

This function is called thermodynamical potential at constant pressure, which is defined by

$$G = U + pV - TS$$

D.

Differentiating

$$dG = dU - d(TS) + d(PV)$$

$$= (dU - TdS) - SdT + PdV + VdP$$

$$\Downarrow$$

$$dG = -dW - \boxed{SdT} + PdV + \boxed{VdP}$$

$dU = TdS - dW$

$-dW = dU - TdS$

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

$$dG = -dW + PdV$$

OR $\qquad dG = -dA$

where dA is the amount of work obtained exclusive of the mechanical work ($P \cdot dV$) involved in the change of the system.

we can write $\quad dG + dA = 0$

This means that in reversible isothermal and isobaric changes the external work, exclusive of any mechanical work is done wholly at the cost of Gibbs free energy.

~~Relation of~~ Gibbs Helmholtz Relation.

we have already defined by Helmholtz free energy F by

$$F = U - TS \longrightarrow$$ ①

$$dF = dU - TdS - SdT$$

$$= (\cancel{TdS} - pdV) - \cancel{TdS} - SdT$$

$$dF = -pdV - SdT \longleftarrow$$ ②

Gibbs potential G by

$$G = H - TS = U + PV - TS \longrightarrow$$ ③

$$dG = dU + pdV + Vdp - TdS - SdT$$

$$= \cancel{TdS} - \cancel{pdV} + \cancel{pdV} + Vdp - \cancel{TdS} - SdT$$

$$dG = Vdp - SdT \longrightarrow$$ ④

Now we consider different process:-

i) Isothermal processes. i.e; when Temperature Constant. in equ ② $dT = 0$.

$$dF_T = -pdV - SdT$$

$$dF_T = -pdV \longrightarrow \left(\frac{\partial F}{\partial V}\right)_T = -P \longrightarrow$$ ③

|||ly $$dG_T = Vdp - SdT$$

$$dG_T = Vdp \longrightarrow \left(\frac{\partial G}{\partial p}\right)_T = V. \longrightarrow$$ ④

ii) Isobaric processes. i.e; when pressure is constant in equ ④ → $dp = 0$

$$dG_p = -SdT$$

$$\left(\frac{\partial G}{\partial T}\right)_p = -S \longrightarrow$$ ⑤

Thus entropy is a measure of th rate of change of Gibb's potential with tempe at constant pressure

Substitute value of S from equ ⑤ in ③

$$G = H + T\left(\frac{\partial G}{\partial T}\right)_{p} \longrightarrow ⑥$$

iii) Isochoric process, ie; when volume is constant.
in equ ② dv=0

$$dF_{v} = -S\,dT \quad \text{or} \quad \left(\frac{\partial F}{\partial T}\right)_{v} = -S \longrightarrow ⑦$$

Thus th entropy is a measure of th rate of change of free energy with temp at constant volume.

apply th value of S from equ ⑦ in equ ①.

$$F = U + T\left(\frac{\partial F}{\partial T}\right)_{v} \longrightarrow ⑧$$

equations ⑥ and ⑧ co relating Gibbs potential Ⓖ with enthalpy Ⓗ and Helmholtz free energy Ⓕ with internal energy Ⓤ are known as Gibbs Helmholtz relations.

Nernst Heat Theorem

It State that " The heat capacities of all the Solids tend to zero as the absolute zero of temperature is approached and that the internal energies and entropies of all Substances become equal there, approaching their Common Value asymtotically".

This simple statement of nernst follows neither from the first law nor from Second law and is thus of the nature of a new law called "Third law of Thermodynamics." This theorem is useful in explaining the nature of bodies in neighbourhood of absolute zero temperature.

Now for isochoric process, we have Gibbs Helmholtz relation

$$F = U + T\left(\frac{\partial F}{\partial T}\right)_V$$

we can express this relation taking two finite States as

$$F_2 - F_1 = (U_2 - U_1) + T\left\{\frac{\partial}{\partial T}(F_2 - F_1)\right\}_V$$

OR

$$F^* = U^* + T\left(\frac{\partial F^*}{\partial T}\right)_V \longrightarrow ①$$

where F^* denote the decrease in free energy during molecular reaction and U^* is the decrease in internal energy. If F^* varies with temperature, Particularly at low temperature is important.

But we know $\frac{dU^*}{dT} = \Sigma nc$

n- number of molecul , c- heat capacity.

If we ~~have~~ Consider the lowest limit of temperature as propositional by Nernst heat theorem to be zero. we have,

$$U^* = \int_0^T \Sigma nc \, dT + \text{constant}$$

If at $T=0$ then $U^* = 0 + \text{Constant}$.

The value of Constant is obtaind as U_0^*

$$U^* = U_0^* + \int_0^T \Sigma nc \, dT \longrightarrow ②$$

In order to Calculate F^* differentiate equ ①

as F to be a function of Temperature.

$$\cancel{\frac{dF^*}{dT}} = \frac{dU^*}{dT} + T\left(\frac{\partial^2 F^*}{\partial T^2}\right)_v + (1)\cancel{\frac{dF^*}{dT}}$$

$$\frac{\partial^2 F^*}{\partial T^2} = -\frac{1}{T}\frac{dU^*}{dT}$$

$$\frac{\partial^2 F^*}{\partial T^2} = -\frac{1}{T}\Sigma nc.$$

By integrating we have.

$$\frac{dF^*}{dT} = -\int_0^T \frac{\Sigma nc}{T} dT + \text{constant}. \longrightarrow ③$$

Again at $T=0$ then

$$\frac{dF^*}{dT} = 0 + \text{constant} \longrightarrow \text{Constant} = \left(\frac{dF^*}{dT}\right)_0$$

$$\frac{dF^*}{dT} = -\int_0^T \frac{\Sigma nc}{T}\, dT + \left(\frac{dF^*}{dT}\right)_0 \longrightarrow \textcircled{4}$$

But "The entropy change in any isothermal reversible process of condensed system approaches zero as the temperature at which the process occurs approaches zero. i.e:-

$$\left(\frac{dF^*}{dT}\right)_0 = 0.$$ Then apply in ④

$$\left(\frac{dF^*}{dT}\right) = -\int_0^T \frac{\Sigma nc}{T}\, dT \longrightarrow \textcircled{5}$$

Combining equ ①, ②, ⑤ then we get

$$F^* = U^* + T\left(\frac{\partial F^*}{\partial T}\right)_V$$

$$= U_0^* + \int_0^T \Sigma nc\, dT - T\int_0^T \frac{\Sigma nc}{T}\, dT$$

If $T=0$ then

$$F_0^* = U_0^*$$

$$\left(\frac{dF^*}{dT}\right)_0 = 0 \quad \text{and} \quad \left(\frac{dU^*}{dT}\right)_0 = 0.$$

This is why the functions F^* and U^* becomes equal ~~at~~ absolute zero. We can write this also.

$$\lim_{T=0}\left(\frac{\partial F^*}{\partial T}\right) = \lim_{T=0}\left(\frac{\partial U^*}{\partial T}\right) = 0$$

This is called Nernst heat theorem.

Phase

Which is defined as
a physically distinct but homogeneous part
a System which is Seperated from other parts
of the system by difinite bounding surfaces.
Thus each different physically homogeneous part of a
system is called phase. (Solid, liquid, gas)

Component :- The number of distinct chemical Species involved.

Degrees of freedom :- Liquid — two DOF (P,T)
Liquid with vapour — One DOF (P or T)

Gibbs phase rule.

Let us Consider a heterogeneous System
Consisting "n" different Components in "r" phases. Thus
we should find the maximum value of 'r' determined
by the number of independent Components. Thus the
mass of the i^{th} Component in K^{th} phase is represented
by M_i^K.

Now the System Said to be in equilibrium, if
the ~~System~~ temperature and pressure are constant
throughout. Now we Consider the System is to be
isothermal - isobaric rather than an isolated one.
Then the Gibbs potential

$$G = U - TS + PV \quad \text{——} (1)$$

The T and P are entirely independent of the
mass the system then the G is proportional
~~to~~ the mass. Then,

$$G = G(M_1, M_2, M_3 \cdots M_n) \longrightarrow ②$$

If all the masses are multiplied by heat energy Q, we have

$$G(QM_1, QM_2 \cdots QM_n = QG(M_1, M_2, M_3 \cdots M_n) \longrightarrow ③$$

differentiating

~~$\frac{\partial G}{\partial(QM_1)} + \frac{\partial G}{\partial(QM_2)} + \cdots \frac{\partial G}{\partial(QM_n)} = G(M_1, M_2 \cdots M_n)$~~

(or) $$\frac{\partial G}{\partial(QM_1)} \cdot \frac{\partial(QM_1)}{\partial Q} + \frac{\partial G}{\partial(QM_2)} \frac{\partial(QM_2)}{\partial Q} \cdots\cdots \frac{\partial G}{\partial(QM_n)} \frac{\partial(QM_n)}{\partial Q} = G(M_1, M_2 \cdots M_n)$$

(or)

$$M_1 \frac{\partial G}{\partial(QM_1)} + M_2 \frac{\partial G}{\partial(QM_2} \cdots\cdots M_n \frac{\partial G}{\partial(QM_n)} = G(M_1, M_2 \cdots M_n)$$

If $Q = 1$ Then we have.

$$M_1 \frac{\partial G}{\partial M_1} + M_2 \frac{\partial G}{\partial M_2} + \cdots\cdots M_n \frac{\partial G}{\partial M_n} = G(M_1, M_2 \cdots M_n) \longrightarrow ④$$

In this equation the RHS is a homogeneous function of first degree in masses. The LHS ~~is a~~ the derivatives $\frac{\partial G}{\partial M_1}$ must be homogeneous function of zero degree.

But the Gibbs potentials of the entire System is equal to sum of Gibbs functions of its phases. Then

$$G = G' + G'' + G''' + \cdots G^r \longrightarrow ⑤$$

The Condition of equilibrium

$$\delta G = \delta G' + \delta G'' + \cdots\cdots \delta G^{r} = 0 \longrightarrow ⑥$$

In these case, The mass of each Component must be remain unaltered, and the total mass of the Substances remains Constant. we have the following n auxillary Conditions

$$\left.\begin{array}{l} \delta M_1' + \delta M_1'' + \delta M_1''' + \cdots\cdots\cdots\cdots \delta M_1^{r} = 0 \\ \delta M_2' + \delta M_2'' + \delta M_2''' + \cdots\cdots\cdots \delta M_2^{r} = 0 \\ \vdots \qquad\qquad \vdots \qquad\qquad \vdots \\ \delta M_n' + \delta M_n'' + \delta M_n''' + \cdots\cdots\cdots \delta M_n^{r} = 0 \end{array}\right\} \longrightarrow ⑦$$

while P and T are Constant then we obtain
Then equ ④ canbe writen as

$$\frac{\partial G'}{\partial M_1'}\delta M_1' + \frac{\partial G'}{\partial M_2'}\delta M_2' \cdots\cdots \frac{\partial G'}{\partial M_n'}\delta M_n' + \frac{\partial G''}{\partial M_1''}\delta M_1'' + \frac{\partial G''}{\partial M_2''}\delta M_2'' + \cdots\cdots \frac{\partial G''}{\partial M_n''}\delta M_n'' + \cdots\cdots \frac{\partial G^{r}}{\partial M_1^{r}}\delta M_1^{r} + \frac{\partial G^{r}}{\partial M_2^{r}}\delta M_2^{r} + \cdots\cdots \frac{\partial G^{r}}{\partial M_n^{r}}\delta M_n^{r} = 0 \longrightarrow ⑧$$

Now the method of Legrangian undetermined multipliers for that multiplying equations ⑦ by $\lambda_1, \lambda_2, \cdots \lambda_n$ and adding them to equ ⑧

weget

$$\left(\frac{\partial G'}{\partial M_1'} + \lambda_1\right)\delta M_1' + \left(\frac{\partial G'}{\partial M_2'} + \lambda_2\right)\delta M_2' \cdots\cdots \left(\frac{\partial G'}{\partial M_n'} + \lambda_n\right)\delta M_n' +$$

$$\left(\frac{\partial G''}{\partial M_1''} + \lambda_1\right)\delta M_1'' + \left(\frac{\partial G''}{\partial M_2''} + \lambda_2\right)\delta M_2'' + \cdots\cdots \left(\frac{\partial G''}{\partial M_n''} + \lambda_n\right)\delta M_n'' +$$

$$\left(\frac{\partial G^r}{\partial M_1^r} + \lambda_1\right)\delta M_1^r + \left(\frac{\partial G^r}{\partial M_2^r} + \lambda_2\right)\delta M_2^r + \cdots \left(\frac{\partial G^r}{\partial M_n^r} + \lambda_n\right)\delta M_n^r = 0 \longrightarrow (9)$$

If above equation is to be satisfied the Coefficiants of δM_n^r must be vanish Seperately. Then we have the following equations 'nr' in number to be satisfied.

$$\left.\begin{matrix} \left(\frac{\partial G'}{\partial M_1'} + \lambda_1\right) = 0 \quad \left(\frac{\partial G'}{\partial M_2'} + \lambda_2\right) = 0 \cdots\cdots \left(\frac{\partial G'}{\partial M_n'} + \lambda_n\right) = 0 \\ \vdots \\ \left(\frac{\partial G^r}{\partial M_1^r} + \lambda_1\right) = 0 \quad \cdots\cdots\cdots \quad \left(\frac{\partial G^r}{\partial M_n^r} + \lambda_n\right) = 0 \end{matrix}\right\} \longrightarrow (10)$$

In above equation there are n Lagrangian ~~numbers~~ multipliers and the derivatives depend on T and p. The T and p are the Common temperature and pressure of the phases and r is the number of phases. Then we have in all $n + r(n-1) + 2$ independent variables. Then

$$nr \le n + r(n-1) + 2$$

If $n = 1$ Then.

$$r \le n+2.$$

Thus ~~any~~ in any system the number of phases may be at the most two greater than the number of independent components. This is called Gibbs phase rule. According to the rule a system consisting of a single substance can have three phases at most.

Chemical potential

Each ~~system~~ potential has got a capacity factor and work done, on the system is expressed by the product of this capacity factor with the change in potential. In a chemical solution mole as the capacity factor and mole free energy as the potential (chemical potential). Then to transfer n moles of substance from a state of molar free energy F_1 to a state of molar free energy F_2 an amount of wor $n(F_2 - F_1)$ is required.

Let us consider a general heterogeneous system consisting n independent components, which specified by the number of moles N_i, its volume V and its entropy S.

then we, may Set the internal energy to be a function of entropy S, volume V and the number of each moles of each Component

$$U = U(S, V, N_1, N_2 \cdots N_i) \longrightarrow ①$$

N_i is the number of particles of i^{th} component.

Differentiate

$$dU = \left(\frac{\partial U}{\partial S}\right)_{V,N} dS + \left(\frac{\partial U}{\partial V}\right)_{S,N} dV + \sum_{i=1}^{n} \left(\frac{\partial U}{\partial N_i}\right)_{S,V} dN_i \longrightarrow ②$$

But we know

$$dU = TdS - PdV \longrightarrow ③$$

Comparing Coefficients of dS and dV from equ ② and equ ③ we get

$$\left(\frac{\partial U}{\partial S}\right)_{V,N} = T \quad \text{and} \quad \left(\frac{\partial U}{\partial V}\right)_{S,N} = -P$$

and we introduce a new symbol (μ_i) to its last part, that is

$$\cancel{\sum_{i=1}^{n}} \left(\frac{\partial U}{\partial N_i}\right)_{S,V} = \mu_i \longrightarrow ④$$

This quantity μ_i is called chemical potential of the component i in the given phase.

with these relations we can write equ ②
in the compact form.

$$dU = T\,dS - P\,dV + \sum_{i=1}^{n} \mu_i\, dN_i \longrightarrow ⑤$$

The chemical potential μ_i may be expressed
in teoms of other thermodynamic functions.

The Helmholtz free energy F may be written
as a fuction of temperature T, volume V and
independent variables $N_1, N_2 \cdots N_i$ Then

$$F = F(T, V, N_1, N_2 \cdots N_i) \longrightarrow ⑥$$

Differentiate

$$dF = \left(\frac{\partial F}{\partial T}\right)_{V,N} dT + \left(\frac{\partial F}{\partial V}\right)_{T,N} dV + \sum_{i=1}^{n} \left(\frac{\partial F}{\partial N_i}\right)_{T,V} dN_i \longrightarrow ⑦$$

we know $dF = -S\,dT - P\,dV \longrightarrow ⑧$

Compare ⑦ and ⑧

$$\left(\frac{\partial F}{\partial T}\right)_{V,N} = -S \quad \text{and} \quad \left(\frac{\partial F}{\partial V}\right)_{T,N} = -P.$$

and $$\left(\frac{\partial F}{\partial N_i}\right)_{T,V} = \mu_i$$

Therefore we can write equ ⑦ as.

$$dF = -sdT - pdv + \sum_{i=1}^{n} \mu_i dN_i \longrightarrow (9)$$

Similarly we can expresse the chemical potential in terms of thermodynamic function Enthalpy (H) ~~and Gibbs fun~~ $H(S, P, N_1, N_2 \cdots N_i)$ and Gibbs fuction $G(T, P, N_1, N_2 \cdots N_i)$

$$dH = Tds + vdp + \sum_{i=1}^{n} \mu_i dN_i \longrightarrow (10)$$

and

$$dG = -sdT + vdp + \sum_{i=1}^{n} \mu_i dN_i \longrightarrow (11)$$

The above formulae show that the chemical potential

$$\mu_i = \left(\frac{\partial U}{\partial N_i}\right)_{S,V,N_i} = \left(\frac{\partial F}{\partial N_i}\right)_{T,V,N_i} = \left(\frac{\partial H}{\partial N_i}\right)_{S,P,N_i}$$

$$= \left(\frac{\partial G}{\partial N_i}\right)_{T,P,N_i}$$

Then the chemical potential of any component in the system can be obtained by differentiating any of the thermodynamic function U, F, H and G with respect to the corresponding thermodynamic variables.

Phase space.

The instantantaneous ~~motion~~ position of a particle is determined by three independent coordinates x, y, z and the instantaneous motion of a particle is described by momentum coordinates P_x P_y P_z. Thus the position of a point in a space will be described by a set of six coordinates x, y, z, P_x, P_y, P_z. This six dimensinal space for a single particle is termed as "phase-space".

If the system contains a large number of particles such that of system represented by n independent position coordinatetes

$$q_1, q_2, q_3 \cdots\cdots q_n.$$

and n momentum coordinates

$$P_1, P_2, P_3 \cdots\cdots P_n.$$

The instantaneous state of a particle in the phase space is represented by a point known as "phase point."

Ensemble

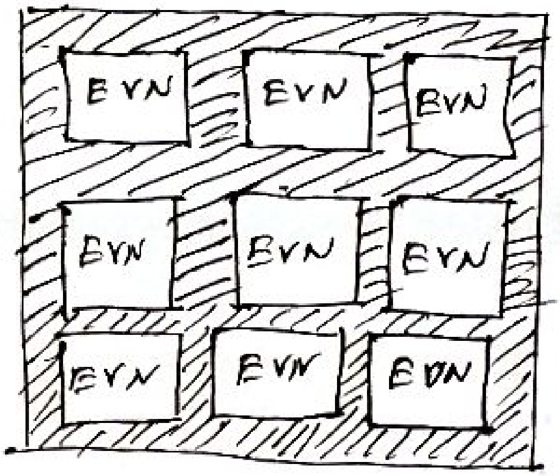
A system defined as a collection of number

A system is defined as a collection of particles. An ensemble is defined as a collection of ~~number~~ large number of macroscopycally identical and ~~microscopically~~ essentially independent systems.

The term macroscopically identical, we mean that each of the systems constituting an ensemble satisfies the same macroscopic condition ex. volume, energy, pressure ...etc. By the term independent systems we mean that the systems constituting an ensemble are mutually non-interacting. The ensemble are classified by micro canonical, canonical and Grand Canonical ensemble.

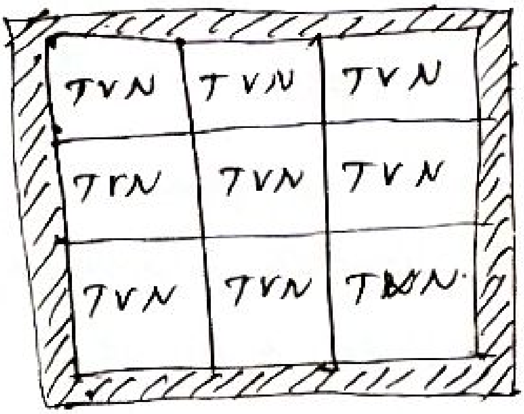
Micro canonical ensemble :-

It is the collection of large number of essentially independent systems having energy (E), volume (V) and number of particles (N). ~~For~~ The each system are separated by rigid, impermeable and well insulated walls.



Canonical Ensemble:-

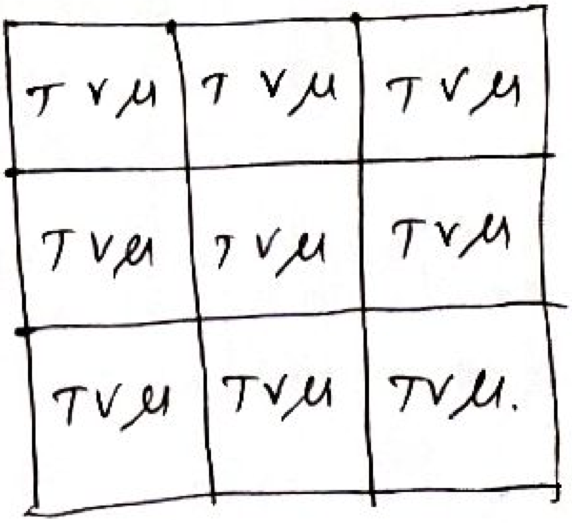
It is the Collection of large number of essentially independent Systems having Same temperature (T), volume (V) and identical number of particles (N). The each individual System is Separated by rigid, impermiable and Conducting walls.



TVN	TVN	TVN
TVN	TVN	TVN
TVN	TVN	TVN.

Grand Canonical ensemble.

It is the Collection of large number of essentially independent Systems having Same Temperature (T), Volume (V) and Chemical potential(μ), Each ~~syst~~ individual System is Seperated by ridid, permiable and Conducting walls.



T V μ	T V μ	T V μ
T V μ	T V μ	T V μ
T V μ	T V μ	T V μ.

Micro states and Macro States.

Let us Consider an ensemble Consisting of a large number of independent systems in the phase Space. Let phase space is divided into cells numbered 1, 2, ... i which having a volume equal to

$$\delta q_1, \delta q_2 \cdots\cdots \delta q_f, \delta p_1, \delta p_2 \cdots\cdots \delta p_f$$

In order to define the micro state of the ensemble we must Specify the individual position of phase points for each systems of the ensemble.

A microstate of the system is defined as a state for which motion of the individual particles are Completely specified

A macro state of the system is defined as Specifying the external parameters and any other Constrains to which the system is Subject. If we are dealing with an isolated system, the macro state might be Specified by giving the values of volume and the Constant energy.

Let us Consider an ensemble with two systems Containing 4 particles a, b, c, d then the ~~possibility~~ probability to distribute as follows

P	Q
a,b,c,d	

(4,0), (3,1) (2,2), (1,3) (0,4)

P	Q
abc	d
abd	c
acd	b
bcd.	a

P	Q
ab	cd.
ac	bd
ad	bc
bc	a,d
bd	ac
cd	ab.

P	Q
a	bcd
b	acd
c	abd
d	abc.

Therefore There are 5 macro state and
$1+4+6+4+1 = 16$ microstate.

Statistical equilibrium

An ensemble is said to be in statistical equilibrium if the probabilities of finding the phase points in the various regions of the phase space and average values of the properties of its Systeme are independent of time.

Mathematically the Condition of an ensemble in statistical equilibrium may be expressed as

$$\left(\frac{\partial \rho}{\partial t}\right)_{q,p} = 0$$

This means that for an ensemble to be in statistical equilibrium the density ρ must be independent of time at all points in phase space.

In general, for any ensemble ρ is a function of some property which in turn, can be expressed as a function of p's and q's. Let this property be represented by ϵ, then we write

$$\rho = \rho(\epsilon) \longrightarrow ①$$

This gives

$$\left.\begin{aligned}\frac{\partial \rho}{\partial q_i} &= \frac{\partial \rho}{\partial \epsilon}\frac{\partial \epsilon}{\partial q_i}\\ \frac{\partial \rho}{\partial p_i} &= \frac{\partial \rho}{\partial \epsilon}\frac{\partial \epsilon}{\partial p_i}\end{aligned}\right\} \longrightarrow ②$$

from Liouville's theorem

$$\left(\frac{\partial \rho}{\partial t}\right)_{q,p} + \sum_{i=1}^{f}\frac{\partial \rho}{\partial q_i}\dot{q}_i + \sum_{i=1}^{f}\frac{\partial \rho}{\partial p_i}\dot{p}_i = 0 \longrightarrow ③$$

apply the equ ② in equ ③

$$\left(\frac{\partial \rho}{\partial t}\right)_{q,p} + \sum_{i=1}^{f}\frac{\partial \rho}{\partial \epsilon}\frac{\partial \epsilon}{\partial q_i}\dot{q}_i + \sum_{i=1}^{f}\frac{\partial \rho}{\partial \epsilon}\frac{\partial \epsilon}{\partial p_i}\dot{p}_i = 0$$

$$\left(\frac{\partial \rho}{\partial t}\right)_{q,p} = \cancel{\sum_{i=1}^{f}}\frac{\partial \rho}{\partial \epsilon}\sum_{i=1}^{f}\left(\frac{\partial \epsilon}{\partial q_i}\dot{q}_i + \frac{\partial \epsilon}{\partial p_i}\dot{p}_i\right) \longrightarrow ④$$

As $\in$ is assumed to be the function of q's and p's such that it's value for any given system in statistical equilibrium does not change with time. we may write

$$\sum_{i=1}^{f}\left(\frac{\partial \in}{\partial q_i}\dot{q}_i + \frac{\partial \in}{\partial p_i}\dot{p}_i\right)=0. \longrightarrow ⑤$$

eqn ⑤ in eqn ④ then

$$\left(\frac{\partial \rho}{\partial t}\right)_{q,p}=0.$$

Hense we conclude that an ensemble of systems will be in statistical equilibrium, if

i) The density ρ is independent of time at all points in the phase space. and

ii) The density ρ is a fuction of some property of the ensemble which depends only on q's and p's and is independent of time.

Law of equipartition of energy (Free energy)

The Law states that "the total kinetic energy of the system of a dynamical system consisting of a large number of particles in thermal equilibrium is equally divided among its all the degrees of freedom and average associated with each degree of freedom is $\frac{1}{2}KT$.

Let us consider a dynamical system with f degrees of freedom. classically This system is described by "f" position coordinates $(q_1 q_2 \cdots q_f)$ and "f" momentum coordinates $(P_1 P_2 \cdots P_f)$.
The total energy E of the system can be written as function of these coordinates

$$E = E(q_1, q_2 \cdots q_f, P_1, P_2 \cdots P_f)$$

Let P_i be any particular momentum then the total energy can be expressed as

$$E = \epsilon_i(P_i) + E'(q_1, q_2 \cdots q_f, P_1, P_2 \cdots P_f) \longrightarrow ①$$

where $\epsilon_i(P_i)$ is the function of momentum P_i alone. and Second term $E'(q_1 \cdots q_f, P_1 \cdots P_f)$ is the function of all the position and momentum coordinates. The

Classically the mean energy ϵ_i is defined as

$$\overline{\epsilon_i} = \frac{E}{N} = \frac{\int \epsilon_i e^{-E/KT} dq_1 dq_2 \dots dq_f}{\int e^{-E/KT} dq_1 dq_2 \dots dq_f}$$

Since $E = \epsilon_i + E'$ then

$$\overline{\epsilon_i} = \frac{\int \epsilon_i e^{-(\epsilon_i + E')/KT} dq_1 dq_2 \dots dq_f}{\int e^{-(\epsilon_i + E')/KT} dq_1 dq_2 \dots dq_f.}$$

apply limits

$$= \frac{\int_{-\infty}^{+\infty} \epsilon_i e^{-\epsilon_i/KT} dp_i}{\int_{-\infty}^{+\infty} e^{-\epsilon_i/KT} dp_i} \cancel{\frac{\int e^{-E'/KT} dq_1 dq_2 \dots dq_f}{\int e^{-E'/KT} dq_1 dq_2 \dots dq_f}}$$

$$\overline{\epsilon_i} = \frac{\int_{-\infty}^{+\infty} \epsilon_i e^{-\epsilon_i/KT} dp_i}{\int_{-\infty}^{+\infty} e^{-\epsilon_i/KT} dp_i}$$

But we know $\epsilon_i = \frac{p_i^2}{2m}$

$$\overline{\epsilon_i} = \frac{\int_{-\infty}^{+\infty} \frac{p_i^2}{2m} e^{-(p_i^2/2m)/KT} dp_i}{\int_{-\infty}^{+\infty} e^{-(p_i^2/2m)/KT} dp_i}$$

Since $\int_{-\infty}^{+\infty} x^2 e^{-ax^2} dx = \frac{1}{2}\sqrt{\left(\pi/a^3\right)}$

$$\int_{-\infty}^{+\infty} e^{-ax^2} dx = \sqrt{\frac{\pi}{a}}$$

Then

$$a = \frac{1}{2mKT}$$

Then

$$\overline{\epsilon_i} = \frac{1}{2m} \frac{\frac{1}{2}\sqrt{\frac{\pi}{(1/2mKT)^3}}}{\sqrt{\frac{\pi}{(1/2mKT)}}}$$

$$= \frac{1}{2m} \frac{1}{2} \sqrt{\frac{\cancel{\pi}}{(1/2mKT)^{\cancel{3}}} \frac{\cancel{1/2mKT}}{\cancel{\pi}}}$$

$$= \frac{1}{2m} \frac{1}{2} \sqrt{(2mKT)^{\cancel{2}}} = \frac{1}{2m} \cancel{2mK}T$$

$$= \frac{1}{\cancel{2m}} \frac{1}{2} \cancel{2m} KT$$

$$\overline{\epsilon_i} = \frac{1}{2} KT$$

This equation states that the mean value of energy expressible as independent quadratic term is equal to $\frac{1}{2}$ KT.

Perfect gas in micro Canonical ensemble.

Let us Consider a micro canonical ensemble of a perfect gas. Let there be n particles of perfect gas each of mass m Confined in a volume V with total energy U with in the energy range δU. The Corresponding volume in the phase space is

$$\Delta\Gamma = \int dq_1 \cdots\cdots dq_{3n} \int dp_1 \cdots\cdots dp_{3n} \qquad \longrightarrow (1)$$

~~where~~ As the particles of Perfect gas are non-interacting, the energy of a perfect gas is independent of position of the particle, so

$$\int dq_1 \cdots dq_{3n} = V^n \qquad \cancel{\longrightarrow (2)}$$

Therefor equ ① become

$$\Delta\Gamma = V^n \int dp_1 \cdots\cdots dp_{3n} \qquad \longrightarrow (2)$$

The integral part of above equation is volume Contained between 3n dimensional hyper-Sphere of radius $(2mU)^{1/2}$ and 3n dimensional hypersphere of radius $[2m(U-\delta U)]^{1/2}$. Therefore the volume occupied between hypersphere of both radius

$$\int dp_1 \cdots\cdots dp_{3n} = \frac{\pi^{3n/2}}{(3n/2)!}\,(2mU)^{3n/2}.$$

apply the above equation in equ② then

$$\Delta\Gamma = V^n \frac{\pi^{3n/2}}{(3n/2)!} (2mU)^{3n/2}$$

According to classical statistical, the entropy (σ) in statistically equilibrium is given by

$$\sigma = \log_e \Delta\Gamma$$

$$= \log_e \left[V^n \frac{\pi^{3n/2}}{(3n/2)!} (2mU)^{3n/2} \right]$$

$$= n \left\{ \log_e \left(V \pi^{3/2} (2mU)^{3/2} \right) \right\} - \log_e \left(\frac{3n}{2}! \right)$$

apply the stirlings approximation.

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

$$\therefore = n \left\{ \log_e \left(V \pi^{3/2} (2mU)^{3/2} \right\} - \frac{3n}{2} \log \frac{3n}{2} + \frac{3n}{2}.$$

$$= n \left\{ \log_e \left(V \pi^{3/2} (2mU)^{3/2} \right\} - \log \left(\frac{3n}{2}\right)^{3n/2} + \frac{3n}{2}.$$

$$= n \log_e \left\{ \frac{V \pi^{3/2} (2mU)^{3/2}}{\left(\frac{3n}{2}\right)^{3/2}} \right\} + \frac{3n}{2}.$$

$$\sigma = \log_e \Delta\Gamma$$

$$= n \log_e \left\{ V \left(\frac{4\pi m}{3}\right)^{3/2} \left(\frac{U}{n}\right)^{3/2} \right\} + \frac{3n}{2}. \longrightarrow ③$$

The entropy should not depend upon the unit of hyper volume $\Delta\Gamma$. To make it dimensionless we divide it by h^{3n}

$$\sigma = \log_e \frac{\Delta\Gamma}{h^{3n}}$$

$$= n \log_e \left[\frac{v \left(\frac{4\pi m}{3}\right)^{3/2} \left(\frac{U}{n}\right)^{3/2}}{h^3} \right] + \frac{3n}{2}$$

n identical particles we must not count as different conditions of the total system. If we take this factor into account, the entropy satisfying this additive property will be given by

$$\sigma = \log_e \frac{\Delta\Gamma}{h^{3n} n!}$$

$$= n \log_e \left[\left(\frac{v}{n}\right) \frac{\left(\frac{4\pi m}{3}\right)^{3/2} \left(\frac{U}{n}\right)^{3/2} e}{h^3} \right] + \frac{3n}{2}.$$

where "e" is the base of the logarithm. Then we can write as.

$$\sigma = n \log_e \left[\left(\frac{v}{n}\right) \frac{\left(\frac{4\pi m}{3}\right)^{3/2} \left(\frac{U}{n}\right)^{3/2}}{h3} \right] + \frac{5n}{2}.$$

where $\frac{V}{n}$ is volume per particle and

$\frac{U}{n}$ is energy per particle.

The properties of the gases.

1. Internal energy :- $U = \frac{3}{2} KT$ which is well known result for the energy of a perfect mono atomic gas.

2. Relation between θ and T :-

$$\theta = KT$$

3. Relation between θ and P :-

$$PV = n\theta$$

4. Thermodynamic entropy of a perfect gas

$$S = nk \log_e \left[\frac{V}{nh^3} (2\pi mkT)^{3/2} e^{5/2} \right]$$

5. Chemical potential of perfect gas :-

$$\mu = \theta \log P + F(T)$$

Where $F(T)$ is function of temperature alone.

Partition function of microcanonical ensemble.

Let consider the ideal gas molecule in which n molecule are occupied i^{th} state with energy range ε_i and $\varepsilon_i + d\varepsilon_i$ and the degeneracy g_i then according to the maxwell's boltzmann the most probable distribution is

$$n_i = g_i e^{-\alpha} e^{-\beta \epsilon_i}$$

where $e^{-\alpha} = A$ and $\beta = 1/KT$ (lagrangian values)

$$n_i = g_i A e^{-\epsilon_i/KT}$$

The total no of particles in the assembly

$$N = \sum_i n_i = \sum_i g_i A e^{-\epsilon_i/KT}$$

$$N = A \sum_i g_i e^{-\epsilon_i/KT}$$

$$\frac{N}{A} = \sum_i g_i e^{-\epsilon_i/KT} = Z \text{ (Partition function)} \longrightarrow ①$$

The quantity Z is called ~~par~~ Boltzmann partition function which indicates how the gas molecules are partitioned or distributed amoung the various energy states of the assembly.

In classical statistics the energy states are considered as continious. Then the number of energy states in momentum range p and p + dp is $\longrightarrow ②$

$$g(p)\,dp = \frac{4\pi V}{h^3} p^2 dp.$$

we know that $\epsilon = \frac{p^2}{2m}$, $p^2 = 2m\epsilon$

$$p = \sqrt{2m\epsilon} \quad \therefore \quad dp = \frac{m\,d\epsilon}{\sqrt{2m\epsilon}}$$

apply these terms in equ ②

$$g(\epsilon)\,d\epsilon = \frac{4\pi V}{h^3}\, 2m\epsilon \,\frac{m\,d\epsilon}{\sqrt{2m\epsilon}}$$

$$= \frac{2\pi V}{h^3}\, 2 \cdot 2^{1/2}\cancel{2^{1/2}}\, m^{1/2}\cancel{m^{1/2}}\, \epsilon^{1/2}\cancel{\epsilon^{1/2}} \,\frac{m\,d\epsilon}{\cancel{\sqrt{2m\epsilon}}}$$

$$= \frac{2\pi V}{h^3}\,(2m)^{3/2}\,\epsilon^{1/2}\,d\epsilon \longrightarrow ③$$

the number of energy levles is continuous in classical statistics therefore equ ① can be write as

$$Z = \int_0^{\infty} g(\epsilon)\,d\epsilon\; e^{-\epsilon/kT}$$

equ ③ apply in above equ

$$Z = \int_0^{\infty} \frac{2\pi V}{h^3}\,(2m)^{3/2}\,\epsilon^{1/2}\,d\epsilon\; e^{-\epsilon/kT}$$

$$= \frac{2\pi V}{h^3}\,(2m)^{3/2} \int_0^{\infty} \epsilon^{1/2}\, e^{-\epsilon/kT}\,d\epsilon$$

$$= \frac{\cancel{2}\pi V}{h^3}\,(2m)^{3/2}\, \frac{\sqrt{\pi}}{\cancel{2}}\,(kT)^{3/2}$$

$$= (2\pi m kT)^{3/2}\,\frac{V}{h^3}$$

$$Z_t = \left(\frac{2\pi m kT}{h^2}\right)^{3/2} V$$

This is called translational partition function.

Relation between partition function and Thermodynamic entropy.

The entropy and weight of the most probable concentration with relation

$$S = k \log \Omega \longrightarrow ①$$

But the weight of the configuration in classical statistical is

$$\Omega = N! \prod_i \frac{g_i^{n_i}}{n_i!}$$

$$\log \Omega = \log N! + \sum_i (n_i \log g_i - \log n_i!)$$

applying stirling approximation.

$$\log \Omega = N \log N - N + \sum_i (n_i \log g_i - n_i \log n_i + n_i)$$

from MB statistics

$$n_i = g_i e^{-\alpha} e^{-\beta \epsilon_i}$$

$$= N \log N - N + \sum_i \left[n_i \log g_i - n_i \log (g_i e^{-\alpha} e^{-\beta \epsilon_i}) + n_i \right]$$

$$= N \log N - \cancel{N} + \cancel{\sum_i n_i \log g_i} - \cancel{\sum_i n_i \log g_i} + \sum_i n_i \alpha + \sum_i n_i \beta \epsilon_i + \cancel{\sum_i n_i} \longrightarrow N.$$

$$\log \Omega = N \log N + \alpha N + \beta E$$

We know $e^{-\alpha} = A \rightarrow -\alpha = \log A \rightarrow \alpha = -\log A$

$$\therefore \log \Omega = N \log N - N \log A + \beta E$$

$$= N(\log N - \log A) + \beta E$$

$$= N \log\left(\frac{N}{A}\right) + \beta E$$

But $\beta = 1/KT$

$$\log \Omega = N \log\left(\frac{N}{A}\right) + \frac{E}{KT} \longrightarrow ②$$

$$S = K\left[N \log\left(\frac{N}{A}\right) + \frac{E}{KT}\right]$$

$$= NK \log\left(\frac{N}{A}\right) + \frac{\cancel{K}E}{\cancel{K}T}$$

$E = 3/2\, NKT$

$$S = N \cdot K \log Z + \frac{E}{T}$$

$$= NK \log Z + \frac{3}{2}\frac{NK\cancel{T}}{\cancel{T}}$$

$$S = NK \log Z + \frac{3}{2} NK$$

The thermodynamical entropy (S) and the partition function (Z) are related.

Helmholtz free energy and partition function.

We know Helmholtz free energy

$$F = E - TS$$

$$F = E - T\left[Nk\log Z + \frac{E}{T}\right]$$

$$= E - NkT\log Z + \cancel{T}E/\cancel{T}$$

$$= \cancel{E} - NkT\log Z + \cancel{E}$$

$$F = -NkT\log Z.$$

Total energy and partition function.

If $\bar{\epsilon}$ is the average energy of system of an assembly contain n number of independent systems then

$$\bar{\epsilon} = \frac{E}{N} = \frac{\sum_i n_i\epsilon_i}{\sum_i n_i}$$

Using MB statistics

$$\bar{\epsilon} = \frac{\sum_i g_i \cancel{e^{\alpha}} e^{-\beta\epsilon_i}\epsilon_i}{\sum_i g_i \cancel{e^{\alpha}} e^{-\beta\epsilon_i}}$$

$$\bar{\epsilon} = \frac{\sum_i g_i\epsilon_i e^{-\beta\epsilon_i}}{\sum_i g_i \bar{e}^{\beta\epsilon_i}}$$

$$\bar{\epsilon} = \frac{\sum_i g_i \epsilon_i e^{-\epsilon_i/kT}}{\sum_i g_i e^{-\epsilon_i/kT}} \qquad \beta = 1/kT$$

$$\bar{\epsilon} = \frac{\sum_i g_i \epsilon_i e^{-\epsilon_i/kT}}{Z} \longrightarrow ①$$

$$Z = \sum_i g_i e^{-\epsilon_i/kT}$$

$$\left(\frac{\partial Z}{\partial T}\right)_v = \sum_i g_i \frac{\epsilon_i}{kT^2} e^{-\epsilon_i/kT}$$

$$kT^2 \left(\frac{\partial Z}{\partial T}\right)_v = \sum_i g_i \epsilon_i e^{-\epsilon_i/kT} \longrightarrow ②$$

~~According to isothermal isochoric transformations~~

~~$\bar{\epsilon} = kT^2 \left(\frac{\partial(\log Z)}{\partial T}\right)$~~

equ ② apply in equ ①

$$\bar{\epsilon} = \frac{kT^2}{Z} \left(\frac{\partial Z}{\partial T}\right)_v .$$

According to isothermal isochoric transformation.

$$\bar{\epsilon} = kT^2 \left[\frac{\partial (\log Z)}{\partial T}\right]_v$$

But $\bar{\epsilon} = \frac{E}{N}$ → $E = \bar{\epsilon} N$

$$\therefore \; E = NKT^2 \left[\frac{\partial(\log z)}{\partial T} \right]_V$$

This is Total energy of the ensemble in terms of partition function.

Enthalpy H and partition function

enthalpy $H = E + PV$ $\quad$ $(PV = RT$

$$H = E + RT$$

We know $\quad H = NKT^2 \left[\frac{\partial(\log z)}{\partial T} \right]_V + RT$

Gibb's potential and partition function

Gibb's potential $\quad G = H - TS$

$$G = NKT^2 \left[\frac{\partial(\log z)}{\partial T} \right]_V + RT - T\left(Nk \log z + \frac{E}{T}\right)$$

$$= NKT^2 \left[\quad \right]_V + RT - NKT \log z + \frac{E\cancel{T}}{\cancel{T}}$$

$$G = NKT^2 \left[\quad \right]_V + RT - NKT \log z + \tfrac{3}{2} NKT$$

Pressure of the gas and partition function

$$P = -\frac{\partial F}{\partial V} = \cancel{-}\frac{\partial}{\partial V}\left(\cancel{-}NKT\,(\log z)\right)$$

$$= NKT\left[\frac{\partial(\log z)}{\partial V}\right]_T$$

Specific heat at constant volume (C_v) and partition function.

$$C_v = \frac{\partial E}{\partial T}$$

$$= \frac{\partial}{\partial T}\left[NKT^2\left(\frac{\partial \log z}{\partial T}\right)_v\right]$$

$$= NK\left[2T\left(\frac{\partial \log z}{\partial T}\right) + T^2\frac{\partial^2(\log z)}{\partial T^2}\right]$$

Maxwell Boltzmann Statistics.

Consider a system containing N number of identical and distinguishable particles of any spin. ~~we know~~ Let the phase space be divided into a large number of cells $1, 2, 3, \dots\dots i$. Let $n_1, n_2 \dots\dots n_i$ be the number of particles whose phase points lie in cell $1, 2, 3 \dots\dots i$ respectively.

As the gas molecules are moving continuously in different ways, but will always keep values close to those for equilibrium state. i.e. the most probable state.

i) The total number of particles is constant

$$n_1 + n_2 + n_3 + \dots\dots n_i = \text{constant}$$

$$\therefore \quad N = n_1 + n_2 + n_3 + \dots\dots n_i$$

~~ii) The total energy of the system is Const~~

$$\delta N = \delta n_1 + \delta n_2 + \dots\dots\dots \delta n_i = 0.$$

$$\sum_i n_i = N \qquad \sum_i \delta n_i = 0 \longrightarrow ①.$$

ii) The total energy of the system is constant.

$$E = \epsilon_1 n_1 + \epsilon_2 n_2 + \dots\dots \epsilon_i n_i = \text{constant}. \qquad \sum_i \epsilon_i n_i = E$$

$$\delta E = \epsilon_1 \delta n_1 + \epsilon_2 \delta n_2 + \dots\dots \epsilon_i \delta n_i = 0.$$

$$\sum_i \epsilon_i \delta n_i = 0. \longrightarrow ②$$

iii) When the gas is in equilibrium, the probability is maximum $\delta P = 0$. When P is maximum the $\log P$ is maximum $\therefore \; \delta(\log P) = 0. \longrightarrow ③$

But the probabilty this distribution 8 particles

$$P = \frac{N!}{n_1!\,n_2!\cdots n_i!}\,(g_1)^{n_1}(g_2)^{n_2}\cdots(g_i)^{n_i}$$

taking natural logarithm

$$\log P = \log N! - \sum_i \log n_i! + \sum_i n_i \log g_i$$

Using Stirling approximation.

$$\log P = N\log N - \cancel{N} - \sum_i n_i \log n_i + \sum_i \cancel{n_i} + \sum_i n_i \log g_i$$

$$\log P = N\log N - \sum_i n_i \log n_i + \sum_i n_i \log g_i$$

Differentiate

~~$\delta(\log p) = 0 - \sum_i n_i$~~

$$\delta(\log p) = 0 + \sum_i \log g_i\,\delta n_i - \sum_i n_i\,\delta(\log n_i) - \sum_i \log n_i\,\delta n_i \longrightarrow ④$$

~~$\sum_i \log g_i\,\delta n_i$~~

$$\delta(\log n_i) = \frac{1}{n_i}\,\delta n_i$$

multiply n_i

$$n_i\,\delta(\log n_i) = \frac{\cancel{n_i}}{\cancel{n_i}}\,\delta n_i$$

$$\sum_i n_i\,\delta(\log n_i) = \sum_i \delta n_i = 0$$

apply in equ ④.

$$\sum_i \log g_i \, \delta n_i - \sum_i \log n_i \, \delta n_i = 0$$

Rearrange

$$\sum_i \log n_i \, \delta n_i - \sum_i \log g_i \, \delta n_i = 0 \longrightarrow ⑤$$

To Solve this equation equ ① and ② are multiplied by Lagrangian undetermined multipliers α and β respectively and added with equ ⑤

Then

$$\sum_i \log n_i \, \delta n_i - \sum_i \log g_i \, \delta n_i + \alpha \sum_i \delta n_i + \beta \sum_i \epsilon_i \, \delta n_i = 0$$

$$\sum_i \left[\log n_i - \log g_i + \alpha + \beta \epsilon_i \right] \delta n_i = 0$$

$$\log n_i - \log g_i + \alpha + \beta \epsilon_i = 0$$

$$\log n_i = \log g_i - \alpha - \beta \epsilon_i$$

$$n_i = g_i \, e^{-\alpha} \, e^{-\beta \epsilon_i}$$

This result determines the most probable distribution of molecules among the various possible individual states and it is called maxwell Boltzmann distribution law.

Liouvill's theorem

Consider an ensemble consisting of large number of identical and non interacting systems. We know that the instantaneous state of a system can be represented by a point in the phase space. The density of this phase points is denoted by 'ρ'. If the state of an ensemble changes with time, the position of the phase points in the phase space will change with time. The motion of the phase points in phase space is governed by canonical equations.

$$\dot{q}_i = \frac{\partial H}{\partial p_i} \quad \text{and} \quad \dot{p}_i = -\frac{\partial H}{\partial q_i} \longrightarrow ①$$

Here $H = H(q_1, q_2 \cdots q_f, p_1 p_2 \cdots p_f)$ is the Hamiltonian of the system.

The Liouvill's theorem gives information about the rate of change of phase density in the phase space. The theorem may be stated in two parts.

1. Principle of Conservation of density in phase space.

This is states that the rate of change of density of phase points in the Γ space is zero.

Consider an arbitrary hyper volume

$\delta\Gamma = \delta q_1 \delta q_2 \cdots \delta q_f \, \delta p_1 \delta p_2 \cdots \delta p_f$ is located between q_1 and $q_1+\delta q_1$ and p_i and $p_1+\delta p_1$. The number of phase points in this volume element changes with time due to the motion of the phase points. If ρ is the density of the phase points the number of phase points in this volume element at any instant time

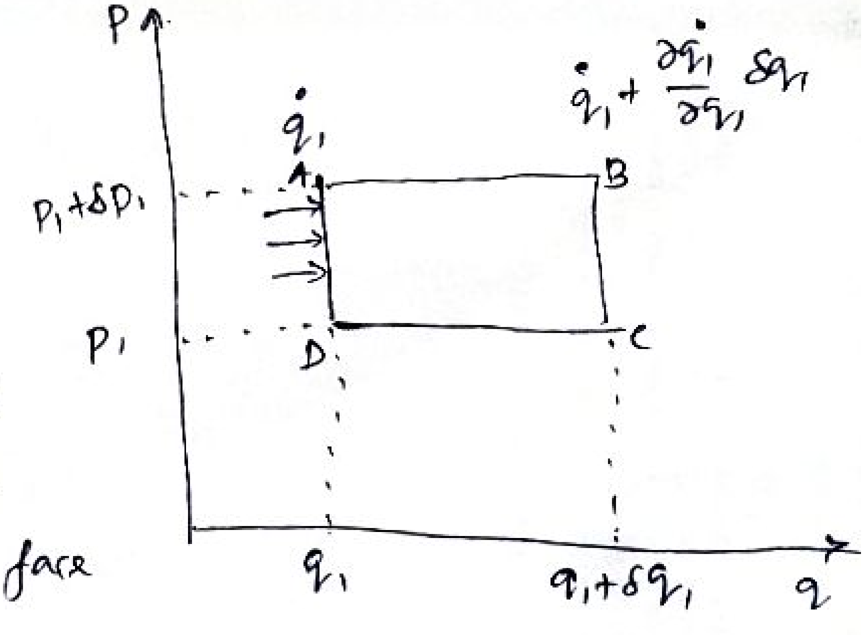
$$\delta N = \rho\, \delta\Gamma = \rho\, \delta q_1 \delta q_2 \cdots \delta q_f\, \delta p_1 \delta p_2 \cdots \delta p_f \qquad \text{——} ②$$

The change in the phase points in the volume element ~~at~~ per unit time

$$\frac{d}{dt}(\delta N) = \frac{d}{dt}(\rho\,\delta\Gamma)$$

$$\frac{d}{dt}(\delta N) = \frac{d\rho}{dt}\, \delta q_1 \delta q_2 \cdots \delta q_f\, \delta p_1 \cdots \delta p_f \qquad \text{——} ③$$

Now consider two faces of hyper volume normal to q_1 axis. If $\dot{q}_1$ is the component of velocity of phase points then the number of phase points entered into AD face per second



$$= \rho\, \dot{q}_1\, \delta q_2 \cdots \delta q_f\, \delta p_1 \cdots \delta p_f. \longrightarrow \cancel{②}\ ④$$

then ρ changes to $\left(\rho + \frac{\partial \rho}{\partial q_1}\delta q_1\right)$ at BC face. Simillarly the velocity componet $\dot{q}_1$ changes to $\left(\dot{q}_1 + \frac{\partial \dot{q}_1}{\partial q_1}\delta q_1\right)$. Therefor the number of phase points leaving from face BC

$$= \left(\rho + \frac{\partial \rho}{\partial q_1}\delta q_1\right)\left(\dot{q}_1 + \frac{\partial \dot{q}_1}{\partial q_1}\delta q_1\right)\delta q_2 \cdots \delta q_f \, \delta p_1 \cdots \delta p_f$$

Inter multiply, then we obtain ~~number~~ ~~the net~~

$$= \rho \dot{q}_1 + \rho \frac{\partial \dot{q}_1}{\partial q_1}\delta q_1 + \dot{q}_1 \frac{\partial \rho}{\partial q_1}\delta q_1 + \left(\frac{\partial \rho}{\partial q_1}\frac{\partial \dot{q}_1}{\partial q_1}\right)$$

$$\delta q_1 \cdots \delta q_f \, \delta p_1 \cdots \delta p_f$$

If we remone the highere order differontial

$$= \rho \dot{q}_1 + \left(\rho \frac{\partial \dot{q}_1}{\partial q_1}\cancel{\delta q_1} + \dot{q}_1 \frac{\partial \rho}{\partial q_1}\right)\delta q_1 \, \delta q_2 \cdots \delta q_f \, \delta p_1 \cdots \delta p_f$$

$\longrightarrow$ ~~④~~ ⑤

Now ~~③~~ 4 − ~~④~~ 5 then we obtain the net change in phase points in q coordinate.

$$= -\left(\rho \frac{\partial \dot{q}_1}{\partial q_1} + \dot{q}_1 \frac{\partial \rho}{\partial q_1}\right)\delta q_1 \cdots \delta q_f \, \delta p_1 \cdots \delta p_f$$

$\longrightarrow$ ~~⑤~~ ⑥

Similarly the net change in the phase points of hyper volume in p coordinctes

$$= -\left(\rho \frac{\partial \dot{p}_1}{\partial p_1} + \dot{p}_1 \frac{\partial \rho}{\partial p_1}\right)\delta q_1 \cdots \delta q_f \, \delta p_1 \cdots \delta p_f$$

$\longleftarrow$ ~~⑥~~ ⑦

Combine the equ ~~⑤~~ 6 & ~~⑥~~ 7 we get the total number of change in the all coordinates

$$\frac{d}{dt}(\delta N) = -\sum_{i=1}^{F}\left\{\rho\left(\frac{\partial \dot{q}_i}{\partial q_i}+\frac{\partial \dot{p}_i}{\partial p_i}\right)+\left(\dot{q}_i\frac{\partial \rho}{\partial q_i}+\dot{p}_i\frac{\partial \rho}{\partial p_i}\right)\right\}\delta q_1\cdots\delta q_F\,\delta p_1\cdots\delta p_F \longrightarrow ~~⑦~~ ⑧$$

using equ ③

$$\frac{d\rho}{dt}\,\cancel{\delta q_1\cdots\delta q_F\,\delta p_1\cdots\delta p_F} = -\sum_{i=1}^{F}\left\{\rho\left(\frac{\partial \dot{q}_i}{\partial q_i}+\frac{\partial \dot{p}_i}{\partial p_i}\right)+\left(\dot{q}_i\frac{\partial \rho}{\partial q_i}+\dot{p}_i\frac{\partial \rho}{\partial p_i}\right)\right\}\cancel{\delta q_1\cdots\delta q_F\,\delta p_1\cdots\delta p_F}$$

$$\frac{d\rho}{dt} = -\sum_{i=1}^{F}\left\{\rho\left(\frac{\partial \dot{q}_i}{\partial q_i}+\frac{\partial \dot{p}_i}{\partial p_i}\right)+\left(\dot{q}_i\frac{\partial \rho}{\partial q_i}+\dot{p}_i\frac{\partial \rho}{\partial p_i}\right)\right\} \longrightarrow ⑨$$

from canonical equations equ ①

$$\frac{\partial \dot{q}_i}{\partial q_i} = \frac{\partial^2 H}{\partial q_i\,\partial p_i} \quad \text{and} \quad \frac{\partial \dot{p}_i}{\partial p_i} = -\frac{\partial^2 H}{\partial p_i\,\partial q_i}$$

$$\frac{\partial^2 H}{\partial q_i\,\partial p_i} = -\frac{\partial^2 H}{\partial p_i\,\partial q_i} \longrightarrow \frac{\partial \dot{q}_i}{\partial q_i} = -\frac{\partial \dot{p}_i}{\partial p_i}$$

$$\sum_{i=1}^{F}\frac{\partial \dot{q}_i}{\partial q_i}+\frac{\partial \dot{p}_i}{\partial p_i} = 0 \quad \text{———} ⑩$$

apply the equ ⑩ in equ ⑨

$$\frac{d\rho}{dt} = -\sum_{i=1}^{f}\left(\dot{q}_i\frac{\partial\rho}{\partial q_i} + \dot{p}_i\frac{\partial\rho}{\partial p_i}\right)$$

$$\frac{d\rho}{dt} + \sum_{i=1}^{f}\left(\dot{q}_i\frac{\partial\rho}{\partial q_i} + \dot{p}_i\frac{\partial\rho}{\partial p_i}\right) = 0 \longrightarrow ⑪$$

equ ⑪ represents the Liouvill's theorem. This may write as

$$\frac{d}{dt}\rho(q_1, q_2 \cdots q_f, p_1 p_2 \cdots p_f) = 0$$

OR $$\boxed{\frac{d\rho}{dt} = 0} \longrightarrow ⑫$$

The first law is proved.

ii) The principle of Conservation of expension in phase space.

Consider a very small region of hyper volume (δτ) in τ space, So that the density ρ can be taken as uniform throughout the hyper volume.

"Any arbitrary element of volume in the τ space Containing number of phase points does not change with time" the number of phase points in hyper volume

$$\delta N = \rho\, \delta\Gamma$$

$$\frac{d}{dt}(\delta N) = \frac{d}{dt}(\rho\, \delta\Gamma)$$

$$\frac{d}{dt}(\delta N) = \frac{d\rho}{dt}\, \delta\Gamma + \rho \frac{d}{dt}(\delta\Gamma) \longrightarrow ⑬$$

As each phase point represents a definite system and systems can neither created or destroyed, therefore the number of phase points δN must remain constant.

Therefore equ ⑬ may write as.

$$\frac{d\rho}{dt}(\delta\Gamma) + \rho \frac{d(\delta\Gamma)}{dt} = 0$$

from equ ⑫ $\frac{d\rho}{dt} = 0$. Then

$$\rho \frac{d}{dt}(\delta\Gamma) = 0$$

(OR) if we neglect ρ

$$\frac{d}{dt}(\delta\Gamma) = 0$$

*

Canonical ensemble

The canonical ensemble describes the systems which are not isolated but are in thermal contact with a heat reservoir. The any part or subsystem of an isolated system in statistical equilibrium can be represented by a canonical ensemble.

If we consider a hyper volume in ~~phase~~ space of canonical ensemble energy range between E and E+dE

$$\Delta\Gamma = \frac{1}{\rho(E)}$$ where $\rho(E)$ is probability density

therefore $\rho(E) =$ [illegible] $= A\, e^{-E/\theta}$ —— ①

If $E = U$ ~~and~~ energy of the system and $\theta = KT$

$$\therefore \quad \Delta\Gamma = A^{-1} e^{U/KT}$$

The statistical entropy (σ) is given by

$$\sigma = \log_e \Delta\Gamma$$

$$= \log_e \left(A^{-1} e^{U/KT}\right)$$

$$\sigma = -\log A + \frac{U}{KT}$$

$$-\log A = \sigma - \frac{U}{KT}$$

$$\log A = \frac{U}{KT} - \sigma = \frac{U - \sigma KT}{KT} = \frac{U - ST}{KT}$$

where $S = K\sigma$ is thermodynamic entropy.

But the Helmholtz free energy is defined as

$$F = U - ST$$

$$\therefore \log A = \frac{F}{KT}$$

$$A = e^{F/KT} \longrightarrow ②$$

equ ② in equ ①

$$\rho(E) = e^{F/KT} e^{-E/KT}$$

$$\rho(E) = e^{(F-E)/KT} \longrightarrow ③$$

Now we applying the normalization condition

$$\int \rho(E)\, d\Gamma = 1$$

$$\int e^{(F-E)/KT}\, d\Gamma = 1$$

$$e^{F/KT} \int e^{-E/KT} = 1$$

$$\int e^{-E/KT}\, d\Gamma = \frac{1}{e^{F/KT}}$$

$$\int e^{-E(q,p)/KT}\, d\Gamma = e^{-F/KT}$$

Now the partition function is defined as

$$Z = \int e^{-E(q,p)/KT} \cdot d\Gamma \longrightarrow ④$$

which is classical partition function

or $Z = \sum_i e^{-E_i/kT} \longleftarrow$ ⑤ quantum statistical partition function

But $e^{-F/kT} = Z$

$$-\frac{F}{kT} = \log z$$

$$-F = kT \log z$$

$$F = -\tau \log z \longrightarrow ⑥$$

This is expression for Helmholtz free energy in terms of partition function.

The statistical entropy of the system in a canonical ensemble is given by

$$\sigma = -\left(\frac{\partial F}{\partial \tau}\right)_V = -\frac{\partial}{\partial \tau}(-\tau \log z)$$

$$\sigma = \log z + \frac{\partial}{\partial \tau} \log z \cdot \tau \longrightarrow ⑦$$

If E_i is the i^{th} energy eigen value of a system we know

$$z = \sum_i e^{-E_i/\tau}.$$

$$\log z = \log\left(\sum_i e^{-E_i/\tau}\right)$$

$$\frac{\partial}{\partial \tau}(\log z) = \frac{\partial}{\partial \tau}\left\{\log\left(\sum_i e^{-E_i/\tau}\right)\right\}$$

$$\frac{\partial}{\partial \tau}(\log z) = \frac{1}{\sum_i e^{-E_i/\tau}} \sum_i E_i e^{-E_i/\tau} \left(\frac{1}{\tau^2}\right)$$

$$\frac{\partial}{\partial \tau}(\log z) = \frac{E_i}{\tau^2} = \underline{\underline{\frac{U}{\tau^2}}} \longrightarrow ⑧$$

apply equ ⑧ in equ ⑦

$$\sigma = \log z + \frac{U}{\tau^{\cancel{2}}} \cancel{\tau}$$

$$\sigma = \log z + \frac{U}{\tau}$$

Thermodynamical entropy of the system of canonical ensemble.

$$S = k\sigma = k\left[\log z + \frac{U}{kT}\right] \quad (\tau = kT)$$

$$S = k \log z + \frac{U}{T}$$

* * *

Perfect monoatomic gas in canonical ensemble.

Now we find the partition fuction and thermodynamic functions of monoatomic perfect gas using canonical ensemble.

If the system containing N number of identical and independent spinless particle we must correct the classical partition function as follows

$$z = \frac{1}{N!\, h^{3N}} \int e^{-E_{qp}/KT}\, d\tau \longrightarrow ①$$

But we know $E = \sum_i \frac{p_i^2}{2m}$

$$d\Gamma_i = \cancel{dq_1 \, dp_1} \prod_i dq_i \, dp_i$$

apply these equations in equ ①

$$Z = \frac{1}{N! \, h^{3N}} \int \left[\prod_{i=1}^{3N} e^{-p_i^2/2mT} dq_i \, dp_i \right] \longrightarrow ②$$

But we can write

$$\int \prod_{i=1}^{3N} dq_i = V^N.$$

$$\therefore Z = \frac{1}{N! \, h^{3N}} V^N \left[\int_{-\infty}^{+\infty} e^{-p_i^2/2mT} dp_i \right]^{3N} \longrightarrow ③$$

we know $\int_{-\infty}^{+\infty} e^{-ax^2} dx = \sqrt{\frac{\pi}{a}}$

$$\therefore \int_{-\infty}^{+\infty} e^{-p_i^2/2mT} dp_i = \sqrt{\frac{\pi}{1/2mT}} = (2\pi m T)^{1/2}$$

apply equ ③.

$$Z = \frac{1}{N! \, h^{3N}} V^N (2\pi m T)^{3N/2}.$$

$$Z = \frac{V^N}{N!} \left(\frac{2\pi m T}{h^2} \right)^{3N/2}.$$

~~Now according~~ to ~~definition of thermal~~ de broglie wavelength

This is ~~One particle partition func~~tion.

$$Z = \frac{V^N}{N!}\left(\frac{2\pi m K T}{h^2}\right)^{3N/2} \longrightarrow ④$$

$\tau = KT$

~~But~~ Now according to definition of thermal de broglie wavelength, we know

$$\lambda = \frac{h}{(2\pi m K T)^{1/2}}$$

~~multiply & divide by~~ . we may write

$$\lambda^{3N} = \frac{h^{3N}}{(2\pi m K T)^{3N/2}} = \frac{h^{3N\,2/2}}{(2\pi m K T)^{3N/2}}$$

$$\frac{1}{\lambda^{3N}} = \left(\frac{2\pi m K T}{h^2}\right)^{3N/2}$$

apply this in equ ④

$$Z = \frac{V^N}{N!}\left(\frac{1}{\lambda^{3N}}\right) \Longrightarrow Z = \frac{1}{N!}\left(\frac{V}{h^3}\right)^N \quad Z = \frac{f^N}{N!} \longrightarrow ⑤$$

This is one particle partition function

where $f = V\left(\frac{2\pi m K T}{h^2}\right)^{3/2} \longrightarrow f = \frac{V}{\lambda^3}$

Helmholtz free energy F.

The Helmholtz free energy F in terms of Partition function is given by

$F = -\tau \log Z$ or $F = -KT \log Z$

$F = -KT \log\left(\frac{Z^N}{N!}\right)$ from equ⑤.

$F = -KT\left[\log Z^N - \log N!\right]$

use stirriling approximation.

$F = -KT\left[N \log Z - N \log N + N\right]$

$= -KT\left[N \log\left(\frac{Z}{N}\right) + N\right]$

$= -NKT \log\left(\frac{Z}{N}\right) - NKT$

Entropy (S)

$$S = -\left(\frac{\partial F}{\partial T}\right)_V$$

$$= -\frac{\partial}{\partial T}\left(-NKT \log\left(\frac{Z}{N}\right) - NKT\right]$$

$$= \frac{\partial}{\partial T}\left[NKT \log\left(\frac{Z}{N}\right) + NKT\right]$$

$$= NK \log\left(\frac{Z}{N}\right) + NKT \frac{\partial}{\partial T}\left(\log \frac{Z}{N}\right) + NK.$$

using equ⑤ we can write

$$S = NK\log\left(\frac{Z}{N}\right) + NKT\frac{\partial}{\partial T}\left[\log\frac{V}{N}\left(\frac{2\pi mkT}{h^2}\right)^{3/2}\right]_V + NK$$

$$= NK\log\left(\frac{Z}{N}\right) + NKT\left\{\frac{1}{\frac{V}{N}\left(\frac{2\pi mkT}{h^2}\right)^{3/2}}\,\frac{V}{N}\left(\frac{2\pi mk}{h^2}\right)^{3/2}\frac{3}{2}T^{1/2}\right\} + NK$$

$$= NK\log\frac{Z}{N} + NK\left\{\frac{3}{2}\,\frac{\frac{V}{N}\cancel{\left(\frac{2\pi mkT}{h^2}\right)^{3/2}}}{\frac{V}{N}\cancel{\left(\frac{2\pi mkT}{h^2}\right)^{3/2}}}\right. + NK.$$

$$= NK\log\left(\frac{Z}{N}\right) + \frac{3}{2}NK + NK.$$

$$S = NK\log\left(\frac{Z}{N}\right) + \frac{5}{2}NK.$$

This equation is also called Sackur – Tetrode equation.

Internal energy.

The mean energy is defined as

$$\bar{\epsilon} = \frac{\sum_i E_i e^{-E_i/KT}}{\sum_i e^{-E_i/KT}} \longrightarrow ①$$

where E_i = energy of the system in i^{th} state.

The partition function $z = \sum_i e^{-E_i/\gamma}$

$$\log z = \log\left(\sum_i e^{-E_i/\gamma}\right)$$

$$\frac{\partial}{\partial T}(\log z) = \frac{1}{\sum_i e^{-E_i/T}} \sum_i E_i e^{-E_i/T} \left(\frac{1}{T^2}\right)$$

$$= \frac{1}{T^2} \frac{\sum_i E_i e^{-E_i/T}}{\sum_i e^{-E_i/T}}.$$

from equ ①

$$\frac{\partial}{\partial T}(\log z) = \frac{\bar{\epsilon}}{T^2}.$$

$$\bar{\epsilon} = T^2 \frac{\partial}{\partial T}(\log z).$$

But we know $F = -T \log z \longrightarrow \log z = -\frac{F}{T}.$

$$\bar{\epsilon} = T^2 \frac{\partial}{\partial T}\left(-\frac{F}{T}\right)$$

from Helmholtz free energy.

$$F = -NKT \log \left(\frac{Z}{N}\right) - NKT$$

~~apply this in~~ $F = -\left\{NT \log\left(\frac{Z}{N}\right) + NT\right\}$

$$\bar{\epsilon} = T^2 \frac{\partial}{\partial T}\left\{\frac{NT \log(Z/N) + NT}{T}\right)$$

$$= T^2 \frac{\partial}{\partial T} \cancel{T} \left\{\frac{N \log(Z/N) + N}{\cancel{T}}\right\}$$

$$\bar{\epsilon} = T^2 \, \partial/\partial T \left(N \log\left(\frac{Z}{N}\right) + N\right\}$$

$$\bar{\epsilon} = NT^2 \, \partial/\partial T \left(\log \frac{Z}{N} + 1\right)$$

$$\bar{E} = N\tau^2 \frac{\partial}{\partial \tau}\left\{\log\left[\frac{V}{N}\left(\frac{2\pi m\tau}{h^2}\right)^{3/2}\right] + 1\right\}$$

$$= N\tau^2 \frac{1}{\frac{V}{N}\left(\frac{2\pi m\tau}{h^2}\right)^{3/2}} \frac{V}{N}\left(\frac{2\pi m}{h^2}\right)^{3/2} \frac{3}{2}\tau^{1/2} + 0$$

$$= \frac{3}{2} N\tau \frac{\cancel{\frac{V}{N}\left(\frac{2\pi m\tau}{h^2}\right)^{3/2}}}{\cancel{\frac{V}{N}\left(\frac{2\pi m\tau}{h^2}\right)^{3/2}}}$$

$$\bar{E} = \frac{3}{2} NkT$$

Thus the internal energy of the system is given by

$$U = \bar{E} = \frac{3}{2} NkT$$

Perfect gas in grand canonical ensemble.

An ensemble which allows the subsystems to exchange the energy as well as number of particle with reservoir is called grand canonical ensemble. In which temperature volume and chemical potential are the independent variables.

Therefore instead of free energy $F = U - TS$ we have the grand potential

$$\Omega = U - TS - \mu n \longrightarrow ①$$

In grand canonical ensemble the density distribution function as well as the phase space will depends on number of particles in the subsystem then the density distribution function

$$f(n) = \exp\left[(\Omega + \mu n - E)/\tau\right] \longrightarrow ②$$

where 'Ω' is grand potential and 'μ' is the chemical potential per particle.

The grand partition function is defined as

$$Z = \exp\left(-\frac{\Omega}{\tau}\right) = \sum_n e^{\mu n/\tau} \int e^{-E/\tau}\, d\Gamma(n).$$

$$\text{or} \quad Z = \sum_n e^{\mu n/\tau} Z_n. \longrightarrow ③$$

where Z_n is the canonical partition function.

taking into account of indistinguishability of the particles, the canonical partition function is written as

$$z_n = \frac{1}{n!\,h^{3n}} \int e^{-E_n/\tau}\, d\Gamma(n) = \frac{\mathcal{F}^{n}}{n!} \longrightarrow ④$$

where $\mathcal{F} = \left(\frac{2\pi m \tau}{h^2}\right)^{3/2} V$

apply equ④ in equ③

$$Z = \sum_n e^{\mu n/\tau} \cdot \frac{\mathcal{F}^n}{n!}$$

$$Z = \sum_n \frac{\left(e^{\mu/\tau}\mathcal{F}\right)^n}{n!}$$

But we know $e^x = \sum_{n=0}^{\infty} \frac{x^n}{n!}$ Then

$$Z = \exp\left(e^{\mu/\tau}\mathcal{F}\right) \longrightarrow ⑤$$

But we know $F = -\tau \log Z$.

modify to ~~grand~~ free energy into grand potential

$$\Omega = -\tau \log Z \longrightarrow ⑥$$

equ⑤ in equ⑥

$$\Omega = -\tau e^{\mu/\tau}\mathcal{F}$$

$$\Omega = -T\, e^{\mu/T} \left(\frac{2\pi m T}{h^2}\right)^{3/2} V \longrightarrow ⑦$$

This is grand potential of grand partition function.

chemical potential(μ) :-

we know $n = -\left(\frac{\partial \Omega}{\partial \mu}\right)_{V,T}$

from equ ⑦

$$n = +\frac{\partial}{\partial \mu}\left[+T\, e^{\mu/T} \left(\frac{2\pi m T}{h^2}\right)^{3/2} V\right]$$ [redacted]

$$= T\,\frac{1}{T}\left[e^{\mu/T} \left(\frac{2\pi m T}{h^2}\right)^{3/2} V\right]$$

$$-n = -\frac{T}{T}\, e^{\mu/T} \left(\frac{2\pi m T}{h^2}\right)^{3/2} V$$

$-n = \frac{\Omega}{T}$ from equ ⑦

$$\Omega = -nT. \longrightarrow ⑧$$

n[redacted]

apply equ ⑧ in equ ⑦

$$\cancel{-}n\cancel{T} = \cancel{-}\cancel{T}\, e^{\mu/T} \left(\frac{2\pi m T}{h^2}\right)^{3/2} V$$

$$e^{\mu/T} = \frac{n}{V}\left(\frac{h^2}{2\pi m T}\right)^{3/2}$$

$$e^{-\mu/\tau} = \frac{V}{n}\left(\frac{2\pi m\tau}{h^2}\right)^{3/2} \longrightarrow \text{⑨}$$

$$-\frac{\mu}{\tau} = \log\left\{\frac{V}{n}\left(\frac{2\pi m\tau}{h^2}\right)^{3/2}\right\}$$

$$\mu = -\tau\log\left\{\frac{V}{n}\left(\frac{2\pi m\tau}{h^2}\right)^{3/2}\right\}$$

$$\mu = -\tau\log\left(\frac{\mathcal{F}}{n}\right) \longrightarrow \text{⑩}$$

Entropy (σ):-

The statistical entropy σ is given by

$$\sigma = -\left(\frac{\partial\Omega}{\partial\tau}\right)_{V,\mu}.$$

from equ ⑦ $\sigma = \cancel{-}\frac{\partial}{\partial\tau}\left\{\cancel{-}\tau\, e^{\mu/\tau}\left(\frac{2\pi m\tau}{h^2}\right)^{3/2}V\right\}$

$$= \left(\frac{2\pi m}{h^2}\right)^{3/2}V\,\frac{\partial}{\partial\tau}\left\{\tau^{5/2}e^{\mu/\tau}\right\}$$

$$\sigma = \left(\frac{2\pi m}{h^2}\right)^{3/2}V\left\{-\frac{\mu}{\tau\cancel{\tau}}e^{\mu/\tau}\,\tau^{\overset{3/2}{\cancel{5/2}}} + e^{\mu/\tau}\,\frac{5}{2}\tau^{3/2}\right\}$$

$$= \left(\frac{2\pi m}{h^2}\right)^{3/2}V\left\{\frac{5}{2}\tau^{3/2}e^{\mu/\tau} - \frac{\mu}{\tau}e^{\mu/\tau}\tau^{3/2}\right\}$$

$$\sigma = \left(\frac{2\pi m\tau}{h^2}\right)^{3/2} V\, e^{\mu/\tau}\left[\frac{5}{2}-\frac{\mu}{\tau}\right] \longrightarrow ⑪$$

from equ ⑩

$$\left.\begin{aligned}\frac{\mu}{\tau} &= -\log\left(\frac{\tau}{n}\right)\\ \frac{\mu}{\tau} &= \log\left(\frac{n}{\tau}\right)\end{aligned}\right\} \longrightarrow ⑫$$

apply equ ⑫ in equ ⑪.

$$\sigma = \left(\frac{2\pi m\tau}{h^2}\right)^{3/2} V\, e^{\log(n/\tau)}\left[\frac{5}{2}+\log\left(\frac{\tau}{n}\right)\right].$$

$$= \left(\frac{2\pi m\tau}{h^2}\right)^{3/2} V\, \frac{n}{\tau}\left[\frac{5}{2}+\log\left(\frac{\tau}{n}\right)\right]$$

$$= \cancel{\left(\frac{2\pi m\tau}{h^2}\right)^{3/2}} \cancel{V}\cdot \frac{n}{\cancel{\left(\frac{2\pi m\tau}{h^2}\right)^{3/2}}\cancel{V}}\left[\frac{5}{2}+\log\left(\frac{V}{n}\left(\frac{2\pi m\tau}{h^2}\right)^{3/2}\right)\right]$$

$$\sigma = n\cdot\left\{\log\left[\frac{V}{n}\left(\frac{2\pi m\tau}{h^2}\right)^{3/2}\right]+\frac{5}{2}\right. \longrightarrow ⑬$$

Therefore the thermodynamical entropy $S = k\sigma$

$$S = nk\log\left[\frac{V}{n}\left(\frac{2\pi m\tau}{h^2}\right)^{3/2}\right]+\frac{5}{2}nk \longrightarrow ⑭$$

Internal energy :-

We obtain an equation from previous Section

$$U = -\Omega + \tau\sigma + \mu n \quad ⑮$$

apply the value of Ω from equ ⑦ and σ from equ ⑪ Then we get

$$U = -\tau e^{\mu/\tau}\left(\frac{2\pi m\tau}{h^2}\right)^{3/2} V + \tau\left(\frac{2\pi m\tau}{h^2}\right)^{3/2} V e^{\mu/\tau}\left(\frac{5}{2}-\frac{\mu}{\tau}\right) + \mu n$$

$$= \tau e^{\mu/\tau}\left(\frac{2\pi m\tau}{h^2}\right)^{3/2} V\left\{-1+\frac{5}{2}-\frac{\mu}{\tau}\right\} + \mu n.$$

$$= \tau \, e^{\mu/\tau}\left(\frac{2\pi m\tau}{h^2}\right)^{3/2} V\left\{\frac{3}{2}-\frac{\mu}{\tau}\right\} + \mu n. \longrightarrow ⑯$$

The value of n from equ ⑨.

$$n = \left(\frac{2\pi m\tau}{h^2}\right)^{3/2} \frac{V}{e^{-\mu/\tau}}.$$

$$n = \left(\frac{2\pi m\tau}{h^2}\right)^{3/2} e^{\mu/\tau} V$$

apply the above equation in equ ⑯

$$U = n\tau\left\{\frac{3}{2}-\frac{\mu}{\tau}\right\} + \mu n.$$

$$= \frac{3}{2} n\tau - \cancel{\frac{\mu n \cancel{\tau}}{\cancel{\tau}}} + \cancel{\mu n}.$$

$$\therefore \boxed{U = \frac{3}{2} nKT}$$

Bose – Einstein statistics

Consider a system having n distinguishable Particles be divided into quantum groups such that $n_1, n_2, \dots n_i$ number of particles in groups whose approximate constant energies are $\epsilon_1, \epsilon_2, \dots \epsilon_i$ respectively. Let g_i be the number of eigen states of i^{th} level.

The condition for bose einstein statistics are.

i) The particles are indistinguishable from each other

ii) Each ~~of~~ eigen state (sub level) of i^{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.

Then the probability of the systems occuring distribution is proportional to total number of eigen states, i.e.

$$W = \prod_i \frac{(n_i+g_i)!}{n_i!\, g_i!} \times \text{constant} \longrightarrow ①$$

taking logrithm in both sides

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

$$= \sum_i \left[\log (n_i+g_i)! - \log n_i! - \log g_i! \right] + \text{const}$$

using stirling approximation.

$$\log W = \sum_i \Big[(n_i+g_i)\log(n_i+g_i) - \cancel{(n_i+g_i)} - n_i \log n_i + \cancel{n_i}$$
$$- g_i \log g_i + \cancel{g_i} \Big] + \text{const}$$

$$\log W = \sum_i \Big[(n_i+g_i)\log(n_i+g_i) - n_i \log n_i - g_i \log g_i \Big] + \text{const}$$

differentiate

$$\delta(\log w) = \sum_i \Big[\delta n_i \log(n_i+g_i) + \cancel{(n_i+g_i)} \frac{1}{\cancel{(n_i+g_i)}} \delta n_i$$
$$- \log n_i \, \delta n_i - \cancel{n_i} \frac{1}{\cancel{n_i}} \delta n_i - 0 \Big] + 0.$$

$$= \sum_i \Big[\log(n_i+g_i)\,\delta n_i + \cancel{\delta n_i} - \log n_i \,\delta n_i - \cancel{\delta n_i} \Big]$$

$$\delta(\log w) = \sum_i \Big[\log(n_i+g_i)\,\delta n_i - \log n_i \,\delta n_i \Big]$$

$$\delta(\log w) = \sum_i \Big[\log(n_i+g_i) - \log n_i \Big] \delta n_i$$

$$\delta(\log w) = -\sum_i \Big[\log \frac{n_i}{n_i+g_i} \Big] \delta n_i \longrightarrow ②$$

But we know

i) The total number of particles of the system is constant.

$$n = \sum_i n_i = \text{const} \longrightarrow \delta n = \sum_i \delta n_i = 0.$$
$$\longrightarrow ③$$

ii) The total amount of energy of the system is constant

$$E = \sum_i n_i \epsilon_i = \text{const}$$

$$\delta E = \sum_i \epsilon_i \,\delta n_i = 0. \longrightarrow ④$$

iii) When the probability is maximum then $\delta(\log w) = 0. \longrightarrow$ (5

According to equ ⑤ the equ ② may write as

$$-\sum_i \left[\log \frac{n_i}{n_i+g_i} \right] \delta n_i = 0 \longrightarrow ⑥$$

now we apply Legrangian method of undetermined multipliers. using equ ③ & ④ then

~~$-\sum_i \left[\log \frac{n_i}{n_i+g_i} \delta n_i + \alpha \sum_i \delta n_i + \beta \sum_i \epsilon_i \delta n_i \right] = 0$~~

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

$$\log \frac{n_i}{n_i+g_i} + \alpha + \beta \epsilon_i = 0$$

$$\log \frac{n_i}{n_i+g_i} = -(\alpha + \beta \epsilon_i)$$

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

$$\frac{n_i+g_i}{n_i} = e^{(\alpha+\beta\epsilon_i)}$$

$$1 + \frac{g_i}{n_i} = e^{(\alpha+\beta\epsilon_i)}$$

$$\frac{g_i}{n_i} = e^{(\alpha+\beta\epsilon_i)} - 1$$

$$\frac{n_i}{g_i} = \frac{1}{e^{\alpha+\beta\epsilon_i} - 1}$$

$$n_i = \frac{g_i}{e^{\alpha+\beta\epsilon_i} - 1}$$

This equation representing most probable distribution of particles among various energy levels for a system obeying Bose-Einstein statistics and also called Bose-Einstein distribution law.

~~Planck's Law of Black body radiation.~~

~~Black body radiation is the example of application of Bose einstein statistics. The radiation emitted~~

Ideal Bose gas

Consider a system of N identical independent and interactive particles with integral spin ~~with~~ having symmetrical wave function. Let the particles are distributed amoung various particle state $n_1, n_2 \cdots n_i$ and energy associated with the states are $\epsilon_1, \epsilon_2 \cdots \epsilon_i$ respectively. Now the most probable distribution of Bose particles is

$$n_i = \frac{g_i}{e^{\alpha+\beta\epsilon_i}-1} \qquad \text{put } e^{\alpha} = D \text{ then}$$

$$n_i = \frac{g_i}{De^{\beta\epsilon_i}-1} \longrightarrow ①$$

The number of particles state lying between momentum p and p+dp is

$$g(p)\,dp = g_s \frac{4\pi V}{h^3} p^2\,dp \longrightarrow ②$$

where $g_s = 2s+1$ spin degeneracy

Now equ ① canbe write in terms of momentum

$$dn(p) = \frac{g(p)\,dp}{De^{\beta\epsilon}-1} \longrightarrow ③$$

apply equ ② in equ ③

$$dn(p) = g_s \frac{4\pi V}{h^3} \frac{p^2\,dp}{De^{\beta\epsilon}-1} \longrightarrow ④$$

But we know $\epsilon = p^2/2m$, $p^2 = 2m\epsilon$, $p = \sqrt{2m\epsilon}$, $dp = \sqrt{\frac{m}{2\epsilon}}\,d\epsilon$

apply the above equations in equ ④

$$dn(\epsilon) = g_s \frac{4\pi V}{h^3} \frac{2m\epsilon \left(\frac{m}{2\epsilon}\right)^{1/2} d\epsilon}{De^{\epsilon/KT}-1} \qquad (\beta = 1/KT$$

$$= g_s \frac{\cancel{4}\pi V}{h^3} \frac{\cancel{2^{1/2}}\,2^{1/2}\, m\, \cancel{\epsilon^{1/2}}\,\epsilon^{1/2} \left(\frac{m}{\cancel{2\epsilon}}\right)^{1/2} d\epsilon}{De^{\epsilon/KT}-1}$$

$$= g_s \frac{4\pi mV}{h^3} (2m)^{1/2} \frac{\epsilon^{1/2}\,d\epsilon}{De^{\epsilon/KT}-1}$$

Put $\frac{\epsilon}{KT} = x$, $\epsilon = xKT$, $d\epsilon = KT\,dx$.

$$dn(\epsilon) = g_s \frac{4\pi mV}{h^3} (2m)^{1/2} \frac{(xKT)^{1/2} \cdot KT\,dx}{De^{x}-1}$$

mult & divi by $\sqrt{\pi}$

$$dn(\epsilon) = g_s \frac{2 \cdot 2\pi mV}{h^3} \frac{\sqrt{\pi}}{\sqrt{\pi}} (2m)^{1/2} \frac{(KT)^{3/2}\, x^{1/2}\,dx}{De^{x}-1}$$

$$= \underline{2g_s} \frac{V}{h^3\sqrt{\pi}} \left(2\pi mKT\right)^{3/2} \frac{x^{1/2}\,dx}{De^{x}-1}$$

$$dn(E) = \frac{2g_s}{\sqrt{\pi}} V \left(\frac{2\pi mkT}{h^2}\right)^{3/2} \frac{x^{1/2}\,dx}{De^{x}-1}$$

$$dn(E) = \frac{2g_s Z_t}{\sqrt{\pi}} \frac{x^{1/2}\,dx}{De^{x}-1} \longrightarrow ⑤$$

where $Z_t = \left(\frac{2\pi mkT}{h^2}\right)^{3/2} V$ is translational partition function.

But the total number of particle can write as

$$n = \int dn. \longrightarrow ⑥$$

apply the equ ⑤ in ~~above~~ equ ⑥.

$$n = \frac{2g_s Z_t}{\sqrt{\pi}} \int_0^{\infty} \frac{x^{1/2}\,dx}{De^{x}-1} \longrightarrow ⑦$$

The total amount of energy

$$E = \int E\,dn. \longrightarrow E = \int xkT\,dn.$$

$$E = \frac{2g_s Z_t}{\sqrt{\pi}} kT \int_0^{\infty} \frac{x^{3/2}\,dx.}{De^{x}-1} \longrightarrow ⑧$$

first we must solve the ~~equ~~ integral part from equ ⑦

$$\int_0^{\infty} \frac{x^{1/2}\,dx}{De^{x}-1} = \int_0^{\infty} x^{1/2}\left(De^{x}-1\right)^{-1} dx.$$

$$= \int_0^{\alpha} x^{1/2} D^{-1} e^{-x} \left(1 - \frac{1}{De^{x}}\right)^{-1} dx$$

$$= \int_0^{\alpha} x^{1/2} \frac{e^{-x}}{D} \left(1 - \frac{e^{-x}}{D}\right)^{-1} dx.$$

The Binomial expansion

$$= \int_0^{\alpha} x^{1/2} \frac{e^{-x}}{D} \left(1 + \frac{e^{-x}}{D} + \frac{e^{-2x}}{D^2} + \cdots\cdots\right) dx.$$

$$= \frac{1}{D}\int_0^{\alpha} x^{1/2} e^{-x} dx + \frac{1}{D^2}\int_0^{\alpha} x^{1/2} e^{-2x} dx + \cdots\cdots$$

$$= \frac{1}{D}\frac{\sqrt{\pi}}{2} + \frac{1}{D^2}\frac{1}{2^{3/2}}\frac{\sqrt{\pi}}{2} + \cdots\cdots$$

$$\int_0^{\alpha} \frac{x^{1/2} dx}{De^{x}-1} = \frac{\sqrt{\pi}}{2D}\left(1 + \frac{1}{2^{3/2}D} + \frac{1}{3^{3/2}D^2} + \cdots\cdots\right) \longrightarrow ⑨$$

IIIly $$\int_0^{\alpha} \frac{x^{3/2} dx}{De^{x}-1} = \frac{1}{D}\int_0^{\alpha} x^{3/2} e^{-x} dx + \frac{1}{D^2}\int_0^{\alpha} x^{3/2} e^{-2x} dx + \cdots\cdots$$

$$\int_0^{\alpha} \frac{x^{3/2} dx}{De^{x}-1} = \frac{3\sqrt{\pi}}{4D}\left(1 + \frac{1}{2^{5/2}D} + \frac{1}{3^{5/2}D^2} + \cdots\cdots\right) \longrightarrow ⑩$$

apply the equ ⑨ in equ ⑦

$$n = \frac{\cancel{2} g_s Z_t}{\cancel{\sqrt{\pi}}} \frac{\cancel{\sqrt{\pi}}}{\cancel{2}D}\left(1 + \frac{1}{2^{3/2}D} + \frac{1}{3^{3/2}D^2} + \cdots\cdots\right)$$

$$n = \frac{g_s Z_t}{D}\left(1 + \frac{1}{2^{3/2}D} + \frac{1}{3^{3/2}D^2} + \cdots\right) \longrightarrow ⑪$$

Similarly equ ⑩ apply in equ ⑧

$$E = \frac{\cancel{2} g_s Z_t}{\cancel{\sqrt{\pi}}} KT \frac{3\cancel{\sqrt{\pi}}}{\cancel{4}D}\left(1 + \frac{1}{2^{5/2}D} + \frac{1}{3^{5/2}D^2} + \cdots\cdots\right)$$

$$E = \frac{3 g_s Z_t KT}{2D}\left(1 + \frac{1}{2^{5/2}D} + \frac{1}{3^{5/2}D^2} + \cdots\cdots\right) \longrightarrow ⑫$$

From equ ⑪

$$g_s Z_t = nD\left(1 + \frac{1}{2^{3/2}D} + \frac{1}{3^{3/2}D^2} + \cdots\right)^{-1}$$

apply this in equ ⑫

$$E = \frac{3KT}{2\cancel{D}}\, n\cancel{D}\left(1 + \frac{1}{2^{5/2}D} + \frac{1}{3^{5/2}D^2} + \cdots\right)\left(1 + \frac{1}{2^{3/2}D} + \frac{1}{3^{3/2}D^2} + \cdots\right)^{-1}$$

$$= \frac{3}{2}nKT\left(1 + \frac{1}{2^{5/2}D} + \cdots\cdots\right)\left(1 - \frac{1}{2^{3/2}D} - \frac{1}{3^{3/2}D^2} - \cdots\right)$$

$$= \frac{3}{2}RT\left(1 - \frac{1}{2^{5/2}D} - \frac{1}{3^{5/2}D^2} - \cdots\cdots\right)$$

$$\boxed{E = \frac{3}{2}RT\ 2.}$$

From the first part of equ ⑩

$$n = \frac{g_s Z_t}{D} \longrightarrow D = \frac{g_s Z_t}{n}.$$

F.

$$\therefore E = \frac{3}{2}RT\left(1 - \frac{1}{2^{5/2}}\left(\frac{n}{g_s Z_t}\right) - \frac{1}{3^{5/2}}\left(\frac{n}{g_s Z_t}\right) - \cdots\cdots\right)$$

Pressure of the Bose gas.

we can calculate the pressure of the gas from the following relation

$$P = -\left(\frac{\partial E}{\partial V}\right) \longrightarrow ①$$

In order to calculate the pressure, first we found out a relation between energy and Volume.

Let us Consider particle of mass m is enclosed in a Container of volume a, b, c. The wave function ψ of the particle must satisfy the schrodinger equation.

$$\nabla^2\psi + \frac{8\pi^2 m}{h^2}(E-V)\psi = 0.$$

where V is potential energy, which is zero for one particle in a box.

$$\therefore \quad \nabla^2\psi + \frac{8\pi^2 m}{h^2} E\psi = 0$$

$$\frac{8\pi^2 m}{h^2} E\psi = -\nabla^2\psi$$

$$E\psi = -\nabla^2\psi \frac{h^2}{8\pi^2 m}$$

$$E\psi = -\frac{h^2}{8\pi^2 m}\left(\frac{\partial^2\psi}{\partial x^2} + \frac{\partial^2\psi}{\partial y^2} + \frac{\partial^2\psi}{\partial z^2}\right)$$

The ψ is form of associated variables.

$$\psi = X_{(x)}\, Y_{(y)}\, Z_{(z)}$$

$$E = -\frac{h^2}{8\pi^2 m}\left(\frac{1}{X}\frac{\partial^2 X}{\partial x^2} + \frac{1}{Y}\frac{\partial^2 Y}{\partial y^2} + \frac{1}{Z}\frac{\partial^2 Z}{\partial z^2}\right)$$

Or we Kan write as.

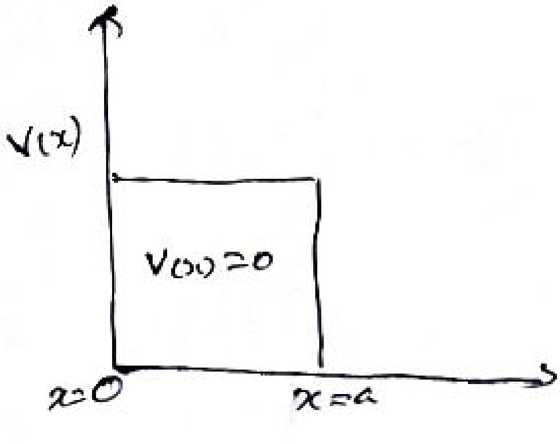
$$\left.\begin{aligned} E_x &= -\frac{h^2}{8\pi^2 m}\left(\frac{1}{X}\frac{\partial^2 X}{\partial x^2}\right) \\ E_y &= -\frac{h^2}{8\pi^2 m}\left(\frac{1}{Y}\frac{\partial^2 Y}{\partial y^2}\right) \\ E_z &= -\frac{h^2}{8\pi^2 m}\left(\frac{1}{Z}\frac{\partial^2 Z}{\partial z^2}\right)\end{aligned}\right\} \longrightarrow ②$$

The general solution equation for above equations is

$$X_{(x)} = A \sin(Bx + C) \longrightarrow ③$$

where A, B, C are constants.

which canbe calculated by applying boundari conditions as mention in figure.



$X_{(x)} = 0$ at $x = 0$.

∴ equ ③

$$0 = A \sin C$$

$$\boxed{C = 0}$$

and $X_x = 0$ at $x = a$ then. equ ③

$$0 = A \sin (Ba + C)$$

where $Ba + C = r_x \pi$
where r_x is an intiguer. and $C = 0$ then.

$$Ba = r_x \pi$$

$$\boxed{B = \frac{r_x \pi}{a}}$$

apply the values of B, C in equ ③

$$X_x = A \sin \frac{r_x \pi}{a} + 0$$

Illy $$Y_y = A \sin \frac{r_y \pi}{b}$$

$$Z_z = A \sin \frac{r_z \pi}{c}$$

Apply in equ ②

$$E_x = -\frac{h^2}{8\pi^2 m} \frac{1}{A \sin \frac{r_x \pi}{a}} \frac{\partial^2}{\partial x^2}\left(A \sin . \frac{r_x \pi}{a}\right)$$

$$= -\frac{h^2}{8\pi^2 m} \cancel{\frac{1}{A \sin \frac{r_x \pi}{a}}} \left(-\frac{r_x^2 \pi^2}{a^2}\right) \cancel{A \sin \frac{r_x \pi}{a}}$$

$$E_x = \frac{h^2 \pi^2 r_x^2}{8\pi^2 m a^2}$$

Similarly

$$E_y = \frac{h^2 \pi^2 r_y^2}{8\pi^2 m b^2}$$

$$E_z = \frac{h^2 \pi^2 r_z^2}{8\pi^2 m c^2}$$

$$\therefore E = E_x + E_y + E_z = \frac{h^2 \pi^2}{8\pi^2 m}\left(\frac{r_x^2 + r_y^2 + r_z^2}{a^2+b^2+c^2}\right)$$

$\therefore a = b = c = l$ Then

$$E = \frac{h^2 \pi^2}{8\pi^2 m}\left(\frac{r_x^2 + r_y^2 + r_z^2}{l^2}\right)$$

But the volume $l^3 = V \rightarrow l = V^{1/3} \longrightarrow \underline{\underline{l^2 = V^{2/3}}}$

$\therefore$ ~~$E = \frac{h^2\pi^2}{8\pi^2 m}$~~ And the indiger $r_x^2 + r_y^2 + r_z^2 = r^2$

$$\therefore E = \frac{h^2 \pi^2 r^2}{8\pi^2 m V^{2/3}} \longrightarrow ④$$

apply the equ ④ in equ ①

$$P = -\frac{\partial}{\partial V}\left(\frac{h^2 \pi^2 r^2}{8\pi^2 m V^{2/3}}\right)$$

$$= -\frac{h^2 \pi^2 r^2}{8\pi^2 m} \frac{\partial}{\partial V}\left(V^{-2/3}\right)$$

$$= -\frac{h^2 \pi^2 r^2}{8\pi^2 m}\left(-\frac{2}{3} V^{-2/3 - 1}\right)$$

$$P = \frac{2}{3} \frac{h^2 \pi^2 r^2}{8\pi^2 m} V^{-5/3}$$

$$= \frac{2}{3} \frac{h^2 \pi^2 r^2}{8\pi^2 m V^{5/3}}$$

$$= \frac{2}{3V} \frac{h^2 \pi^2 r^2}{8\pi^2 m V^{2/3}}$$

$$= \frac{2}{3} \frac{E}{V}$$

from the energy of the gas.

$$P = \frac{\cancel{2}}{\cancel{3}V} \frac{\cancel{3}}{\cancel{2}} RT\, 2$$

$$\boxed{P = \frac{RT}{V}\, 2}$$

From the equations of energy (E) and pressure (P), we can find out the deviations of the gas from ideal Bose gas Behaviour.

Bose Einstein Condensation.

We know the equation of number of particles from Bose gas.

$$n = \frac{g_s Z_t}{D}\left(1 + \frac{1}{2^{3/2} D} + \cdots\right) \longrightarrow ①$$

If we neglect the second term

$$n = \frac{g_s Z_t}{D} \longrightarrow D = \frac{g_s Z_t}{n}.$$

$$\frac{1}{D} = \frac{n}{g_s Z_t}$$

$$= \frac{n}{g_s V}\left(\frac{2\pi m k T}{h^2}\right)^{-3/2}.$$

We ~~[illegible]~~ note that the temperature approach to "0" then the value of $\frac{1}{V}$ will get large values. It means the gas deviate highly from perfect gas behaviour. Now we find the reason as follows.

The number of particles lying between energy range E and E+dE

$$dn(E) = g_s \frac{g(E)dE}{De^{E/kT} - 1}$$

But the number of eigen state lying between the ~~energy~~ range E and dE

$$g(E) = \frac{4\pi V}{h} \frac{\epsilon^{1/2} d\epsilon}{De^{\epsilon/kT}-1}$$

where for ground state the energy $\epsilon_i = 0$
~~above the ground state $\epsilon_i \neq 0$~~

we know the equation for most probable distribution of Bose-Einstein statistics

$$n_i = \frac{g_i}{e^{\alpha+\beta\epsilon}-1}$$

for the ground state $\epsilon_i = \epsilon_0 = 0$

Then $g_i = 1$ Therefore

$$n_0 = \frac{1}{e^{\alpha}-1}$$

For total number of particles in all the particles states $n = n_0 + \int dn$.

$$n = n_0 + \frac{2 g_s Z_t}{\sqrt{\pi}} \int_0^{\alpha} \frac{x^{1/2} dx}{De^{x}-1}$$

we may write this equation

$$n = n_0 + g_s Z_t \, F_{3/2}(\alpha) \quad \text{———} ②$$

where $F_{3/2}(\alpha) = \frac{2}{\sqrt{\pi}} \int_0^{\alpha} \frac{x^{1/2} dx}{De^{x}-1}$

$$F_{3/2}(\alpha) = \frac{2}{\sqrt{\pi}} \frac{\sqrt{\pi}}{2D}\left(1+\frac{1}{2^{3/2}D}+\cdots\cdots\right)$$

$$F_{3/2}(\alpha) = \frac{1}{D}\left(1+\frac{1}{2^{3/2}D}+\cdots\cdots\right)$$

~~Fo~~ If $\alpha = 0$ then $e^{\alpha} = 1 = D$

$$\therefore F_{3/2}(0) = 1+\frac{1}{2^{3/2}}+\frac{1}{3^{3/2}}+\cdots\cdots$$

$$\therefore F_{3/2}(0) = 2.612.$$

If $T = T_0$ ~~and $\alpha = 0$ then $D = 1$ then~~

~~from equations for Bosons~~

then the equ ① may write. as

$$n = \frac{g_s Z_t(T=T_0)}{D}\left(1+\frac{1}{2^{3/2}D}+\cdots\cdots\right)$$

But $\alpha = 0$ and $D = 1$ then

$$n = g_s Z_t(T=T_0)\left(1+\frac{1}{2^{3/2}}+\frac{1}{3^{3/2}}+\cdots\right)$$

$$n = g_s Z_t(T=T_0)\, F_{3/2}(0) \; . \longrightarrow ③.$$

$$g_s = \frac{n.}{Z_{t(T=T_0)}\, F_{3/2}(0)}$$

apply this in equ ②.

$$n = n_0 + n \frac{Z_t}{Z_{t\,(T=T_0)}} \quad \frac{F_{3/2}(\alpha)}{F_{3/2}(0)}$$

$$= n_0 + n \cdot \frac{\left(\frac{2\pi \cancel{m} kT}{h^2}\right)^{3/2} \cancel{V}}{\left(\frac{2\pi \cancel{m} kT_0}{h^2}\right)^{3/2} \cancel{V}} \cdot \quad \frac{F_{3/2}(\alpha)}{F_{3/2}(0)}$$

$$n = n_0 + n \left(\frac{T}{T_0}\right)^{3/2} \frac{F_{3/2}(\alpha)}{F_{3/2}(0)} \longrightarrow ⑦$$

And number of particle states above the ground states

$$n' = n - n_0 = n \left(\frac{T}{T_0}\right)^{3/2} \frac{F_{3/2}(\alpha)}{F_{3/2}(0)}$$

If $\alpha = 0$ then $D = 1$

$\alpha \neq 0$ then $D > 1$

$$\therefore \quad n' = n \left(\frac{T}{T_0}\right)^{3/2} \quad \text{where } T < T_0$$

$$n_0 = n - n'$$
$$= n - n \left(\frac{T}{T_0}\right)^{3/2} = n\left[1 - \left(\frac{T}{T_0}\right)^{3/2}\right]$$

$$n_0 = n\left[1 - \left(\frac{T}{T_0}\right)^{3/2}\right] \quad \text{when } T = T_0.$$

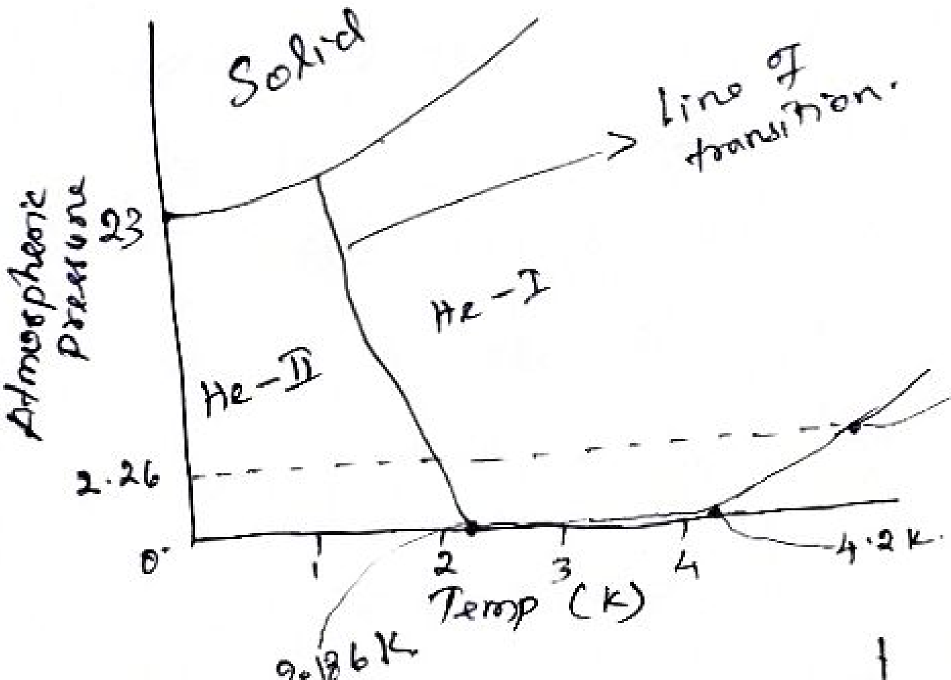
At this stage all the particles must Condensed into ground state. From this equation ~~the~~ while the temp. is lowered all the particles are fall rapidly into the ground state.

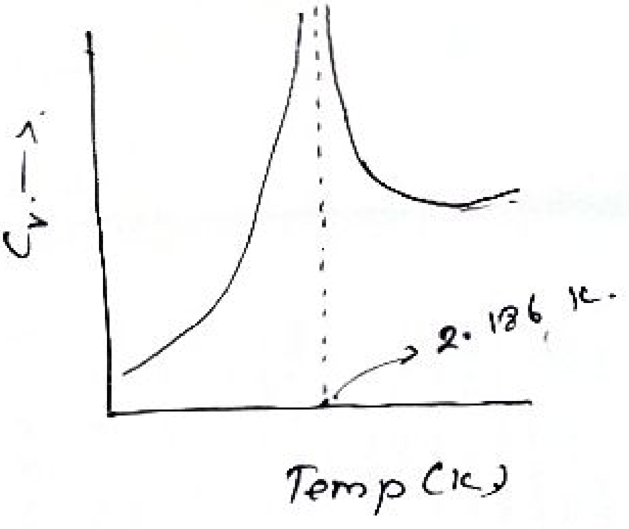
Liquid Helium

Liquid Helium is the application of B.E Statistics, we may investigate the quantitative nature of Superfluid transition of Liquid helium at 2.186 K. The Helium exhibits peculier properties at low temperature as follows.

1. Helium gas at atmospheric pressure condensed at 4.3 K into liquid of low density about 0.124 g/cm³.
2. Further cooling, upto absolute zero at normal pressure it does not freeze and it is believed to remain liquid. The Solid State of Helium does not exist unless it Subjected to external pressure of 23 atmospheric pressure.
3. Helium in liquid phase there is another phase transition called "λ" transition which divides the liquid state into two phases He-I and He-II. ~~The investi~~

The investigation ~~reviewed~~ revealed that the transition temperature is at 2.186 K and it represents a transition to be a new State of matter known as Liquid He-II.





The properties of Liquid He-II :-

a) Heat conductivity is very large in order of 3×10^6 times grater.

b) The Coefficient of viscosity is reduced as lowering the temperature and approaches zero at absolute zero temperature.

c) The specific heat is increased upto 2.19 K. The Cv is discontinued. at that point the Cv is decreases and above that point then increases.

The Specific heat - temperature curve at 2.186 K. looks like lamda (λ) and hence this temperature 2.186 K at which Specific heat changes abruptly is called λ-point. we can notice that there is no heat is absorbed during this transition from ~~one~~ He-I to He-II.

London's theory of Liquid He-II

Explanation based on the B.E condensation. He-II Liquid analogues to B.E gas and that λ transition in liquid helium the Counter part of B.E Condensation in ideal gas.

In B.E gas the degeneracy is

$$\frac{1}{D} = \frac{n}{g_s V}\left(\frac{2\pi mKT}{h^2}\right)^{3/2}$$

London suggested that the helium atoms are light enough. And the density of liquid is sufficiently high. The degeneracy to be well marked but is low ~~cop~~ enough for the liquid becom as a gas.

The Bose Einstein Condensation temperature T_0 is defined ~~as~~ from equ ③ of B.E Condensation.

$$n = g_s Z_t \; F_{3/2}(0)$$

$$\frac{n}{V F_{3/2}(0)} = g_s \left(\frac{2\pi m k T_0}{h^2} \right)^{3/2}$$

$$T_0 = \frac{h^2}{2mk\pi} \left(\frac{n g_s}{V F_{3/2}(0)} \right)^{2/3}$$

~~$T_0 = 3.12\ K.$~~ $T_0 = 3.12\ K.$

In this expression we apply the values of Volume $V = 27.2\ cm^3$ for gram molecule of helium in liquid state we get $T_0 = 3.12\ K.$ which is closed to the value of λ point (T_λ). This agreement in the value T_0 and T_λ favours the london explanation.

Further for the discontineuty is of specific heat curve at λ point, London suggest that similar discondinuity occurs in the specific heat of B.E gas.

The decrease in the entropy below T_λ being zero at 0.5 K. which is well explained by B.F Condensation.

Einstein's theory of Specific heat of Solid.

Einstein modified the classical results by making the following simple assumptions.

i) The atoms in a solid are all independent and each atom acts as a simple harmonic oscillator with a common frequency 'ν'. Thus the solid is characterized by monochromatic vibrations.

ii) Each atom of a solid has three degrees of freedom.

iii) The mean energy per degree of freedom of an oscillator vibrating with the frequency is not $\frac{1}{2}KT$, But $h\nu/e^{h\nu/KT}-1$ as obtained by planck by the application of quantum theory.

Hence energy of each atom is $= \dfrac{3h\nu}{e^{h\nu/KT}-1}$

The energy content of a gram-atom of the solid consisting N atoms then

$$E = \frac{3Nh\nu}{e^{h\nu/KT}-1}$$

Then the specific heat at constant volume

$$C_V = \frac{dE}{dT} = \frac{d}{dT}\left[\frac{3Nh\nu}{e^{h\nu/KT}-1}\right]$$

$$= 3Nh\nu\left[-\frac{1}{(e^{h\nu/KT}-1)^2}\right]e^{h\nu/KT}\left(-\frac{h\nu}{KT^2}\right)$$

$$= \frac{3Nh^2\nu^2}{KT^2}\left[\frac{e^{h\nu/KT}}{(e^{h\nu/KT}-1)^2}\right]$$

× and ÷ by k

$$C_V = 3Nk\left(\frac{h^2\nu^2}{k^2T^2}\right)\left[\frac{e^{h\nu/kT}}{(e^{h\nu/kT}-1)^2}\right] \longrightarrow ①$$

$$C_V = 3R\left[\frac{e^{h\nu/kT}}{(e^{h\nu/kT}-1)^2}\left(\frac{h\nu}{kT}\right)^2\right]$$

where $\frac{h\nu}{k} = \theta$ →

$$C_V = 3R\left[\frac{e^{\theta/T}}{(e^{\theta/T}-1)^2}\left(\frac{\theta}{T}\right)^2\right] \longrightarrow ②$$

where θ_E is Einstein's temperature and ν_E is Einstein's frequency then this term is function of Einstein's temperature

$$\theta_E = \frac{h\nu_E}{k}$$

~~This~~ The equ ② represents that the specific heat is a function of temperature. There are two cases to discuss as follows:-

1. <u>At high temperature</u>. $\frac{h\nu}{kT}$ approaches very small values due to the T is in denominator.

$$\therefore (e^{h\nu/kT}-1)^2 = \left[1 + \frac{h\nu}{kT} + \frac{1}{2!}\left(\frac{h\nu}{kT}\right)^2 + \ldots\ldots -1\right]$$

$$(e^{h\nu/kT}-1)^2 \approx \left(\frac{h\nu}{kT}\right)^2$$ apply in equ ①

$$C_V = 3R \frac{\left[1+\frac{h\nu}{KT}+\cdots\right]}{\left[\left(\frac{h\nu}{KT}\right)\right]^2}\left(\frac{h\nu}{KT}\right)^2$$

$$= 3R\left[1+\frac{h\nu}{KT}+\cdots\right]$$

As $T \to \infty$ then $\frac{h\nu}{KT} \to 0$

$\therefore$ $C_V = 3R$

2- At very low temperature :- that is $T \to 0$ then $\frac{h\nu}{KT} \to \infty$ and hence 1 may be neglected in the expression $\left(e^{h\nu/KT}-1\right)^2$

$$\therefore \quad C_V = 3R\frac{\cancel{e^{h\nu/KT}}}{\left(e^{h\nu/KT}\right)^2}\left(\frac{h\nu}{KT}\right)^2$$

$$= 3R\frac{\left(\frac{h\nu}{KT}\right)^2}{\left[1+\frac{h\nu}{KT}+\frac{1}{2!}\left(\frac{h\nu}{KT}\right)^2+\cdots\right]}$$

$$= 3R\frac{1}{\left[\frac{1}{\left(\frac{h\nu}{KT}\right)^2}+\frac{1}{\left(\frac{h\nu}{KT}\right)}+\frac{1}{2!}+\frac{1}{3!}\left(\frac{h\nu}{KT}\right)+\cdots\right]}$$

Thees The T in denominator $\frac{h\nu}{KT} \to \infty$

$$\boxed{C_V = 0}$$

The Specific heat tends to zero as temperature tends to absolute zero.

~~Debye's theory of Specific heat of Solid.~~

~~The essential of Debye considered the vibratio~~

Debye's theory of Specific heat of Solid.

Debye Considered that the vibrational modes of Crystal as a whole, while Einstein Consider the vibration of Single atom and that to be independent of other atoms. Thus the atoms do not vibrate independently, the vibration of any individual atom will set neighbouring atoms in oscillation and the free vibrations of the system are identical with the elastic vibrations. There are two kinds of vibrations are proposed: 1. longitudinal vibrations 2. Transverse vibrations.

The number of modes of longitudinal vibrations per unit volume in frequency range ν and $\nu + d\nu$

$$= \frac{4\pi\nu^2 d\nu}{C_l^3}$$

where C_l is velocity of longitudinal vibrations.

The number of modes of Transverse vibrations per unit volume in frequency range ν and $\nu + d\nu$

$$= \frac{8\pi\nu^2 d\nu}{C_t^3}$$

C_t is velocity of transverse vibrations.

Here the expressions in Second case is doubled because one longitudinal vibration is equal to two Transverse vibrations due to displacement perpendicular to direction of ~~vibs~~ propagation.

Therefore the number of independent vibrations per unit volume with frequency rang ν and $\nu+d\nu$

$$= 4\pi\left[\frac{1}{C_l^3}+\frac{2}{C_t^3}\right]\nu^2 d\nu$$

If V is volume of gram atom of Solid then

$$= 4\pi V\left[\frac{1}{C_l^3}+\frac{2}{C_t^3}\right]\nu^2 d\nu \longrightarrow ①$$

Debye assumes this results holds for all the frequencies from lowest ($\nu=0$) to highest ($\nu=\nu_m$)

Then

$$= 4\pi V\left[\frac{1}{C_l^3}+\frac{2}{C_t^3}\right]\int_0^{\nu_m}\nu^2 d\nu$$

$$= 4\pi V\left[\quad\right]\frac{\nu_m^3}{3} \longrightarrow ②$$

But this must be equal to the number of degrees of freedom(3) of all the atoms (N) Then

$$4\pi V \left[\qquad \right] \frac{\nu_m^3}{3} = 3N$$

$$4\pi V \left[\qquad \right] = \frac{9N}{\nu_m^3} \longrightarrow ③$$

apply equ: ③ in equ ①

∴ Then we have the total number of modes of vibrations in a volume V having a frequency range ν and $\nu + d\nu$

$$= \frac{9N\nu^2 d\nu}{\nu_m^3} \longrightarrow ④$$

Debye assumes that the mean energy of each vibrations has the value given by quantum theory $\left(h\nu / e^{h\nu/KT} - 1\right)$. Therefore total energy for one gram atom of the solid is given by

$$E = \int_0^{\nu_m} \frac{9N\nu^2 d\nu}{\nu_m^3} \frac{h\nu}{e^{h\nu/KT} - 1}$$

$$E = \frac{9Nh}{\nu_m^3} \int_0^{\nu_m} \frac{\nu^3 d\nu}{e^{h\nu/KT} - 1} \longrightarrow ⑤$$

But $C_V = \frac{dE}{dT}$

$$C_V = \frac{9Nh}{\nu_m^3}\int_0^{\nu_m} \nu^3 \left\{ \frac{-1}{(e^{h\nu/KT}-1)^2}\, e^{h\nu/KT}\left(-\frac{h\nu}{KT^2}\right)\right\} d\nu$$

$$= \frac{9N}{\nu_m^3}\int_0^{\nu_m} \frac{\frac{h^2\nu^4}{KT^2}\, e^{h\nu/KT}}{(e^{h\nu/KT}-1)^2}\, d\nu$$

x and ÷ by K the

$$C_v = \frac{9NK}{\nu_m^3}\int_0^{\nu_m} \frac{\frac{h^2\nu^4}{(KT)^2}\, e^{h\nu/KT}}{(e^{h\nu/KT}-1)^2}\, d\nu \longrightarrow ⑥$$

we put $\frac{h\nu}{KT} = \xi \longrightarrow \nu = \frac{KT}{h}\xi$

$$d\nu = \frac{KT}{h}\, d\xi$$

||ly for maximum value of frequency of vibration

$$\frac{h\nu_m}{KT} = \xi_m = x. \longrightarrow \nu_m = \frac{KT}{h}x.$$

apply these values in equ.

$$v = \frac{9NK}{\left(\frac{KT}{h}x\right)^3}\int_0^{x} \frac{\frac{h^{\cancel{2}}\nu^4}{K^{\cancel{2}}T^{\cancel{2}}}\, e^{\xi}\, \frac{K\cancel{T}}{\cancel{h}}\, d\xi}{(e^{\xi}-1)^2}$$

$$C_V = \frac{9NK}{x^3}\int_0^{x} \frac{\frac{h^3}{K^3T^3}\,\frac{h\nu^4}{KT}\, e^{\xi}\, d\xi}{(e^{\xi}-1)^2}$$

$$C_V = \frac{9NK}{x^3}\int_0^{x} \frac{\left(\frac{h\nu}{KT}\right)^4 e^{\xi}\, d\xi}{(e^{\xi}-1)^2}$$

$$C_V = \frac{9NK}{x^3}\int_0^{x} \frac{\xi^4 e^{\xi}\, d\xi}{(e^{\xi}-1)^2} \longrightarrow ⑦$$

The integral part may be written as.

$$\int_0^{x} \frac{\xi^4 e^{\xi}\, d\xi}{(e^{\xi}-1)^2} = -\int_0^{x} \xi^4 \frac{d}{d\xi}\left(\frac{1}{e^{\xi}-1}\right)$$

$$= -\left[\xi^4 \frac{1}{e^{\xi}-1}\right]_0^{x} + \int_0^{x} \frac{1}{e^{\xi}-1}\,\frac{d\xi^4}{d\xi}$$

$$= -\left[\frac{x^4}{e^{x}-1}\right] + 0 + \int_0^{x} \frac{4\xi^3}{e^{\xi}-1}\, d\xi \longrightarrow ⑧$$

apply equ ⑧ in equ ⑦.

$$C_V = \frac{9NK}{x^3}\left[\int_0^{x} \frac{4\xi^3\, d\xi}{e^{\xi}-1} - \frac{x^4}{e^{x}-1}\right]$$

~~$C_v = 3R\left[\frac{12}{x^3}\int_0^x \xi^4\right.$~~

$$C_v = 3R\left[\frac{12}{x^3}\int_0^x \frac{\xi^3\, d\xi}{e^\xi - 1} - \frac{3x^4}{x^3(e^x - 1)}\right]$$

$$C_v = 3R\left[\frac{12}{x^3}\int_0^x \frac{\xi^3\, d\xi}{e^\xi - 1} - \frac{3x}{e^x - 1}\right] \longrightarrow ⑨$$

OR $C_v = 3R\left[D(x)\right]$

where $D(x)$ is represents Debye's function.

We shall here Consider two cases here.

i) <u>At high temperature:-</u> when T is large.

The function $x = \frac{h\nu_m}{KT} = \frac{\theta}{T}$ is small values. Then

$$e^x = 1 + x + 2x^2 + 3x^3 \ldots\ldots \approx 1 + x.$$

also $\xi\left(= \frac{h\nu}{KT}\right)$ is also small Then

$$e^\xi = 1 + \xi$$

apply these function in Debye's function. equ ⑨

$$\therefore C_v = 3R\left[\frac{12}{x^3}\int_0^x \frac{\xi^{\overset{2}{\cancel{3}}}\,d\xi}{\cancel{1}+\cancel{\xi}-\cancel{1}} - \frac{3\cancel{x}}{\cancel{1}+\cancel{x}-\cancel{1}}\right]$$

$$C_v = 3R\left[\frac{12}{x^3}\int_0^x \xi^2\,d\xi - 3\right]$$

$$= 3R\left[\frac{\overset{4}{\cancel{12}}}{\cancel{x^3}}\cdot\frac{\cancel{x^3}}{\cancel{3}} - 3\right] = 3R\left[4-3\right]$$

$$\therefore \boxed{C_v = 3R}$$

The specific heat of all substants tends to a maximum value 3R at high temperature.

ii) At low temperature :-

when T is very small values the x and ξ become large, so that the last term in equ ⑨ can be neglegible, since the value of x and ξ in exponential factor, and also the limit is changed.

$$C_v = 3R\left[\frac{12}{x^3}\int_0^\infty \frac{\xi^3\,d\xi}{e^{\xi}-1}\right]$$

$$\text{But} \int_0^\infty \frac{\xi^3\,d\xi}{e^{\xi}-1} = \frac{\pi^4}{15}$$

$$\therefore \quad C_V = 3R \, \frac{12}{x^3} \, \frac{\pi^4}{15}$$

$$C_V = 3R \, \frac{12\pi^4}{15} \left(\frac{T}{\theta} \right)^3 = \frac{464 \cdot 4}{\theta^3} T^3$$

~~Since~~ $C_V = 464 \cdot 4 \left(\frac{T^3}{\theta^3} \right)$

Since θ is Constant then The Specific heat of a Solid at extremly low temperature in directly proportional to the cube of absolute Temperature.

$$\boxed{C_V \propto T^3}$$

This is Called Debye's T^3 law.

Black-body radiation and Plank's Radiation Law

This is an application of Bose-Einstein statistics to photons. Radiation from a black body at absolute temperature T and in thermal equilibrium is supposed consist of photons of energy content $h\nu$ moving in all possible directions with speed of light 'c' and it possesses the momentum $h\nu/c$

Some important properties of photons.

i) photons are particles of zero rest mass.

ii) Photons are indistinguishable from one another and their number in a system is not necessary. If a photon of frequency 'ν' is absorbed by the wall of black body, it can be replaced by the emission of several photons of frequencies $\nu_1, \nu_2 \cdots\cdots$ therefore $h\nu = h\nu_1 + h\nu_2 + \cdots\cdots$

there $\sum_i \delta n_i \neq 0$ therefore the undetermined multiplier $\alpha = 0$.

iii) The photons are Bose particles with spin 1 having two modes of propagation.

According to quantum idea each allowed eigen state of a system has a volum h^3 in the phase space. The volume of each allowed eigen state

$$d\tau = dx\,dy\,dz\,dp_x\,dp_y\,dp_z = h^3$$

According to Heisenberg's uncertainity relation an element of volume in the momentum space

$$\sigma_p = \frac{h^3}{V}$$

σ_p denotes the size of an elementary cell in the momentum space. Therefor the total number of eigen states between momentum p and $p+dp$ is

$$g(p)\,dp = \frac{4\pi p^2 dp}{\frac{h^3}{V}} \qquad \text{but} \quad p = \frac{h\nu}{c}$$

$$dp = \frac{h\,d\nu}{c}$$

$$g(p)dp = \frac{4\pi V p^2 dp}{h^3} \longrightarrow ①$$

apply these functions in equ ①

$$g(\nu)\,d\nu = \frac{4\pi V}{h^3}\left(\frac{h\nu}{c}\right)^2 \frac{h\,d\nu}{c}$$

$$= \frac{4\pi V}{\cancel{h^3}} \cancel{h^3} \frac{\nu^2}{c^3} d\nu$$

$$g(\nu)\,d\nu = 4\pi V \frac{\nu^2}{c^3} d\nu. \longrightarrow ②$$

Taking into account the doubling of the states due to polarization of photons. we can write equ ② as

$$g(\nu)\,d\nu = 8\pi V \frac{\nu^2}{c^3} d\nu.$$

But we know the B.E distribution law

$$dn = \frac{g(\nu)\,d\nu}{e^{\alpha+\beta E}-1}$$

In this case the undetermined multipliers $\alpha = 0$ and $\beta = 1/KT$

$$dn = \frac{g(\nu)\,d\nu}{0+e^{h\nu/KT}-1}$$

apply the equ ② in above equation

$$dn = 8\pi V \frac{\nu^2}{c^3} \frac{d\nu}{e^{h\nu/KT}-1} \longrightarrow ③$$

This equation represents the number of photons per unit volume lying between the frequency rang ν and $\nu+d\nu$

The energy density of radiation of frequencies ν and $\nu+d\nu$ can be found by multiplying '$h\nu$' with equ ③. Therefore the energy density $E_\nu\,d\nu$ is

$$\boxed{\frac{dn}{V} = \frac{8\pi\nu^3}{c^3}\frac{d\nu}{e^{h\nu/KT}-1}}$$

$$E_\nu\,d\nu = \frac{dn}{V}\,h\nu = \frac{8\pi\nu^2}{c^3}\frac{h\nu\,d\nu}{e^{h\nu/KT}-1}$$

$$E_\nu d\nu = \left(\frac{8\pi h \nu^3}{c^3}\right)\left(\frac{d\nu}{e^{h\nu/kT}-1}\right) \longrightarrow ④$$

This is plank's radiation law in terms of frequency.

But we kno $\nu = \frac{c}{\lambda}$ and $d\nu = -\frac{c}{\lambda^2} d\lambda$

apply in equ ④

$$E_\lambda d\lambda = \frac{8\pi h}{\cancel{c^3}} \left(\frac{\cancel{c}}{\lambda}\right)^3 \left(-\frac{c}{\lambda^2} d\lambda\right) \frac{1}{e^{h\nu/kT}-1}$$

$$E_\lambda d\lambda = -\frac{8\pi hc}{\lambda^5} \frac{d\lambda}{e^{h\nu/kT}-1}$$

This is plank's radiation law in terms of wavelength.

Fermi-Dirac Statistics

Consider a system having n indistinguishable particles of half integral ~~p~~ spin that have anti-symmetric wave function as

$$= \sum_i \Big[g_i \log g_i - \cancel{g_i} - n_i \log n_i \cancel{+n_i} - (g_i - n_i) \log(g_i - n_i) + \cancel{(g_i - n_i)} \Big] + \text{cons.}$$

$$= \sum_i \Big[(n_i - g_i) \log (g_i - n_i) + \boxed{g_i \log g_i} - n_i \log n_i \Big] + \text{cons}$$

$$\delta(\log w) = \sum_i \Big[(n_i - g_i)\, \delta\{ \cancel{\log}\, (g_i - n_i) + \log (g_i - n_i)\, \delta n_i - n_i\, \delta(\log n_i) - \log n_i\, \delta n_i \Big] + 0$$

$$(n_i - g_i) \frac{1}{(g_i - n_i)}\, \delta n_i \qquad \delta \log n_i \qquad \cancel{n_i} \frac{1}{\cancel{n_i}} \delta n_i.$$

$$\cancel{\delta(\log w) = -\sum_i \Big[\log (g_i - n_i - \log n_i \Big] \delta n_i = 0.}$$

$$\log N = \sum_i \Big[g_i \log g_i - (g_i - n_i) \log (g_i - n_i) - n_i \log n_i \Big] + \text{cons}$$

$$\delta(\log w) = \sum_i \Big[0 - (g_i - n_i)\, \delta\{ \log (g_i - n_i) \} - \log (g_i - n_i)\, \delta n_i - n_i\, \delta(\log n_i) - \log n_i\, \delta n_i \Big] + 0$$

$$\cancel{g_i - n_i}\, \frac{1}{\cancel{g_i - n_i}} \sum_i \delta n_i$$

Fermi-Dirac Statistics

Consider a System having n indistinguishable Particles. Let these particles are divided into quantum levels such that there are $n_1, n_2 \dots n_i$ number of Particles in groups whose Constant energies are $\epsilon_1\ \epsilon_2 \dots \epsilon_i$ respectively. Let g_i denote the number of Sublevels of i^{th} level

In F.D Statistics the Conditions are

i) The particles are indistinguishable from each other.

ii) The particles obey pauli's excluction principle according to which each Sub level may contain 0 (or) 1 particle.

iii) The Sum of energies of all the particles in the different quantum groups taken together Constitutes the total energy of the System.

Then the probability W of the System for occurring with the Specified distribution is proportional to the total number of eigen States;

$$W = \prod_i \frac{g_i}{n_i!\,(g_i - n_i)!} \times \text{Constant.}$$

taking log in both sides

$$\log W = \log \left[\prod_i \frac{g_i}{n_i!\,(g_i - n_i)!} \times \text{const} \right] \longrightarrow ①$$

But we know

1) The total number of particle is Constant.

$$\therefore \quad n = \sum_i n_i$$

$$\delta n = \sum_i \delta n_i = 0 \longrightarrow ②$$

② The total energy of the system is const

$$E = \sum_i \epsilon_i n_i$$

$$\delta E = \sum_i \epsilon_i \delta n_i = 0 \longrightarrow ③$$

③ If the probability is maximum then

$$\delta(\log w) = 0 \longrightarrow ④$$

now the equ① can be write as

$$\log w = \sum_i \left[\log g_i! - \log n_i! - \log(g_i - n_i)! \right] + \text{const}$$

Using Stirling approximation

$$\log w = \sum_i \Big[g_i \log g_i - \cancel{g_i} - n_i \log n_i + \cancel{n_i} - (g_i - n_i)\log(g_i - n_i) + \cancel{(g_i - n_i)} \Big] + \text{const.}$$

$$\log w = \sum_i \Big[(n_i - g_i)\log(g_i - n_i) - n_i \log n_i + g_i \log g_i \Big] + \text{const}$$

Differentiate

~~$\delta(\log w) = \sum_i \Big[$~~

Differentrate

$$\delta(\log w) = \sum_i \Big[(n_i - g_i)\,\delta\{\log(g_i - n_i)\}$$

$$+ \log(g_i - n_i)\,\delta n_i - n_i\,\delta(\log n_i) - \log n_i\,\delta n_i \Big] + 0 \longrightarrow ⑤$$

To solve the terms.

$$(n_i - g_i)\,\delta\{\log(g_i - n_i)\} = n_i - g_i \,\frac{1}{g_i - n_i}\,\delta n_i$$

$$-(g_i \cancel{-n_i})\,\frac{1}{(\cancel{g_i - n_i})}\,\delta n_i \Rightarrow -\left(\sum_i \delta n_i\right) = 0.$$

IIIly. $n_i\,\delta(\log n_i) = \sum_i \delta n_i = 0$

apply thes terms in equ ⑤

$$\delta(\log w) = \sum_i \Big[0 + \log(g_i - n_i)\,\delta n_i - \log n_i\,\delta n_i \Big]$$

$$-\sum_i \Big[\log n_i - \log(g_i - n_i) \Big]\,\delta n_i = 0.$$

$$\sum_i \left\{ \log \frac{n_i}{g_i - n_i} \right\} \delta n_i = 0 \longrightarrow ⑥$$

Now we apply the Legrangian method of undetermined multipliers equ ⑥ can be writen as

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

$$\log \frac{n_i}{g_i - n_i} = -(\alpha + \beta \epsilon_i)$$

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

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

$$\frac{g_i}{n_i} - 1 = e^{(\alpha+\beta\epsilon_i)}$$

$$\frac{g_i}{n_i} = e^{(\alpha+\beta\epsilon_i)} + 1$$

$$\frac{n_i}{g_i} = \frac{1}{e^{\alpha+\beta\epsilon_i} + 1}$$

$$\boxed{n_i = \frac{g_i}{e^{\alpha+\beta\epsilon_i} + 1}}$$

This equation represents the most probable distribution of the particles among various energy levels and is called F.D distribution law.

Ideal Fermi gas.

Participants of F D assembly are the Particles with half integral spin like electrons, Protons and neutrons. The general expressions for the most probable distribution in energy for the F.D gas.

$$n_i = \frac{g_i}{e^{\alpha+\beta\epsilon_i}+1} \longrightarrow ①$$

Putting $D = e^{\alpha}$ then $n_i = \frac{g_i}{De^{\beta\epsilon_i}+1}$

The number of particle states lying between momentum p and $p+dp$ is determined from

$$g(p)dp = g_s\frac{4\pi V p^2 dp}{h^3} \longrightarrow ②$$

where $g_s = 2s+1$ is spin degeneracy factor

Since $\epsilon = \frac{p^2}{2m} \longrightarrow p^2 = 2m\epsilon$, $dp = \sqrt{\frac{m}{2\epsilon}}\,d\epsilon$

∴ equ ② can be write as

$$g(\epsilon)\,d\epsilon = g_s\frac{4\pi V}{h^3}\,2m\epsilon\left(\frac{m}{2\epsilon}\right)^{1/2}d\epsilon$$

$$g(\epsilon)\,d\epsilon = g_s\frac{4\pi mV}{h^3}(2m)^{1/2}\,\underline{\epsilon^{1/2}d\epsilon} \longrightarrow ③$$

apply the equ ③ in equ ① we get the number of particles in energy range between ϵ and $\epsilon+d\epsilon$

[illegible])

$$dn(\epsilon) = g_s\frac{4\pi mV}{h^3}(2m)^{1/2}\frac{\epsilon^{1/2}d\epsilon}{De^{\beta\epsilon_i}+1}$$

But wee know $\beta = 1/KT$

$$\therefore dn(\epsilon) = g_s \frac{4\pi m V}{h^3} (2m)^{1/2} \frac{\epsilon^{1/2} d\epsilon}{De^{\epsilon/KT}+1}$$

Putting $\frac{\epsilon}{KT} = x. \rightarrow \epsilon = xKT \rightarrow d\epsilon = KT\,dx.$

$$\therefore dn(\epsilon) = g_s \frac{4\pi m V}{h^3} (2m)^{1/2} \frac{(xKT)^{1/2} KT\,dx.}{De^{x}+1}$$

$$= g_s \frac{4\pi m V.}{h^3} (2m)^{1/2} (KT)^{3/2} \frac{x^{1/2} dx,}{De^{x}+1}$$

x and ÷ by $\sqrt{\pi}$

$$dn(\epsilon) = g_s \frac{4\pi m V}{h^3} \frac{\sqrt{\pi}}{\sqrt{\pi}} (2m)^{1/2} (KT)^{3/2} \frac{x^{1/2} dx}{De^{x}+1}$$

$$= \frac{2 g_s V}{h^3 \sqrt{\pi}} (2\pi m KT)^{3/2} \frac{x^{1/2} dx}{De^{x}+1}$$

$$dn(\epsilon) = \frac{2 g_s V}{\sqrt{\pi}} \left(\frac{2\pi m KT}{h^2}\right)^{3/2} \frac{x^{1/2} dx.}{De^{x}+1}$$

$$dn(\epsilon) = \frac{2 g_s Z_t}{\sqrt{\pi}} \frac{x^{1/2} dx}{De^{x}+1} \longrightarrow ④$$

where the translational partition function is

$$Z_t = \left(\frac{2\pi m KT}{h^2}\right)^{3/2} V.$$

The total number of particles

$$n = \int dn$$

$$n = \frac{2 g_s Z_t}{\sqrt{\pi}} \int_0^{\infty} \frac{x^{1/2}\, dx}{D e^{x} + 1} \longrightarrow ⑤$$

The total energy of the system is

$$E = \int \epsilon\, dn = KT \int x\, dn \qquad \boxed{\epsilon = x KT}$$

$$E = \frac{2 g_s Z_t}{\sqrt{\pi}} KT \int_0^{\infty} \frac{x^{3/2}\, dx}{D e^{x} + 1} \longrightarrow ⑥$$

F.D gas has two cases, that is when ~~D~~ D > 1 then it is reffered as weak degeneracy. When D < 1 then it is referred as strong degeneracy.

(A) Case of weak degeneracy :-

$$\int_0^{\infty} \frac{x^{1/2}\, dx}{D e^{x} + 1} = \int_0^{\infty} x^{1/2}\, dx\, \frac{e^{-x}}{D} \left(1 + \frac{e^{-x}}{D}\right)^{-1}$$

$$= \int_0^{\infty} x^{1/2}\, dx\, \frac{e^{-x}}{D} \left(1 - \frac{e^{-x}}{D} + \frac{e^{-2x}}{D^2} - \cdots\right)$$

$$= \frac{1}{D} \int_0^{\infty} x^{1/2} e^{-x}\, dx - \frac{1}{D^2} \int_0^{\infty} x^{1/2} e^{-2x}\, dx + \frac{1}{D^3} \int_0^{\infty} x^{1/2} e^{-3x}\, dx \cdots$$

$$\int_0^\alpha \frac{x^{1/2}\,dx}{De^x+1} = \frac{\sqrt{\pi}}{2D}\left[1-\frac{1}{2^{3/2}D}+\frac{1}{3^{3/2}D^2}-\cdots\cdots\right]$$

∴ Apply the above equation in equ ⑤

$$n = \frac{\cancel{2}g_s Z_t}{\cancel{\sqrt{\pi}}}\,\frac{\cancel{\sqrt{\pi}}}{\cancel{2}D}\left[1-\frac{1}{2^{3/2}D}+\frac{1}{3^{3/2}D}-\cdots\cdots\right]$$

$$n = \frac{g_s Z_t}{D}\left[\qquad\qquad\qquad\right] \longrightarrow ⑦$$

Similarly $\displaystyle\int_0^\alpha \frac{x^{3/2}\,dx}{De^x+1} = \frac{1}{D}\int_0^\alpha x^{3/2}e^{-x}\,dx - \frac{1}{D^2}\int_0^\alpha x^{3/2}e^{-2x}\,dx\cdots\cdots$

$$\int_0^\alpha \frac{x^{3/2}\,dx}{De^x+1} = \frac{3\sqrt{\pi}}{4D}\left(1-\frac{1}{2^{5/2}D}+\frac{1}{3^{5/2}D^2}-\cdots\cdots\right)$$

Then equ ⑥ may writ as.

$$E = \frac{\cancel{2}g_s Z_t}{\cancel{\sqrt{\pi}}}\,KT\,\frac{3\cancel{\sqrt{\pi}}}{\cancel{2}\cancel{4}D}\left(1-\frac{1}{2^{5/2}D}+\frac{1}{3^{5/2}D^2}-\cdots\cdots\right)$$

$$E = \frac{3}{2D}KT\,g_s Z_t\left(1-\frac{1}{2^{5/2}D}+\frac{1}{3^{5/2}D^2}-\cdots\cdots\right) \longrightarrow ⑧.$$

from the equ ⑦ the value of $g_s Z_t$ then

$$E = \frac{3KT}{2\cancel{D}}\,n\cancel{D}\left(1-\frac{1}{2^{5/2}D}+\frac{1}{3^{5/2}D^2}-\cdots\right)\left(1-\frac{1}{2^{3/2}D}+\frac{1}{3^{3/2}D^2}-\cdots\right)^{-1}$$

$$E = \frac{3}{2}nKT\left(1+\frac{1}{2^{5/2}D}-\frac{1}{3^{5/2}D^2}+\cdots\cdots\right)$$

Putting $D = \frac{g_s Z_t}{n}$ from ~~Secon~~ first part of equ ① Then

$$E = \frac{3}{2} RT \left[1 + \frac{1}{2^{5/2}} \left(\frac{n}{g_s Z_t} \right) - \frac{1}{3^{5/2}} \left(\frac{n}{g_s Z_t} \right)^2 + \cdots\cdots \right]$$

The pressure of the ideal fermi gas is

$$P = - \left(\frac{\partial E}{\partial V} \right)_{T,S}$$

$$= \frac{2}{3} \frac{E}{V}$$

$$P = \frac{RT}{V} \left(1 + \frac{1}{2^{5/2}} \left(\frac{n}{g_s Z_t} \right) - \frac{1}{3^{5/2}} \left(\frac{n}{g_s Z_t} \right)^2 + \cdots\cdots \right)$$

The value of D is smaller or value of $\frac{1}{D}$ is greater then the degeneracy is more marked.

B) Case of Strong degeneracy

If $D << 1$ then this increases the value of $1/D$ and hence the degeneracy will become more prominent.

$$\frac{1}{D} = \frac{n}{g_s Z_t} = \frac{n}{g_s V} \left(\frac{h^2}{2\pi m k T} \right)^{3/2}$$

which shows the gas will be highly degenerate at low temperature and high density $\left(\frac{n}{V} \right)$.

Shall discuss this case of strong degeneracy at two temperatures.

i) At T = 0 The energy of the FD gas is

$$E_0 = \frac{3nh^2}{10m}\left(\frac{3n}{4\pi g_s V}\right)^{2/3}$$

and pressure is

$$\therefore \quad P_0 = \frac{n}{V}\frac{h^2}{5m}\left(\frac{3n}{4\pi g_s V}\right)^{2/3}.$$

The energy and pressure in terms of ~~for~~

Fermi energy.

$$\epsilon_F = \frac{h^2}{2m}\left(\frac{3n}{4\pi V g_s}\right)^{2/3}$$

which represents the energy of the highest level filled at T = 0 K.

∴ The energy

$$E = \frac{3}{5} n \epsilon_F$$

$$P = \frac{2}{5}\frac{n\epsilon_F}{V}.$$

Thermodynamic functions of degenerate Fermi-Dirac gas.

i) Thermal Capacity (C_V).

At low temperature the gas will have thermal capacity given by

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

But we know the energy of the gas at strong degeneracy

$$E = \frac{3}{5} n \epsilon_F \left\{ 1 + \frac{5}{12}\left(\frac{\pi k T}{\epsilon_F}\right)^2 - \cdots \right\}$$

$$\therefore C_V = \frac{\partial}{\partial T}\left[\frac{3}{5} n \epsilon_F \left\{ 1 + \frac{5}{12}\left(\frac{\pi k T}{\epsilon_F}\right)^2 - \cdots \right\} \right]$$

$$= \frac{3}{5} n \epsilon_F \left\{ 0 + \frac{5}{12}\left(\frac{\pi k}{\epsilon_F}\right)^2 2T - \cdots \right\}$$

$$= \frac{\cancel{3}}{\cancel{5}} n \epsilon_F \frac{\cancel{5}}{\underset{\cancel{4}\,2}{\cancel{12}}} \left(\frac{\pi k}{\epsilon_F}\right)^2 \cancel{2}T - \cdots$$

$$= n \cancel{\epsilon_F} \left(\frac{\pi k}{\cancel{\epsilon_F}}\right)^2 \frac{T}{2} \longrightarrow ①$$

$$= \frac{nT}{2} (\pi k)^2 \frac{1}{\epsilon_F} - \cdots$$

$$C_V = \frac{nT}{2} (\pi k)^2 \frac{1}{\frac{h^2}{2m}\left(\frac{3n}{4\pi V g_s}\right)^{2/3}}$$

$$C_v = \frac{n\pi}{\cancel{2}} (\pi k)^2 \frac{\cancel{2}m}{h^2}\left(\frac{4\pi V g_s}{3n}\right)^{2/3}$$

$$C_v = \frac{n\pi^2 m k^2}{h^2}\left(\frac{4\pi V g_s}{3n}\right)^{2/3} T$$

We infer that the heat capacity per particle would be small for large densities and small particle mass m.

ii) Entropy :- The entropy S can be obtained from

$$S = \int_0^T \frac{C_v}{T}\, dT = \int_0^T \frac{n\pi^2 m k^2}{\cancel{T} h^2}\left(\frac{4\pi V g_s}{3n}\right)^{2/3}\cancel{T}\, dT$$

$$S = \frac{n\pi^2 m k^2}{h^2}\left(\frac{4\pi V g_s}{3n}\right)^{2/3} T$$

It is similar to equation of specific heat.
Then the alternatively use equ ① Then

$$S = \int_0^T \frac{1}{\cancel{T}}\; n\epsilon_f \left(\frac{\pi k}{\epsilon_f}\right)^2 \frac{\cancel{T}}{2} \cdots\cdots dT$$

$$= \frac{n\epsilon_f}{2}\left(\frac{\pi k}{\epsilon_f}\right)^2 T - \cdots\cdots$$

× and ÷ by T Then

$$S = \frac{n\epsilon_f}{2T}\left(\frac{\pi k}{\epsilon_f}\right)^2 T^2 - \cdots\cdots$$

$$= \frac{n\epsilon_f}{T}\left\{\frac{\pi^2}{2}\left(\frac{kT}{\epsilon_f}\right)^2 - \cdots\cdots\right\}$$

iii) Helmholtz free energy

$$F = E - TS$$

$$F = \frac{3}{2} n \epsilon_F \left[1 + \frac{5}{12} \left(\frac{\pi K T}{\epsilon_F} \right)^2 - \dots \right] - \cancel{T} \left(\frac{n \epsilon_F}{\cancel{T}} \right) \left\{ \frac{\pi^2}{2} \left(\frac{KT}{\epsilon_F} \right)^2 - \dots \right\}$$

$$= \frac{3}{\cancel{5}} n \epsilon_F + \frac{\cancel{3}}{\cancel{5}} n \epsilon_F \frac{\cancel{5}}{\underset{4}{\cancel{12}}} \left(\frac{\pi K T}{\epsilon_F} \right)^2 - n \epsilon_F \left\{ \frac{\pi^2}{2} \left(\frac{KT}{\epsilon_F} \right)^2 - \dots \right\}.$$

$$F = \frac{3}{5} n \epsilon_F + \frac{n \epsilon_F}{4} \left(\frac{\pi K T}{\epsilon_F} \right)^2 - \frac{n \epsilon_F}{2} \left(\frac{\pi K T}{\epsilon_F} \right)^2 - \dots$$

$$F = n \epsilon_F \left[\frac{3}{5} + \frac{1}{4} \left(\frac{\pi K T}{\epsilon_F} \right)^2 - \dots \dots \right]$$

Electron gas.

A metal canbe considered to be Composed of a System of fixed positive nuclei and number of mobile electron to as electron gas. Let Study the properties of an electron gas at low tempr. we know the spin $S = 1/2$ and the spin degenaracy is

$$g_s = 2S + 1 = 2 \cdot \tfrac{1}{2} + 1$$

$$g_s = 2$$

The fermi energy is $\epsilon_F = \frac{h^2}{2m} \left(\frac{3n}{4\pi V 2} \right)^{2/3}$

$$\epsilon_F = \frac{h^2}{2m}\left(\frac{3n}{8\pi V}\right)^{2/3}.$$

$$\epsilon_F = \frac{h^2}{8m}\left(\frac{3n}{8\pi V}\right)^{2/3}.$$

~~[illegible] the energy of Fermi gas at [illegible] temperature [illegible]~~

$$\epsilon_F = \frac{h^2}{2m}\left(\frac{3n}{8\pi V}\right)^{2/3}$$

$$\epsilon_F = \frac{h^2}{8m}\left(\frac{3n}{\pi V}\right)^{2/3}$$

$$E_0 = \frac{3}{5}\frac{nh^2}{8m}\left(\frac{3n}{\pi V}\right)^{2/3}$$

which means that in the limit $T \to 0$ each one of the states is occupied fully upto the energy level ϵ_F whereas all the states above this energy level is empty.

We can calculate the degeneracy factor from an electron gas. For electrons $m = 9.1 \times 10^{-28}$ gm and $g_s = 2$ Then the degeneracy

$$\frac{1}{D} = \frac{h^2}{2mKT}\left(\frac{3n}{4\pi V g_s}\right)^{2/3}$$

$$= \frac{h^2}{2 \times 9.1 \times 10^{-28} \times 1.38 \times 10^{-16}\, T}\left(\frac{3n}{8\pi V}\right)^{2/3}$$

Taking a typical metal of atomic weight 100 and density 10 so that the volume of gm-atom is 10 cc. and the avagadoo number 6.02×10^{23} then

$$\frac{1}{D} = \frac{(6.62\times10^{-27})^2}{2\times1.9\times10^{-28}\times1.38\times10^{-6}\times T}\left(\frac{3\times6.02\times10^{23}}{8\times3.14\times10'}\right)^{2/3}$$

$$\frac{1}{D} = \frac{10^5}{1.5T} \longrightarrow$$

$$D = 1.5\times10^{-5}T$$

which means degeneracy is sufficiently high.

At low temperature electronic contribution to the specific heat of metals is

$$C_v = \cancel{\frac{1}{2}nk}\ \frac{nT}{2}(\pi k)^2\frac{1}{\epsilon_F}$$

$$= \frac{1}{2}nk\pi^2\left(\frac{kT}{\epsilon_F}\right)$$

But we know $D = \frac{kT}{\epsilon_F}$

$$\therefore\ C_v = \frac{1}{2}nk\pi^2 D$$

$$= \frac{1}{2}nk\pi^2\ 1.5T\times10^{-5}$$

where $nk = R = 1.978$ cal/deg/mol ≈ 2.

$\pi^2 \approx 10$

$$\therefore\ C_v = \frac{1}{\cancel{2}}\cancel{2}\times10\times1.5T\times10^{-5}$$

$$C_v = 1.5\times10^{-4}T$$

The pressure is

$$P_0 = \frac{2}{5}\frac{n\epsilon_F}{V}$$

$$= \frac{\cancel{2}n}{5V}\frac{h^2}{\cancel{2}m}\left(\frac{3n}{4\pi V g_s}\right)^{2/3}$$

$g_s = 2.$

$$P_0 = \frac{nh^2}{20mV}\left(\frac{3n}{\pi V}\right)^{2/3}$$

for the metal of atomic weight 100 and density 10 the the volume 10 cc the

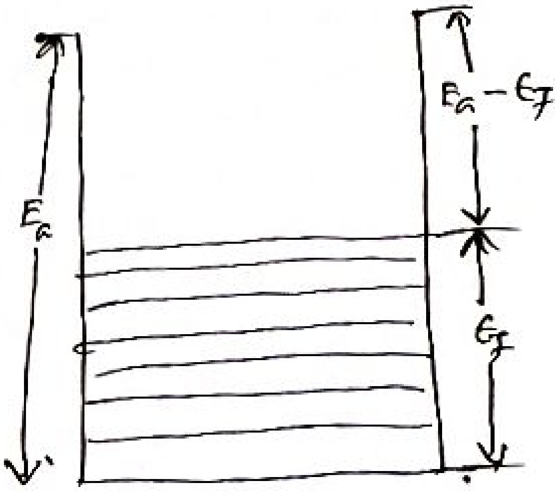
$$P_0 \approx 10^5 \text{ atoms}$$

which means at normal temperature the pressure of the gas is sufficiently high.

Free electron model and Electronic emission or thermionic emission.

In free electron model of a metal, At absolute zero of temperature the electrons will fill $n/2$ lowest energy states upto the energy value ϵ_F. The minimum amount of energy necessary to remove an electron from the metal is equal to $(E_a - \epsilon_F)$ and is defined as the work function ϕ of the metal.

According to F.D distribution the number of electrons per unit volume lying between momentum space p and $(p+dp)$ is given by



$$dn = \frac{g(p)\,dp}{V\,De^{E/kT}+1}$$

E_a – Surface energy

ϵ_F – Fermi energy

$E_a - E_F = e\phi$ work function.

But $g(p)dp = g_s \frac{4\pi V}{h^3} p^2 dp$

For electrons $g_s = 2$. then

$$dn = 2\,\frac{4\pi \cancel{V}}{h^3}\,\frac{p^2\,dp}{\cancel{V} D e^{\epsilon/kT}+1}$$

Put $D = e^{-\epsilon_f/kT}$

$$\therefore\ dn = \frac{8\pi p^2\,dp}{h^3\left[e^{(\epsilon-\epsilon_f)/kT}+1\right]}$$

But $p = mv$ and $dp = m\,dv$.

$$dn = \frac{8\pi\,(mv)^2\,m\,dv}{h^3\left[e^{(\epsilon-\epsilon_f)/kT}+1\right]}$$

$$= 8\pi\left(\frac{m}{h}\right)^3 \frac{v^2\,dv}{\left[e^{(\epsilon-\epsilon_f)/kT}+1\right]}$$

$$dn = 2\left(\frac{m}{h}\right)^3 \frac{4\pi v^2\,dv}{e^{(\epsilon-\epsilon_f)/kT}+1}$$

If v_x v_y v_z be the velocity Components of the electrons in x, y, z directions, then the phase space volume between v_x and v_x+dv_x, v_y and v_y+dv_y, v_z and v_z+dv_z will be

$$\therefore\ 4\pi v^2\,dv = dv_x\,dv_y\,dv_z$$

$$\therefore\ dn = 2\left(\frac{m}{h}\right)^3 \frac{dv_x\, dv_y\, dv_z}{e^{(\epsilon-\epsilon_F)/kT}+1}$$

where the quantity $e^{(\epsilon-\epsilon_F)/kT}$ is much greater than one. Therefore in the denominator we neglect the 1. Therefore

$$dn = 2\left(\frac{m}{h}\right)^3 e^{(\epsilon_F-\epsilon)/kT}\, dv_x\, dv_y\, dv_z$$

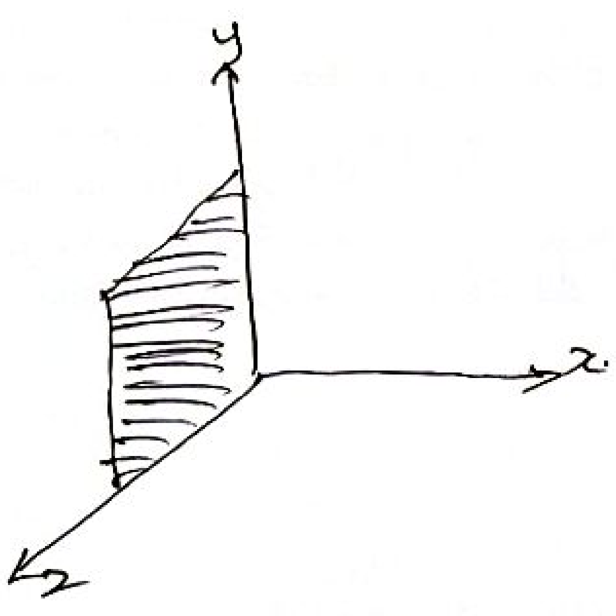
if the kinetic energy

$$\epsilon = \tfrac{1}{2} mv^2 = \tfrac{1}{2} mv_x^2 + \tfrac{1}{2} mv_y^2 + \tfrac{1}{2} mv_z^2$$

apply this the

$$dn = 2\left(\frac{m}{h}\right)^3 e^{\epsilon_F/kT}\, e^{-\frac{1}{2}mv_x^2/kT} dv_x\, e^{-\frac{1}{2}mv_y^2/kT} dv_y\, e^{-\frac{1}{2}mv_z^2/kT} dv_z$$

If the surface of the metal to be a plane surface perpendicular to x-direction with the number of electrons with a velocity component v_x and dv_x is given by



$$dn_x = n(v_x)\,dv_x$$

$$= 2\left(\frac{m}{h}\right)^3 e^{E_F/kT}\; e^{-\frac{1}{2}mv_x^2/kT}\,dv_x.$$

$$\int_{-\infty}^{+\infty}\int_{-\infty}^{+\infty} e^{-\frac{1}{2}m(v_y^2+v_z^2)/kT}\,dv_y\,dv_z.$$

But only those electrons which are travelling in x-direction will come out in yz plane. Only those electrons will come out which have got energy greater than $(E_a - E_F)$ the work function. Therefore number of electrons arriving per second per unit ~~volume~~ area of the metal surface.

$$n_x = \int_{\sqrt{2E_a/m}}^{\infty} n(v_x)\,v_x\,dv_x$$

$$= 2\left(\frac{m}{h}\right)^3 e^{E_F/kT}\int_{\sqrt{2E_a/m}}^{\infty} v_x\, e^{-\frac{1}{2}mv_x^2/kT}\,dv_x$$

$$\int_{-\infty}^{+\infty}\int_{-\infty}^{+\infty} e^{-\frac{1}{2}m(v_y^2+v_z^2)/kT}\,dv_y\,dv_z$$

$$n_x = \frac{4\pi m k^2}{h^3}\,T^2 e^{-(E_a-E_F)/kT}$$

The emission current density per unit area

$$J = e n_x = \frac{4\pi m e k^2}{h^3} T^2 e^{-(E_a - \epsilon_f)/kT}$$

where we put $$\frac{4\pi m e k^2}{h^3} = A$$

$$(E_a - \epsilon_f) = e\phi$$

$$\therefore \quad J = A T^2 e^{-e\phi/kT}$$

This equation is called Richardson – Dushman equation of thermionic emission.

Brownian motion.

when the pollen grains suspended in water and viewed under a powerful ~~motion~~ microscope showed an irregular continuous dancing motion. These random motion of the particles is called as Brownian motion. In case of Brownian motion the following facts were found.

i) The motions are completely irregular and random.
ii) Smaller the particle, the faster is the motion.
iii) For lower viscosity of the liquids the faster is the motion.
iv) At the same temperature, the two particles of the same size move equally fast.

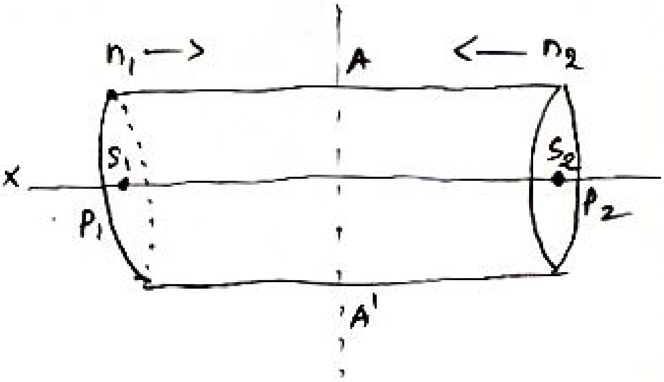
Einstein's theory of translational brownian motion:-

This theory is based on the fact that due to the random motion of the Brownian particles they diffuse into the medium in due course of time. The process of diffusion must be an ordinary one.

Einstein calculated the coefficient of diffusion in following two ways.

i) Calculation of Coefficient of Diffusion (D) from random molecular motion:-

Let us assume that the Concentration is not uniform and there exist a Concentration gradient along to X-axis which causes diffusion. we assume that each particle suffers a displacement Δ in time t.



For Simple, consider a Cylinder of length Δ along x axis with unit area of cross section. The Let the two end faces be S_1 and S_2. Let n_1 and n_2 Concentrations of S_1 and S_2 are respectively and assume $n_1 > n_2$. AA' is a reference plane in the middle of the cylinder. Now we can assume that half of the particles passing through AA' from left to right in time 't' is equal to $\frac{1}{2}\Delta n_1$ and $\frac{1}{2}\Delta n_2$ particles passing through AA' right to left.

Then net number of particles passing through AA' in time t is

$$= \frac{1}{2}\Delta n_1 - \frac{1}{2}\Delta n_2$$

$$= \frac{1}{2} \Delta \, (n_1 - n_2) \longrightarrow ①$$

As the concentration changes uniformly we can calculate the concentration gradiant $\left(\frac{dn}{dx}\right)$ Therefore

$$-\left(\frac{dn}{dx}\right) = \left(\frac{n_1 - n_2}{\Delta}\right)$$

$$n_1 - n_2 = -\Delta\left(\frac{dn}{dx}\right) \text{ --- } ②$$

apply this equ② in equ①

Number of particle passing through AA' in time t

$$= \frac{1}{2} \Delta \left[-\Delta \frac{dn}{dx}\right]$$

Hence number of particles crossing the plane AA' per unit area per second

$$= -\frac{1}{2} \frac{\Delta}{t} \left[\Delta \frac{dn}{dx}\right]$$

$$= -\frac{1}{2} \frac{\Delta^2}{t} \left(\frac{dn}{dx}\right).$$

But the Diffusion coefficient (D) is defined as the number of particles passing across the plane of one sq.cm area per second when the concentration gradient is unity.

According to this difinition the number of particles should be $-D\left(\frac{dn}{dx}\right)$ therefore

$$\cancel{-}D\left(\cancel{\frac{dn}{dx}}\right) = \cancel{-}\frac{1}{2}\frac{\Delta^2}{t}\left(\cancel{\frac{dn}{dx}}\right)$$

$$D = \frac{\Delta^2}{2t}$$

ii) Determination of D from osmatic pressure difference.

Le P_1 and P_2 represent the pressure at the end surfaces S_1 and S_2, respectively from the gas equation

$$P_1 = n_1 KT \quad \& \quad P_2 = n_2 KT$$

due to this pressure difference a force acts on the cylinder which given by the product of pressure difference and area of cross section of the face.

$$(P_1 - P_2) = (n_1 - n_2) KT$$

If n is the mean concentration then this force acts on Δn particles. This force acting on a single particle is given by

$$F = \frac{(n_1 - n_2) KT}{n\Delta}$$

$$= \frac{(n_1 - n_2)}{\Delta} \frac{KT}{n}$$

From equ ② $\quad \frac{n_1 - n_2}{\Delta} = -\left(\frac{dn}{dx}\right)$

apply this

$$F = -\frac{KT}{n} \frac{dn}{dx} \longrightarrow ③$$

when the particles of radius r moves in a viscous medium with velocity v, then the force acting on the particle is given by stoke's law

$$F = 6\pi\eta r v$$

η is coefficient of viscosity. apply in equ ③

$$6\pi\eta r v = -\frac{KT}{n}\left(\frac{dn}{dx}\right)$$

$$nv = -\frac{KT}{6\pi\eta r}\left(\frac{dn}{dx}\right)$$

Hence nv represents the number of particles moving to the right side per second per unit area. According to definition of diffusion coefficient D the number ~~of~~ should be ~~of~~

$$-D\left(\frac{dn}{dx}\right)$$

$$\therefore\ nv = \cancel{-}D\left(\cancel{\frac{dn}{dx}}\right) = \cancel{-}\frac{KT}{6\pi\eta r}\left(\cancel{\frac{dn}{dx}}\right)$$

$$D = \frac{KT}{6\pi\eta r}$$

× Eq ÷ by N.

$$D = \frac{NKT}{N\,6\pi\eta r} =$$

$$D = \frac{RT}{N}\left(\frac{1}{6\pi\eta r}\right)$$

We know $D = \frac{\Delta^2}{2t}$

$$\therefore\ \frac{\Delta^2}{2t} = \frac{RT}{N}\left(\frac{1}{6\pi\eta r}\right)$$

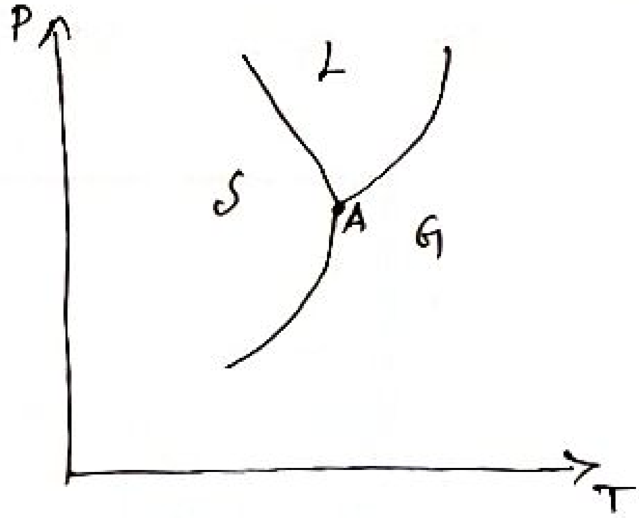
$$\Delta^2 = \frac{RT}{N}\left(\frac{\cancel{2}t}{3\cancel{6}\pi\eta r}\right)$$

$$\Delta^2 = \frac{RT}{N}\left(\frac{t}{3\pi\eta r}\right)$$

This expression represents the average Square displacement of a particle due to Brownian motion along x axis in a time 't'.

Phase transition.

Simple substances are capable of existing three phases: solid, liquid and gas.



The three lines in a phase diagram seperating these phases are called phase equilibrium lines. The common point A where lines meet is called triple point, At this unique temperature and pressure all three phases can coexist in equilibrium with each other.

Consider a system whose phases are in equilibrium. A slight variation of external conditions results in a certain amount of the substance passing from one phase to another. This process is called phase transition.

Now we consider condition of equilibrium of two phases. The Gibb's free energy is a function of T, P, N. At constant temperature pressure Gibb's free energy is proportional to the number of particle.

$$\therefore \quad G(T,P,N) = N g(T,P)$$

where $g(T,P)$ is gibb's free energy per particle and we know

$$G(T,P,N) = \mu N$$

$$\therefore \quad \mu = g(T,P)$$

i) First order phase transition

Let us consider a vapour liquid mixture in equilibrium at vapour pressure and temperature. If v and s is the specific volume and entropy then

$$dg = v\,dP - s\,dT \longrightarrow ①$$

also $\quad g = g(P,T)$

taking its derivatives

$$dg = \left(\frac{\partial g}{\partial P}\right)_T dP + \left(\frac{\partial g}{\partial T}\right)_P dT \longrightarrow ②$$

As comparing equ ① and equ ②

$$\left(\frac{\partial g}{\partial p}\right)_T = v \quad \text{and} \quad \left(\frac{\partial g}{\partial T}\right)_p = -S$$

In general $\left(\frac{\partial G}{\partial P}\right)_{T,N}$ and $\left(\frac{\partial G}{\partial T}\right)_{P,N}$ are discontinues at the transition point the v and S have different values in two phases and this transition is called first order transition.

The first order transitions can be characterized by the following statements,

i) The first order derivatives of Gibb's function change discontinuously.

ii) The density changes are discontinuous at transition temperature and pressure.

ii) Second order phase transition:

If the derivatives $\left(\frac{\partial G}{\partial P}\right)_{T,N}$ and $\left(\frac{\partial G}{\partial T}\right)_{P,N}$ are continuous at the transition point then this phase transition is called continuous or Second order phase transition.

In Second order phase transition

$$\left(\frac{\partial g_1}{\partial T}\right)_P = \left(\frac{\partial g_2}{\partial T}\right)_P \quad \text{and}$$

$$\left(\frac{\partial g_1}{\partial P}\right)_T = \left(\frac{\partial g_2}{\partial P}\right)_T$$

The well known excamble to the Second order phase transition is the transition of liquid helium - I into liquid helium - II for Common isotope of $_2He^4$. The other excample is the transition from non - ferromagnetic state to a ferromagnetic state.

Thus we Conclude that phase transition of Second kind is Continuous in the Sense that the state of ~~body chan~~ body changes Continuously

Ising model: phase transition.

We Consider a ferromagnetic Substance like iron and nickel. without any external field being applied, Some of the spins of the atoms become Spontaneously polarized in Same direction below the Curie temperature (T_c). The Spontaneous magnetisation vanishes if temperature is higher than T_c because thermal energy makes Some of the aligned spins to flip over.

Ising setup a model to investigate the behaviour of Substances whose molecules possess a magnetic moment, which model is known as Ising model. In this model the System Considered is an array of N fixed points called lattice Sites that form n-dimentional periodic lattice ($n = 1, 2, 3$). Associated with each lattice site is a spin variable S_i ($+1$ or -1). If $S_i = +1$ the i^{th} State is said to be Spin up and $S_i = -1$ then it Said to be Spin down. whose energy is defined to be

$$E(S_i) = -\sum_{i,j} \varepsilon_{ij} S_i S_j - \mu H \sum_{i=1}^{N} S_i$$

where the symbol (ij) denotes the nearest neighbour pair of spins. ϵ_{ij} is the interaction energy and μH is the interaction energy associated with an external magnetic field H.

we apply the model to the case of isotopic interaction so that all ϵ_{ij} have the same value ϵ. we write for energy

$$E_I(s_i) = -\epsilon \sum_{ij} s_i s_j - \mu H \sum_i s_i$$

If $\varepsilon > 0$ then it corresponds to ferromagnetism and if $\varepsilon < 0$ to anti-ferromagnetism. For the stable equilibrium, the energy E tends to be minimum. Therefore the spontaneous configuration of least energy is completed polarized, in which all the Ising spins are oriented in same direction.

Boltzmann transport equation

Let us Consider a system of particles that is dynamical equilibrium under external force. For example, the system may consist of electrons in a metal that are acted upon by stationary external electric and magnetic field. when the steady state current is flowing the system is in equilibrium of the type we wish to consider.

Let x, y, z be the coordinates of an electron and v_x v_y v_z be the velocity components. then the distribution function is

$$F(x, y, z, v_x, v_y, v_z, t)$$

The number of electrons in the volume $dx\,dy\,dz$ which at the instant have velocity range $dv_x\,dv_y\,dv_z$ is given by

$$dn = F(\underbrace{x, y, z}_{\downarrow}, \underbrace{v_x, v_y, v_z}_{\swarrow}, t)\, dx\,dy\,dz\, dv_x\,dv_y\,dv_z$$

$$dn = F(\vec{r}, \vec{v}, t)\, dr, dv.$$

where $F(r, v, t)$ is distribution function

This may be variation of the function with time due to the two independent ways.

i) Drift variation

The function 'f' may vary because the electrons are moving from one region of space to another and they are accelerated by external fields during their motion. This variation is called drift variation.

Let $\alpha_x, \alpha_y, \alpha_z$ be the components of acceleration which are acting on the electrons. As the velocities and spatial coordinates of the electrons will now be different at different points of time, then at the instant time $t+dt$

$$x+v_x dt, \quad y+v_y dt, \quad z+v_z dt$$

$$v_x+\alpha_x dt, \quad v_y+\alpha_y dt, \quad v_z+\alpha_z dt$$

Now the number of electrons at the instant $t+dt$ having the representing points in into element $dv_x\, dv_y\, dv_z$, ~~the fun~~ function, therefore,

$$f\,(x+v_x dt, y+v_y dt, z+v_z dt, v_x+\alpha_x dt, v_y+\alpha_y dt, v_z+\alpha_z dt)\, dx\, dy\, dz\, dv_x\, dv_y\, dv_z$$

It may write as

$$f\,(r+v\,dt, v+\alpha\,dt\,;\,t+dt)$$

The change due to drift of number of electrons in time dt is

$$\left(\frac{df}{dt}\right)_{drift} = f(r+vdt, v+\alpha dt; t+dt) - f(r,v,t)$$

Using Taylor's expansion and retaining only the first order terms and in the limit $dt \to 0$ consequently the rate change of f caused by drift is

$$\left(\frac{df}{dt}\right)_{drift} = -v_x\frac{\partial f}{\partial x} - v_y\frac{\partial f}{\partial y} - v_z\frac{\partial f}{\partial z}$$
$$-\alpha_x\frac{\partial f}{\partial v_x} - \alpha_y\frac{\partial f}{\partial v_y} - \alpha_z\frac{\partial f}{\partial v_z}$$

or simply

$$\left(\frac{df}{dt}\right)_{drift} = -v\cdot \text{grad}_r f - \alpha\cdot\text{grad}_v f$$

when collisions are not taken into consideration, there is only drift variation, then variation in function f is expressed as

$$\left(\frac{df}{dt}\right) = \left(\frac{df}{dt}\right)_{drift}$$

$$\frac{df}{dt} = -v\,\text{grad}_r f - \alpha\,\text{grad}_v f$$

$$\frac{df}{dt} + v\,\text{grad}_r f + \alpha\,\text{grad}_v f = 0.$$

This is Boltzmann transport equation when the collisions are not taken into account.

ii) Collision interaction.

The function F may vary due to collisions among the particles. Some particles leave the volume element $dr\,dv$ and some the particles pass from $dr\,dv_1$ to $dr\,dv$. Then the change in number of particles in volume element $dr\,dv$ during the time interval from t to $t+dt$ is given by

$$F(r+v\,dt,\ v+\alpha\,dt\ ;\ t+dt)\,dr\,dv - F(r,v,t)\,dr\,dv = \left(\frac{df}{dt}\right)_{coll} dt\,dr\,dv$$

If $\theta(v_x, V_y + v_z\ ;\ v_x', v_y', v_z')\,dv_x'\,dv_y'\,dv_z'$ represents the probability per unit time that an electron will change its velocity. Then the velocity of which alters from v_x, v_y, v_z to some other value is

$$a = F(x,y,z; v_x, v_y, v_z)\int \theta(v_x, v_y + v_z : v_x', v_y^2\, v_z'\ dv_x'\,dv_y'\,dv_z'$$

Similarly the number of particles the velocity of which changes to v_x, v_y, v_z from some other value is

$$b = \int F(x,y,z\ ;\ v_x'', v_y'', v_z'')\ \theta(v_x'', v_y'', v_z''\ ;\ v_x, v_y, v_z)\ dv_x''\,dv_y''\,dv_z''$$

Thus the time rate of change of a function by collisions is

$$\left(\frac{df}{dt}\right)_{coll} = b - a$$

The time rate of change of a function F may be expressed as

$$\left(\frac{dF}{dt}\right) = \left(\frac{df}{dt}\right)_{drift} + \left(\frac{df}{dt}\right)_{coll}$$

~~$\left(\frac{df}{dt}\right) = \left[v \cdot \mathrm{grad}_r F \cdot \alpha\, \mathrm{grad}_v F\right] + \left(\frac{df}{dt}\right)_{coll}$~~

$$\frac{dF}{dt} = \left[-v \cdot \mathrm{grad}_r F - \alpha\, \mathrm{grad}_v F\right] + b - a$$

$$\frac{dF}{dt} + v\, \mathrm{grad}_r F + \alpha\, \mathrm{grad}_v F = b - a$$

This is the Boltzmann transport equation in general form.

Boltzmann - H Theorem

when we have homogeneous electric and magnetic fields ~~respectively~~ in z-direction, then the acceleration $\vec{\alpha}$ is given by

$$F = m\bar{\alpha} = -e\left[\vec{\xi} + \frac{1}{e} v \times H_z\right] \longrightarrow ①$$

where $\bar{\xi}$ and H are electric and magnetic fields respectively and e is the absolute value of electronic charge. Now

$$m\alpha_x = -e\left[\xi_x + \frac{1}{e} v_y \times H_z\right]$$

$$\alpha_x = -\left[\frac{e\xi_x}{m} + \frac{e}{e}\frac{v_y}{m} H_z\right]$$

$$m\alpha_y = -e\left[\xi_y + \frac{1}{e} v_x \times H_z\right]$$

$$\alpha_y = -\left[\frac{e\xi_y}{m} + \frac{e}{e}\frac{v_x}{m} H_z\right]$$

and $m\alpha_z = 0$

$$\alpha_z = 0 \qquad ②$$

But we know $$\frac{df}{dt} = \left.\frac{df}{dt}\right)_{drift} + \left.\frac{df}{dt}\right)_{coll} \longrightarrow ③$$

In case the total rate of change is sum of drift variation and scattering interactions. For equilibrium the sum should vanish then

$$\cancel{\left.\frac{df}{dt}\right)_d + \left.\frac{df}{dt}\right)_c} = 0$$

$$\frac{df}{dt} = 0$$

Therefore the equ ③ become

$$\left(\frac{df}{dt}\right)_d + \left(\frac{df}{dt}\right)_c = 0$$

from the former section

$$\left(-v_x \frac{\partial f}{\partial x} - v_y \frac{\partial f}{\partial y} - v_z \frac{\partial f}{\partial z} - \alpha_x \frac{\partial f}{\partial v_x} - \alpha_y \frac{\partial f}{\partial v_y} - \alpha_z \frac{\partial f}{\partial v_z}\right) + (b-a) = 0$$

$$v_x \frac{\partial f}{\partial x} + v_y \frac{\partial f}{\partial y} + v_z \frac{\partial f}{\partial z} + \alpha_x \frac{\partial f}{\partial v_x} + \alpha_y \frac{\partial f}{\partial v_y} + \alpha_z \frac{\partial f}{\partial v_z} = (b-a)$$

apply the value of equ ② in above equation

$$v_x \frac{\partial f}{\partial x} + v_y \frac{\partial f}{\partial y} + v_z \frac{\partial f}{\partial z} - \left(\frac{e\xi_x}{m} + \frac{e}{e}\frac{v_y}{m} H_z\right)\frac{\partial f}{\partial v_x} - \left(\frac{e\xi_y}{m} - \frac{e}{e}\frac{v_x}{m} H_z\right)\frac{\partial f}{\partial v_y} + 0 = b-a$$

$$v_x \frac{\partial f}{\partial x} + v_y \frac{\partial f}{\partial y} + v_z \frac{\partial f}{\partial z} - \left(\frac{e\xi_x}{m} + \frac{e}{e}\frac{v_y}{m} H_z\right)\frac{\partial f}{\partial v_x} - \left(\frac{e\xi_y}{m} - \frac{e}{e}\frac{v_x}{m} H_z\right)\frac{\partial f}{\partial v_y} = \left(\frac{\partial f}{\partial t}\right)_{coll} \longrightarrow ④$$

~~which is th~~ equ ④ is the Boltzmann transport equation for electrons. we shall discuss this equation in homogeneous medium and the electric field is in x-direction as first of all treated by Lorentz. Therefore equ ④ becomes

$$\left(\frac{\partial f}{\partial t}\right)_{coll} = v_x \frac{\partial f}{\partial x} - \frac{e\mathcal{E}_x}{m} \frac{\partial f}{\partial v_x} \longrightarrow ⑤$$

as the function is independent of t, y and z.

Lorentz simplified the collision term by making the following three assumptions.

i) The electrons undergo only elastic collisions
ii) The electronic scattering is isotropic
iii) If the distribution function were the equilibrium distribution function, there would be no change in f due to scattering.

If the distribution fuction differs from the equilibrium fuction, it decays exponentially in time to the equilibrium form. Mathematically

$$\left(\frac{\partial f}{\partial t}\right)_{coll} = -\frac{(f - f_0)}{\tau} \longrightarrow ⑥$$

where τ is a parameter and is called mean free time. f_0 is equilibrium distribution function.

From equ ⑤ and ⑥ we have

$$\left.\frac{\partial f}{\partial t}\right)_{coll} = v_x \frac{\partial f}{\partial x} - \frac{e\mathcal{E}_x}{m} \cdot \frac{\partial f}{\partial v_x} = -\frac{(f - f_0)}{\tau} \longrightarrow ⑦$$

when the electric field. temperature gradient is small, equ ⑦ can be solved by putting $f = f_0$ on left side.

$$\therefore \; v_x \frac{\partial f_0}{\partial x} - \frac{e \xi_x}{m} \frac{\partial f_0}{\partial v_x} = -\frac{(f - f_0)}{\tau}$$

$$f - f_0 = -\tau \left[v_x \frac{\partial f_0}{\partial x} - e \frac{\xi_x}{m} \frac{\partial f_0}{\partial v_x} \right]$$

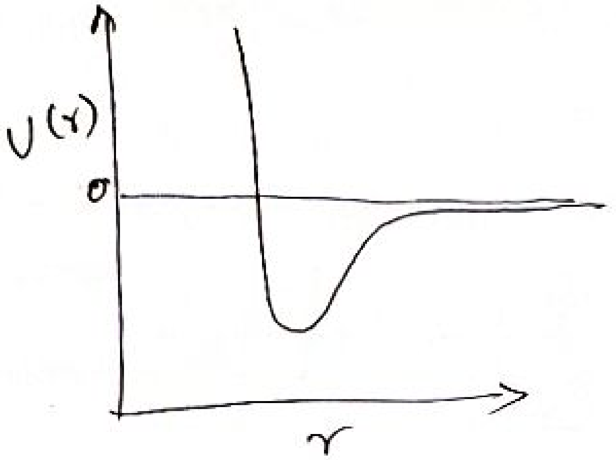
$$f = f_0 - \tau \left[v_x \frac{\partial f_0}{\partial x} - e \frac{\xi_x}{m} \frac{\partial f_0}{\partial v_x} \right]$$

This is the required solution and which is called Boltzmann-H theorem.

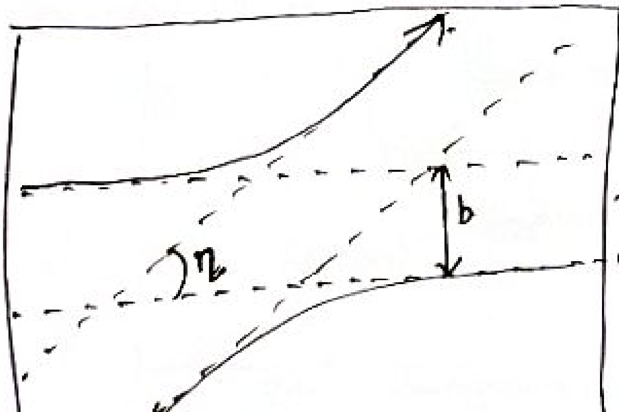
* * *

Binary Collision

The kinematics of a binary Collision between two spherically symmetric molecules are easily desired. The forces between two such molecules act along the intermolecular axis and are a function of the seperation r only. The potential energy U(r) stored in the inter molecular forces therefore also a function only of the seperation. The general form of this function is illustrated in Fig. 1.



The kinetic energy of a pair of molecules can be seperated into the sum of two independent terms; one relating to the motion of the center of mass and the other to the relative motion of the two molecules. In this terms the relative trajectories of two molecules are always parallel. A typical case is illustrated in fig. 2. The initial and final trajectories are specified by the initial relative kinetic energy (E), the impact parameter (b) and the angle of deflection (η).



Both energy and angular momentum are conserved in the encounter and the angle of deflection is

$$\eta(b,E) = \pi - 2b \int_{r_0}^{\infty} \frac{dr/r^2}{\sqrt{1-\left(\frac{U}{E}\right)-\left(\frac{b^2}{r^2}\right)}}$$

where r_0 is the distance of closest approach during the encounter.

Maxwell-Boltzmann distribution law of velocity.

The molecules of a gas donot move with same speed due to frequent collisions and so their velocities vary. In deriving this law certain assumptions are made as follows.

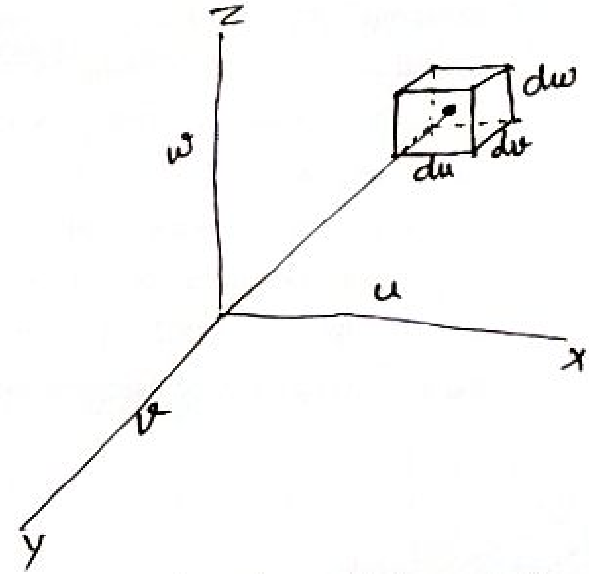
i) In steady state the density of the gas remains uniform on an average throughout the gas.

ii) The velocities along the three coordinate axis are independent of each other.

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

Let u, v, w be the component of velocities of a molecule along x, y and z axis respectively.

The number of molecules per c.c having the velocities lying between u and $u+du$ can be denoted by $n_u\,du$. Obviously n_u must be some function of u say $n f(u)$ where n is the number of molecules per c.c. and $f(u)$ is the function of u to be determined.



Hence the probability that molecules may have its velocity Simultaneously between u and u+du, v and v+dv and w and w+dw is

$$F(u)\,F(v)\,F(w)\,du\,dv\,dw \longrightarrow ①$$

All molecules whose velocity Components lie in the range u and u+du, v and v+dv, w and w+dw will be Contained in the element volume du,dv dw. The change that a single velocity of value c ends in this volume element ~~du~~ is given by the assumption .3. as f(c) dudv dw. For convinience we write the function as $\phi(c^2)$.

$$\therefore F(u)\,F(v)\,F(w)\,du\,dv\,dw = \phi(c^2)\,du\,dv\,dw$$

$$F(u)\,F(v)\,F(w) = \phi(c^2) = \phi(u^2+v^2+w^2) \longrightarrow ②$$

differentiate equ ②.

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

$$\therefore F'(u)\,F(v)\,F(w)\,du + F(u)\,F'(v)\,F(w)\,dv + F(u)\,F(v)\,F'(w)\cdot dw = 0$$

dividing by $F(u)\,F(v)\,F(w)$ then

$$\frac{F'(u)}{F(u)}\,du + \frac{F'(v)}{F(v)}\,dv + \frac{F'(w)}{F(w)}\,dw = 0 \longrightarrow ③$$

again

$c^2 = u^2 + v^2 + w^2$ on differentiating

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

OR $0 = \lambda u\,du + \lambda v\,dv + \lambda w\,dw \longrightarrow ④$

where λ is an arbitrary constand.

Adding equ ③ and equ ④. Then

$$\left(\frac{F'(u)}{F(u)} + \lambda u\right)du + \left(\frac{F'(v)}{F(v)} + \lambda v\right)dv + \left(\frac{F'(w)}{F(w)} + \lambda w\right)dw = 0 \longrightarrow ⑤$$

According to assuption ② the velocity components are independent

$$\therefore \left.\begin{aligned}\left(\frac{F'(u)}{F(u)} + \lambda u\right)du &= 0\\ \left(\frac{F'(v)}{F(v)} + \lambda v\right)dv &= 0\\ \left(\frac{F'(w)}{F(w)} + \lambda w\right)dw &= 0\end{aligned}\right\} \longrightarrow ⑥$$

Integrating ⑥ a Then

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

remove logrithim. (where $\frac{\lambda}{2} = \frac{1}{\alpha^2}$)

$$F(u) = A\,e^{-\lambda u^2/2}.$$

$$\therefore F(u) = A\,e^{-u^2/\alpha^2} \longrightarrow ⑦$$

Similarly

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

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

$$\therefore F(u) F(v) F(w) = A^3 e^{-(u^2+v^2+w^2)/\alpha^2} \longrightarrow ⑩$$

Thus the probability that a molecule has the velocity between u and u+du is given by

$$F(u)\, du = A e^{-u^2/\alpha^2} du \longrightarrow ⑪$$

Evaluation of Constants A and α :-

Let n be the number of molecules per cc of the gas with all possible velocities from $-\alpha$ to $+\alpha$ then the number of molecules per cc with velocity components between u and u+du, v and v+dv, w and w+d

is

$$\iiint_{-\alpha}^{+\alpha} F(u) F(v) F(w)\, du\, dv\, dw = n$$

$$\iiint_{-\alpha}^{+\alpha} A^3 e^{-(u^2+v^2+w^2)/\alpha^2} du\, dv\, dw = 1 \longrightarrow ⑫$$

But the value of definit integral

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

Then the equ ⑫ will be

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

$$A^3 = \frac{1}{\sqrt{\pi}^3 \alpha^3} \longrightarrow A = \frac{1}{\alpha\sqrt{\pi}}$$

In order to calculate the value of α, we calculate the pressure exerted by the gas on the walls of the eclosure. Let us consider the case of a molecule moving along x-axis with velocity u. The charge in momentum of the molecule will be $2mu$. If n_u be the number of molecules per unit volume having velocity u, then the number of impacts on an area ∂A in time ∂t will be $n_u u \partial A \partial t$. Now the pressure p on the wall, averaged through the time interval ∂t is

$$p \cancel{\partial A \partial t} = \sum_{u=0}^{\alpha} 2mu\, n_u u \cancel{\partial A}\, \partial t$$

$$p = 2m \sum_{u=0}^{\alpha} n_u u^2 \longrightarrow ⑬$$

The number of molecules per cc having velocity component lying between u and $u+du$ is given in accordance with equ ⑪

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

$$= n \frac{1}{\alpha\sqrt{\pi}} e^{-u^2/\alpha^2}$$

apply in equ ⑬

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

Replacing summation into integration.

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

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

$$= \cancel{2}mn \frac{1}{\alpha\cancel{\sqrt{\pi}}} \left[\frac{1}{\cancel{4}_2}\cancel{\sqrt{\pi}}\sqrt{\cancel{\alpha}^3}\right]$$

$$= \frac{mn}{2\cancel{\alpha}} \alpha^{\cancel{3}}$$

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

But we know $P = nKT$

apply in above equation.

$$\cancel{n}KT = \frac{m\cancel{n}}{2} \alpha^2$$

$$\frac{1}{\alpha^2} = \frac{m}{2KT}$$

$$\alpha^2 = \frac{2KT}{m} \rightarrow \boxed{\alpha = \sqrt{\frac{2KT}{m}}} \quad ⑭$$

multiply with $\sqrt{\pi}$

$$\alpha\sqrt{\pi} = \sqrt{\frac{2\pi KT}{m}}$$

$$\frac{1}{\alpha\sqrt{\pi}} = \sqrt{\frac{m}{2\pi KT}} = A \longrightarrow ⑮$$

∴ Now the number of molecules dn having velocity components lying between u and u+du

- v and v+dv , w and w+dw is given by

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

⇒ From equ ⑯

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

From equ ⑭ and ⑧.

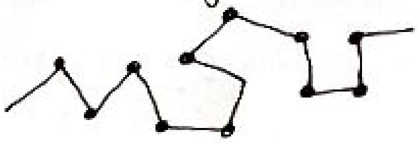
$$dn = n \left(\frac{m}{2\pi KT}\right)^{3/2} \exp\left[-\frac{m(u^2+v^2+w^2)}{2KT}\right] du\, dv\, dw$$

This is known as Maxwell's distribution law of velocities.

Mean free path.

According to kinetic theory of gases the molecules of a gas moving with very large velocities even at ordinary temperature. when the molecules moves forward, it Collides with other molecules in shoot intervals and the path is zig-zag of diffreent lengths. The path traveled by the molecule between two Consecutive Collisions will be a straight line with a uniform velocities, the straight line path is known as free path. The average of the paths is known as mean free paths. and is denoted by 'λ'.

Then the mean free path is the average distance That a molecule travels between Successive Collisions.



If $\lambda_1, \lambda_2, \lambda_3 \cdots \lambda_n$ are the velocities of the Successive free paths and t is the total time in which they ~~traveld~~ traveled then

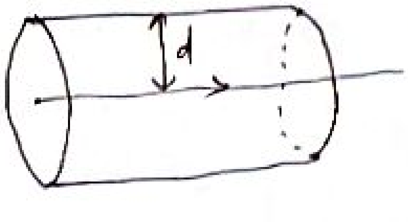
$$\lambda_1+\lambda_2+\cdots\cdots\lambda_n = \vec{v}t$$

where $\bar{v}$ is the mean Speed and n is the number of Collision in time t. then the mean free path

$$\lambda = \frac{\lambda_1+\lambda_2+\lambda_3\cdots\cdots\lambda_n}{n} = \frac{\bar{v}t}{n}$$

Expression of mean free path:-

Let us consider that, except one, all other molecules are at rest. If $\bar{v}$ be the average velocity of the molecules, it will collide with all the molecules ~~with~~ which are contained in a cylinder of radius d and length $\vec{v}$ as shown in the figure. The volume of cylinder would be $\pi d \bar{v}$. If n be the number of molecules per unit volume then the number of collision made in ~~unit time~~ one second by the moving molecules is $\pi d^2 \bar{v} n$. Hence



$$\lambda = \frac{\text{Total distance covered in } \cancel{\text{unit time}} \text{ one second}}{\text{number of Collisions in one Second}}$$

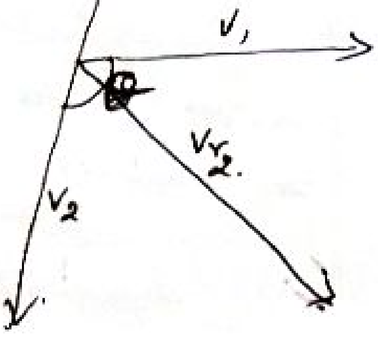
λ [illegible]

Let v_r represent the relative velocity of the molecule with respect to other molecule. Then

$$\lambda = \frac{\bar{v}}{\pi d^2 n v_r} \longrightarrow ①$$

Now the problem is to calculate the value of $\bar{v}$ in terms of known quantities. ~~There are~~

Let the particular molecule under consideration move with velocity v_1. Its relative velocity v_{r_2} with respect to other molecules of velocity v_2



making an angle θ with v_1 is represented by

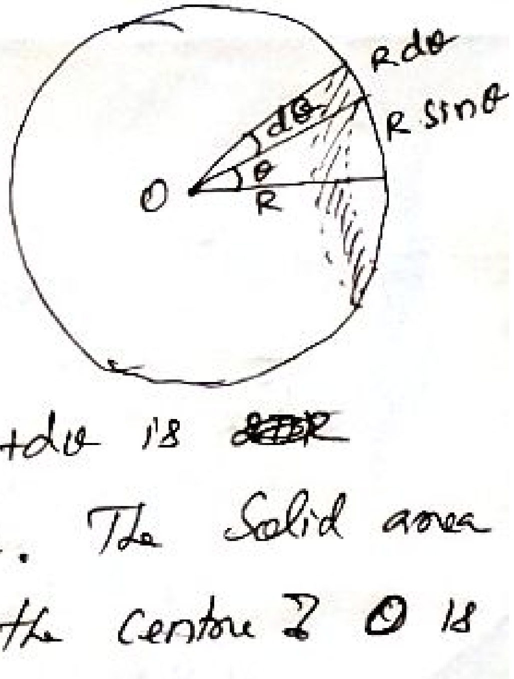
$$v_{r_2} = v_1 + v_2.$$

Applying the law of parallelogram of forces we have

$$v_{r_2}^2 = v_1^2 + v_2^2 - 2v_1 v_2 \cos\theta$$

$$v_{r_2} = \left[v_1^2 + v_2^2 - 2v_1 v_2 \cos\theta\right]^{1/2} \longrightarrow ②$$

Now the probability that the molecules lie within the solid angle between θ and θ+dθ is divided by the total number of molecules present in the whole area.



The surface area of the ring lying between θ and θ+dθ is $2\pi R\sin\theta R d\theta = 2\pi R^2 \sin\theta\, d\theta$. The Solid area substended by this ring at the centre of O is

$$= \frac{\text{Surface area}}{\text{Square of the distance}}$$

$$= \frac{2\pi \cancel{R^2} \sin\theta\, d\theta}{\cancel{R^2}}$$

$$= 2\pi \sin\theta\, d\theta$$

Hence the probability of molecules lying in Solid angle between θ and θ+dθ is

$$= \frac{\cancel{2}\pi \sin\theta\, d\theta}{\cancel{4}_{2}\pi} = \frac{1}{2}\sin\theta\, d\theta. \longrightarrow ③$$

Hence the average relative velocity $\overline{v_{r_2}}$ is given by

$$\overline{v_{r_2}} = \int_{\theta=0}^{\theta=\pi} v_{r_2}.\ \frac{1}{2}\sin\theta\, d\theta$$

$$= \int_{0}^{\pi} \frac{1}{2}\sin\theta\, d\theta\ \left[v_1^2+v_2^2-2v_1v_2\cos\theta\right]^{1/2} \longrightarrow ④$$

Let $v_1^2+v_2^2-2v_1v_2\cos\theta = t$

differentiate $2v_1v_2\sin\theta\, d\theta = dt$

$$\sin\theta\, d\theta = \frac{dt}{2v_1v_2}.$$

apply the above in equ ④

$$\overline{v_{r_2}} = \int_{(v_1-v_2)^2}^{(v_1+v_2)^2} \frac{1}{2}\ \frac{dt}{2v_1v_2}\ t^{1/2}$$

$$= \frac{1}{4v_1v_2}\int_{(v_1-v_2)^2}^{(v_1+v_2)^2} t^{1/2}\,dt = \frac{1}{4v_1v_2}\left[\frac{2}{3}\,t^{3/2}\right]_{(v_1-v_2)^2}^{(v_1+v_2)^2}$$

$$\overline{v_{r_2}} = \frac{1}{6v_1v_2}\left[(v_1+v_2)^3-(v_1-v_2)^3\right] \longrightarrow ⑤$$

∴ If $v_1 > v_2$ then $\overline{v_{r_2}} = \dfrac{3v_1^2+v_2^2}{3v_1^2} \longrightarrow$ (6a)

If $v_1 < v_2$ then $\overline{v_{r_2}} = \dfrac{3v_2^2+v_1^2}{3v_2.} \longrightarrow$ (6b)

Now consider that v_2 has all possible values varying from zero to infinity. Let the mean of v_{r_2} be denoted by $\overline{v_{r_2}}$ then

$$\overline{v_{r_1}} = \int_{v_2=0}^{v_2=\alpha} \overline{v_{r_2}} \times \left\{ \begin{matrix} \text{probability that molecules have} \\ \text{velocity between } v_2 \text{ and } (v_2+dv_2) \end{matrix} \right.$$

$$= \int_{v_2=0}^{v_2=\alpha} \overline{v_{r_2}} \times \frac{4v_2^2 e^{-v_2^2/\alpha^2}}{\alpha^3\sqrt{\pi}}\, dv_2$$

Then

$$\left. \begin{aligned} \overline{v_{r_1}} &= \int_{v_2=0}^{v_2=\alpha} \frac{3v_1^2+v_2^2}{3v_1} \cdot \frac{4v_2^2 e^{-v_2^2/\alpha^2}}{\alpha^3\sqrt{\pi}}\, dv_2 \\ \overline{v_{r_1}} &= \int_{v_2=v_1}^{v_2=\alpha} \frac{3v_2^2+v_1^2}{3v_2} \cdot \frac{4v_2^2 e^{-v_2^2/\alpha^2}}{\alpha^3\sqrt{\pi}}\, dv_2 \end{aligned} \right\} \rightarrow \textcircled{I}$$

Similarly we think a particular molecule having velocity $\overline{v_1}$ may take any velocity in time limit ~~zero~~ 0 to ∞. The average velocity v_r of any molecule

$$v_r = \int_{v_1=0}^{v_1=\infty} \frac{4v_1^2 e^{-v_1^2/\alpha^2}}{\alpha^3\sqrt{\pi}}\, dv_1 \times \overline{v_{r_1}}$$

$$v_r = \int_{v_1=0}^{v_1=\infty} \frac{4v_1^2 e^{-v_1^2/\alpha^2}}{\alpha^3\sqrt{\pi}}\, dv_1 \int_{v_2=0}^{v_2=v_1} \frac{3v_1^2+v_2^2}{3v_1}\, \frac{4v_2^2 e^{-v_2^2/\alpha^2}}{\alpha^3\sqrt{\pi}}\, dv_2$$

$$v_r = \int_{v_1=v_2}^{v_1=\infty} \frac{4v_1^2 e^{-v_1^2/\alpha^2}}{\alpha^3\sqrt{\pi}}\, dv_1 \int_{v_2=0}^{v_2=v_1} \frac{3v_2^2+v_1^2}{3v_2}\, \frac{4v_2^2 e^{-v_2^2/\alpha^2}}{\alpha^3\sqrt{\pi}}\, dv_2 \longrightarrow ⑧$$

~~Ito~~ Integrating and simplifying equ ⑧ then we get

$$v_r = \frac{2\sqrt{2}\,\alpha}{\sqrt{\pi}} = \sqrt{2}\left[\frac{2\alpha}{\sqrt{\pi}}\right]$$

$$v_r = \sqrt{2}\,\bar{v} \longrightarrow ⑨$$

where $\bar{v}$ = Average velocity $= \frac{2\alpha}{\sqrt{\pi}}$

Subtituting the value of v_r from equ ⑨ in equ ① we get

$$\lambda = \frac{\cancel{\bar{v}}}{\pi d^2 n \sqrt{2}\,\cancel{\bar{v}}}$$

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

This is the expression of mean free path.

* * *

14 16, 17, 18 19 20, 21, 22, 23

3, 4, 5, 8