Model Answer

For

M. Sc. (Chemistry) (Fourth Semester) Examination, 2013

CHEMISTRY

Paper: Statistical Mechanics

(PHYSICAL CHEMISTRY)

AR-7153

Section – A
(Short Answer Type Questions)

Model Answer for AR-7153

M.Sc. (IV Sem) : Physical chemistry specilization

Section-A [STATISTICAL MECHANICS]

① ⟨1⟩ To determine the complete state of a moving particle in a space we have to set up a six-dimensional space with configuration coordinates (x, y, z) & momentum coordinates (p_x, p_y, p_z) in which every point represents a state of the molecule. Such a six dimensional space for a single particle is called its μ-space.

For a system of N molecules a set of 6N cartesian coordinates $(x_{11}, x_{21}, x_{31}, \ldots, x_{1N}, x_{2N}, x_{3N}, p_{11}, p_{21}, p_{31}, \ldots, p_{1N}, p_{2N}, p_{3N})$ represents the positions & momenta of all the molecules at a given time that corresponds to a phase point. Such a 6N-dimensional space is called Γ-space.

Graphically μ-space & Γ-space can be represented as follows :-
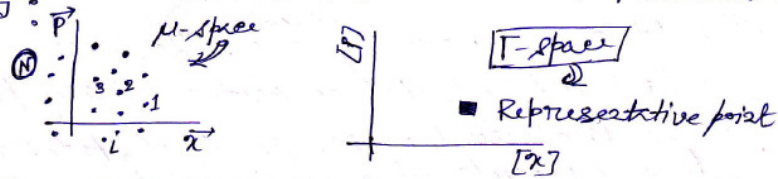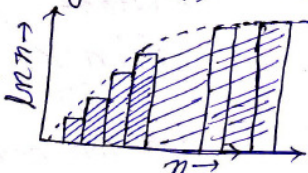
⟨ii⟩ Stirling Approximation :-

To calculate the probability of a binomial distribution Stirling provided a formula known as Stirling Approximation; which is applicable for large n. of particles $(\sim 10^{20})$.

Since $N = 1, 2, 3, \ldots, N$

$$\ln N! = \ln 1 + \ln 2 + \ln 3 + \cdots + \ln N$$

$$= \sum_{n=1}^{N} \ln n$$

If we plot $\ln n$ vs n then area for $\sum \ln n$ is 'S' which is shaded one.

For continuous variable the area under the curve is given by

$$S' = \int_1^N \ln x \, dx = [x \ln x]_1^N - \int_1^N dx = N \ln N - N + 1$$

$$\therefore \ln N! = \sum_{n=1}^{N} \ln n = N \ln N - N + 1 \quad \langle \text{As for large 'N';} \ S = S' \rangle$$

When 'N' is very large; $\boxed{\ln N! = N \ln N - N} \Rightarrow$ This is stirling approximation.

Model Answers for AR-7153
Physical Chemistry Specialization

(iii) Partition function → It can be defined as the reciprocal of fraction of particles occupying the lowest energy state i.e. $Z = \frac{n}{n_i}$; where n is the total no. of particles in the system & n_i is the no. of particles in the lowest energy state.

For MB-distribution; $Z = \sum e^{-\beta \epsilon_i}$

Significances of Partition function →

(i) It indicates the mode of distribution of particles in various energy state.

(ii) It is a pure no. & is a dimensionless quantity.

(iii) It can never be/zero. The lowest value is one.

(iv) It can be applied to system of any physical state.

(V) It indicates the average no. of states that are accessible to a molecule at a particular temp. of the system.

(vi) All the thermodynamic properties including internal energy (U); entropy (S), chemical potential (µ); etc. can be calculated with the help of this function.

(iv) The effect of temperature (T) on equilibrium constant (K_p) can be explained by using van't Hoff equation.

$$\frac{d \ln K_p}{dT} = \frac{\Delta H}{RT^2} \xrightarrow{\text{upon integration}} \ln \left(\frac{K_{p_2}}{K_{p_1}} \right) = \frac{\Delta H}{R} \left[\frac{T_2 - T_1}{T_1 T_2} \right] \text{---}①$$
$$(\text{where } T_2 > T_1)$$

For an exothermic reacn, ΔH is (−)ve then from eqn ① $K_{p_2} < K_{p_1}$; that is with rise in temp. eqvlm const. of the exothermic reaction decreases.

For an endothermic reacn $\Delta H = (+)$ve & $T_2 > T_1$ then from eqn ①; $K_{p_2} > K_{p_1}$; that is with rise in temp. eqvlm const. of endothermic reaction increases.

← for endothermic reacn.   ← For exothermic reacn
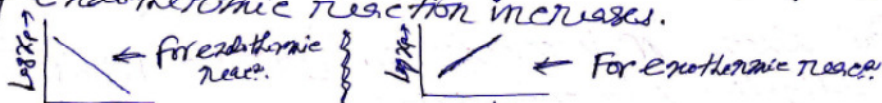
(V) When the temperature of the system (T) become less than the critical temp. of the system (T_0) (where absolute activity, $z_a \to 1$) i.e. when $T < T_0$ then more & more particles begain to occupy the ground state (ϵ_0). Under such condition Bose-Einstein gas became degenerate, which is characterised by $\mu \to 0$ where μ is the Chemical potential.

(VI) The amount of heat required to raise the temperature of one gm of a substance by 1K is called its specific heat. If the substance is an ideal gas then the gas molecules may obey either MB; FD or BE-distribution law. The comparative curve for the heat capacity of a gas according to the above three statistics is as follows—

For MB ⇒ $C_V = \frac{3}{2} NR$

BE ⇒ $C_V = 1.926\, NR \left(\frac{T}{T_0}\right)^{3/2}$

$C_{V+} = \frac{3}{2} NR \left[1 + 0.231 \left(\frac{T_0}{T}\right)^{3/2} + \ldots \right]$

FD ⇒ $C_V = \frac{\pi^2 NR}{2} \cdot \frac{T}{T_F}$
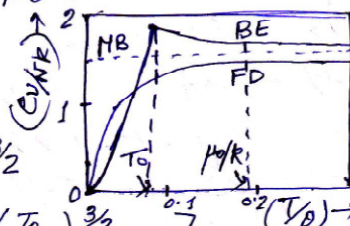
From the curve we can conclude that (C_V/NR) is invariant with (T/θ) for MB-distribution. For BE-distribution we observed a kink at $T = T_0$. If the gas follows FD-distribution then there is a smooth variation observed but it has lower value compare to other two distributions.

(vii) Fermi temperature can be defined as; $\boxed{T_F = \frac{\epsilon_F(0)}{k}}$ where $\epsilon_F(0)$ is the energy of the highest level occupied at 0K. When $T \ll T_F$ or $kT_F \ll \epsilon_F(0) \to$ the distribution is called degenerate. When $T \gg T_F \to$ the distribution is nondegenerate. $k \to$ Boltzmann constant.

⟨viii⟩ Let 'x' is the physical parameter of a system with average value $\bar{x}$. Then the deviation or fluctuation defined as →

$$\delta x = x - \bar{x}$$

$$\therefore \overline{\delta x} = \overline{x - \bar{x}}$$

$$= \bar{x} - \bar{x} = 0$$

Therefore the mean of δx is zero.

Now if we consider mean-square deviation that can be defined as →

$$(\overline{\delta x})^2 = \overline{(x - \bar{x})^2}$$

$$= \overline{x^2 - 2\bar{x}x + \bar{x}^2}$$

$$= (\overline{x^2} - \overline{x}^2)$$

∴ The mean square i.e. $(\overline{\delta x})^2$ is a measure of the strength of the fluctuations.

⟨ix⟩ We usually calculate the average values of the thermodynamic quantities like energy, entropy, free energy etc; that are the properties of a system. With the passage of time the properties of a system vary about the mean/average of equilibrium values. Such deviation from the mean value is known as fluctuation.

⟨x⟩ The steady state Boltzmann transport equation in τ-approximation is represented by —

$$V_x \frac{df}{dx} = - \left[\frac{f - f_0}{\tau} \right]$$

The nonequilibrium distribution function(f) varies in the x-direction from its equilibrium value f_0.

$\tau →$ is the relaxation time. Usually it depends on cartesian coordinates (r) & velocity (v).

Section – B

②   Entropy is an extensive property. Then when we consider the mixing of two different gas entropy of the mixture increases as it is an additive property.

i.e. $S_{AB} = S_A + S_B + 2Nk \ln 2$

This means that if the molecules are different then increase in entropy occur by the factor $2Nk \ln 2$. This increase in entropy is known as the entropy of mixing. Now if A & B contains same type of molecule this increase in entropy of mixing makes no sense. This is called Gibb's paradox.

Gibbs solved the puzzling problem by considering the two systems are same, hence the gas molecules are completely identical & indistinguishable. Introducing indistinguishability in partition function we have $Z = \dfrac{Z^N}{N!}$ & the corresponding Helmholtz free energy is given by —

$$A = - RT \ln \left\{ \dfrac{Z^N}{N!} \right\}$$

$$= - NRT \ln Z + NRT \ln N - NRT \quad \cdots ②$$

∴ Entropy, $S = - \left(\dfrac{\partial A}{\partial T} \right)_V$

$$= Nk \ln \left\{ \left(\dfrac{2\pi m kT}{h^2} \right)^{3/2} V \right\} + \dfrac{3}{2} Nk$$

$$- Nk \ln N + Nk \quad \cdots ③$$

The entropy for the system A & B can be expressed as —

$$S_A = Nk \ln \left\{ \left(\dfrac{2\pi m_A kT}{h^2} \right)^{3/2} V \right\} + \dfrac{3}{2} Nk - Nk \ln N + Nk \quad ④$$

$$S_B = Nk \ln \left\{ \left(\dfrac{2\pi m_B kT}{h^2} \right)^{3/2} V \right\} + \dfrac{3}{2} Nk - Nk \ln N + Nk \quad ⑤$$

Now if the two systems are placed in contact the volume will be $2V$ & the no of molecules will be $2N$.

∴ The entropy for the combined system (S_{AB}) is given by—

$$S_{AB} = 2Nk \ln \left\{ \left(\frac{2\pi mkT}{h^2} \right)^{3/2} 2V \right\} + \frac{3}{2} \cdot 2Nk - 2Nk \ln 2N + 2NR$$

$$= 2Nk \ln \left\{ \left(\frac{2\pi mkT}{h^2} \right)^{3/2} \left(\frac{V}{N} \right) \right\} + 5Nk \quad \text{------} ⑥$$

Now from eqns. ④ & ⑤;

$$(S_A + S_B) = 2Nk \ln \left\{ \left(\frac{2\pi mkT}{h^2} \right)^{3/2} \left(\frac{V}{N} \right) \right\} + 5NR$$

$$= S_{AB}$$
[from eqn. ⑥]   [As the two gases are identical;
                        $m_A = m_B = m$]

Thus Gibb's paradox is resolved.

Section-B

③ Assumptions of Einstein theory of specific heat :

(i) He considered a solid as an aggregate of atomic oscillators.

(ii) Each of these oscillators is vibrating with a common mean frequency, ν in a simple harmonic manner.

(iii) Each atom of solid has three degrees of freedom like a molecule of monoatomic gas.

Now if the normal modes of vibrations do not interact then the total frequency is characterised by one but the total energy will be different for different normal modes. Therefore the partition function for the solid can be written as —

$$Z_N^{crystal} = Z_1^{\nu} \, Z_2^{\nu} \, Z_3^{\nu} \cdots Z_N^{\nu}$$

$$= \left(\frac{e^{-\theta/2T}}{1-e^{-\theta/T}}\right)_1 \cdots \left[\frac{e^{-\theta/2T}}{(1-e^{-\theta/T})}\right]_N$$

where θ is the Einstein's characteristic temp. $\theta = \dfrac{h\nu}{R}$

$$= \left[\frac{e^{-\theta/2T}}{1-e^{-\theta/T}}\right]^N \text{ per degree of freedom.}$$

Using third assumption;

$$Z_N^{crystal} = \left[\frac{e^{-\theta/2T}}{1-e^{-\theta/T}}\right]^{3N} \cdots ①$$

Now the total energy of the crystal can be expressed as—

$$E = kT^2\left[\frac{\delta \ln Z_N^{crystal}}{\delta T}\right]_V = kT^2\left[\frac{\delta}{\delta T}\left(\frac{e^{-\theta/2T}}{1-e^{-\theta/T}}\right)^{3N}\right] \quad (\text{from eqn.①})$$

$$= \left[\frac{3}{2}NK\theta + \frac{3NK\theta}{(e^{\theta/T}-1)}\right] \cdots ②$$

∴ Specific heat of the solid can be written as —

$$c_V = \left(\frac{\delta E}{\delta T}\right)_V = \frac{\delta}{\delta T}\left[\frac{3}{2}NK\theta + \frac{3NK\theta}{(e^{\theta/T}-1)}\right] \quad (\text{from eqn.②})$$

$$= 3R\left(\frac{\theta}{T}\right)^2 \cdot \frac{e^{\theta/T}}{(e^{\theta/T}-1)^2} \quad (\text{where } R = NK)$$

This is the Einstein eqn. for the atomic heat of a solid at constant volume. This eqn. represents that atomic heat is a function of temperature.

Limitations of Einstein theory :

(i) Einstein theory is in good agreement with the exfts for various metals. But for some metals like copper, aluminium, iron, etc. it is observed that the atomic heat at low temp. decreases more slowly than that predicted from Einstein theory.

(ii) In this theory, ν & θ are obtained emperically and can not be verified from any other p independent physical data.

⑭ ④

The particles which follows Bose-Einstein distribution law is known as BOJONS. B-E law is applicable for identical and indistinguishable particles. The wave functh for such distribution should be symmetric. There is no restriction on the occupancy of the particle in a given quantum state. Particles having spin zero or integral number obey Bose-Einstein law such particles are called Bojons.

Examples: (a) α-particles ; (b) Photons; (c) Deutrons;
(d) 12c ; (e) ^{14}N ; (f) ^{16}O etc.

Derivation of Bose-Einstein distribution law :

Consider a system containing 'n' distinguishable particles having a total energy 'E'. Let n_1 particles are present in energy state/level ϵ_1 ; n_2 particles in energy state ϵ_2 ; $n_3 \to \epsilon_3$ ..... $n_i \to \epsilon_i$ & so on for a given distribution. Then we have ;

$$E = n_0 \epsilon_0 + n_1 \epsilon_1 + \cdots + n_i \epsilon_i = \sum n_i \epsilon_i$$
$$\left\{ n = n_1 + n_1 + n_2 + \cdots + n_i = \sum n_i \right\} ①$$

The thermodynamic probability considering B-E statistics is —

$$H = \prod_i \frac{(n_i + g_i - 1)!}{n_i! (g_i - 1)!} \; ; \quad \text{where } g_i \text{ is the degree of degeneracy of ith level.}$$

or; $\ln H = \sum_i [\ln (n_i + g_i - 1)! - \ln n_i! - \ln (g_i - 1)!]$

Applying Stirling's approximation & considering $(n_i + g_i - 1) \simeq$ $(n_i + g_i)$ & $(g_i - 1) \simeq g_i$ [we have —

$$\ln W = \sum_i [(n_i + g_i) \ln (n_i + g_i) - n_i \ln n_i - g_i \ln g_i] \quad \cdots \cdots \textcircled{2}$$

The condition of maximizing the probability i.e. at equilibrium $d \ln W = 0 \quad \cdots \textcircled{3}$

Differentiating eqn $\textcircled{2}$ w.r.t. n_i —

$$\frac{d \ln W}{d n_i} = \sum_i [-\ln n_i + \ln (n_i + g_i)] = \sum_i \left[-\ln \frac{n_i}{(n_i + g_i)} \right] \quad \cdots \textcircled{4}$$

At equilibrium; from eqn $\textcircled{3}$ & $\textcircled{4}$;

$$\sum_i \left[\ln \frac{n_i}{(n_i + g_i)} \right] d n_i = 0 \quad \cdots \cdots \textcircled{5}$$

From eqn $\textcircled{1}$ we have; $n = \sum n_i \rightarrow \sum d n_i = d n = 0 \quad \textcircled{6}$

$$\& \quad E = \sum n_i \epsilon_i \rightarrow \sum \epsilon_i d n_i = dE = 0 \quad \textcircled{7}$$

〈As for a given system the total energy (E) & the total no. of particles (n) is always constant〉

Multiplying eqn $\textcircled{6}$ by $-\alpha$ & eqn $\textcircled{7}$ by $-\beta$ and adding these with eqn $\textcircled{5}$ we have;

$$\sum_i \left[-\ln \frac{n_i}{(n_i + g_i)} - \alpha - \beta \epsilon_i \right] d n_i = 0 \quad \Big\langle \begin{array}{l} \alpha \& \beta \to \text{Lagrange's} \\ \text{undetermined} \\ \text{multiplier} \end{array}$$

for the sum to be equal to zero; each coeff. of $d n_i$ is equal to zero. Then —

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

or; $\qquad \frac{n_i}{n_i + g_i} = e^{-\alpha} e^{-\beta \epsilon_i}$

or; $\qquad \frac{n_i + g_i}{n_i} = e^{+\alpha} e^{\beta \epsilon_i}$

or; $\qquad \left(1 + \frac{g_i}{n_i}\right) = e^{+\alpha} e^{\beta \epsilon_i}$

or; $\qquad \frac{g_i}{n_i} = (e^{+\alpha} e^{\beta \epsilon_i} - 1) = [e^{(\alpha + \beta \epsilon_i)} - 1]$

$$\therefore \boxed{n_i = \frac{g_i}{(e^{\alpha} e^{\beta \epsilon_i} - 1)}} \Rightarrow \begin{array}{l} \text{This is the expression for} \\ \text{Bose – Einstein distribution} \end{array}$$

⑤ Electrons in metals:

According to Drude (1900) the electrical & thermal behaviour of the metals can be correlated if we assume that free electrons exist in thermal equilibrium with the atoms of the metal. If electrons in metals obey Maxwell–Boltzmann statistics then according to Lorentz (1905) the heat capacity should be $9R/2$ per-gm atom. But metals obey Dulong & Petit's law ($c_v = 3R$) quite accurately. This discrepancy can be overcome if free electrons in metals obey Fermi-Dirac statistics. To apply FD-statistics we have to first consider that the mutual interaction of electrons is absent due to the neutralizing effect of positive ions inside a metal.

We know that; FD-distribution depends only slightly on temp. (T). As the temp. is raised from $0K$ to T, each free electron does not gain energy by an amount kT as most of them are occupying states of energy less than Fermi energy; ($\cancel{\epsilon_F}$) $\epsilon_F(T=0) \equiv \mu_0$.

By the Pauli principle they cannot be excited to these states as they are already fully occupied. The electrons that can be excited to empty states which have energy close to μ lying in the range kT is given by —

$$N_{exc} \simeq g(\mu)kT = \frac{3N}{2\mu_0}kT \qquad \left\langle As\ g(\mu) = \frac{3N}{2\mu}\right\rangle$$

$$= \frac{3}{2}N\left(\frac{T}{T_F}\right) \qquad \left\langle T_F \to \text{Fermi temp.}\right\rangle$$

∴ The corresponding electronic energy is given by —

$$U(T) \simeq N_{exc}\cdot kT = \frac{3}{2}Nk\left(\frac{T^2}{T_F}\right)$$

∴ The electronic heat capacity is; $c_v(T) = \left(\frac{\partial U}{\partial T}\right)_V = 3Nk\left(\frac{T}{T_F}\right)$

→ Which is close to c_v ~~that~~ due to Sommerfeld;
$c_v = \frac{\pi^2}{2}Nk\cdot(T/T_F)$

Thus at room temperature the electronic heat capacity per electron calculated according to FD-statistics.3k is very small compared to the atomic specific heat of about 3k per atom; which is in good agreement with the experiments.

At low temp; the lattice heat capacity is proportional to T^3 whereas the electronic heat capacity varies linearly with 'T'. For very low temp. lattice heat capacity decreases very rapidly and the electronic heat capacity begins to dominate. This is also in good agreement with experiments.

From the above we conclude that free electrons in metal follows FD-statistics.

The comparison curve of FD & BE distribution function is as follows:
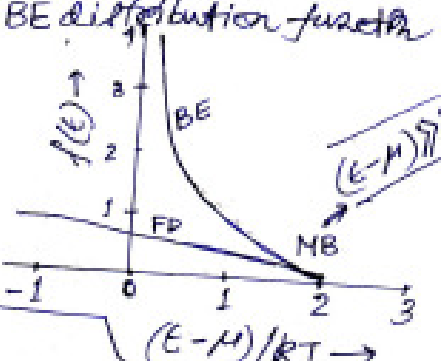
(6) Consider a system of total 'N' no. of particles having energy 'E'.

Let us consider $\bar{n_i}$ is the average no. of particles in the single particle quantum state 'i' then $g_i = 1$.

Then following BE statistics; $\bar{n_i} = \left[\dfrac{1}{e^{(\epsilon_i - \mu)/\theta} - 1} \right]$, where $\theta = k$, & $\mu = -\alpha k$

Differentiating w.r.t. μ →

$$\left(\frac{\delta \bar{n_i}}{\delta \mu} \right) = \frac{\delta}{\delta \mu} \left[\frac{1}{e^{(\epsilon_i - \mu)/\theta} - 1} \right] = \frac{1}{\theta} \bar{n_i}(1 + \bar{n_i}) \quad \text{----①}$$

The fluctuation in grand canonical ensemble can be expressed as —

$$(\delta n_i)^2 = \left[\bar{n_i^2} - \bar{n_i}^2 \right] = \theta \cdot \left(\frac{\delta \bar{n_i}}{\delta \mu} \right) = \bar{n_i}(1 + \bar{n_i}) \quad \text{----②}$$

12

At $T \to 0$, for BE gas a large no. of particles coalesce on the ground state; $\epsilon_{gr.} = 0$, $\bar{n}_{gr.} \simeq N$

for ground state the mean square fluctuation is given by-

$$(\delta n_0)^2 = \left[\overline{n^2} - (\bar{n})^2\right] \simeq (\overline{n^2} - N^2) \quad \text{——③}$$

But from eqn ② we have;

$$(\delta n_0)^2 = \bar{n}_0 (1 + \bar{n}_0) = \bar{n}_0 + \bar{n}_0^2$$
$$= (N + N^2)$$
$$\simeq N^2 \quad \text{——④}$$

Comparing eqns ③ & ④; we have; $\overline{n^2} \simeq 2N^2$

Now if we consider a group of g neighbouring states having same mean particle instead of single particle state $\bar{n}_i$ then we have;

$$\bar{N} = g\bar{n}.$$

Due to the statistical independence of the probability distribution of the different single particle states we may write;

$$(\delta \bar{N})^2 = g(\overline{\delta n})^2 = g\bar{n}(1 + \bar{n})$$
$$= \bar{N}\left(1 + \frac{1}{g}\bar{N}\right) \quad \text{——⑤}$$

The eqn ⑤ is applicable to photons although the eqn① can not be used as $\mu = 0$ for photons.

As photons obey BE statistics; $n(\epsilon) = \left(e^{\epsilon/\theta} - 1\right)^{-1}$
The no. of quantum states of the photons with frequencies between ν & ($\nu + d\nu$) is given by→ $g = 8\pi V (\nu^2/c^3) d\nu$.
The total energy of the quanta in the frequency range is → $E_{(d\nu)} = N h\nu$

If we multiply eqn ⑤ by $(h\nu)^2$ then

$$\left[\delta E_{(d\nu)}^{Photon}\right]^2 = \left[h\nu E_{(d\nu)} + \frac{c^3 \{E_{(d\nu)}\}^2}{8\pi V \nu^2 d\nu}\right] \quad \text{——⑥}$$

This relation was derived by Einstein.

The first term in R.H.S. is due to the corpuscular nature of the radiation as it involves Planck constant; h. The second term represents the classical result for the energy fluctuations of black body radiation. The eqn ⑥ implies that photons like to travel in bunches.

⑦ The Fermi-Dirac distribution for diffusion of particles at the equilibrium can be expressed as —

$$f_0 = \left[\frac{1}{e^{(E-\mu)/RT} + 1} \right] \quad \text{where; } \mu = -\alpha RT$$

At low temp; $\frac{df_0}{d\mu} = - \left(\frac{df_0}{dE} \right)$ is small everywhere except in the region $E \simeq \mu$. Thus $\frac{df_0}{d\mu}$ resembles a delta function, i.e. $\frac{df_0}{d\mu} \simeq \delta(E-\mu)$

$$\therefore \quad \frac{df_0}{dx} = \delta(E-\mu) \left(\frac{d\mu}{dx} \right) \quad \dots \textcircled{1}$$

The particle flux density in the x-direction can be expressed as →

$$\dot{J}_x = \int v_x f g(E) dE = - \frac{d\mu}{dx} \int \frac{\tau v_x^2 f_0}{RT} g(E) dE$$

$$= - \frac{d\mu}{dx} \tau(\mu) \int v_x^2 \delta(E-\mu) g(E) dE \quad \dots \textcircled{2}$$

Where $\tau(\mu)$ is the relaxation time at $E = \mu$. $\langle$ from eqn ①$\rangle$

If we put $g(E) = g(\mu) = 3n/2\mu_0$ at absolute zero; then the above integral has the value $\frac{1}{3} v_F^2 \frac{3n}{2\mu_0} = \frac{n}{m}$

Where $\mu_0 \equiv E_F(T=0) \equiv \frac{1}{2} m v_F^2$; $v_F \to$ Fermi velocity on the Fermi surface.

We know; $\frac{d\mu}{dx} = \frac{2}{3} \cdot \frac{h^2}{2m} \left(\frac{3}{8\pi} \right)^{2/3} n^{-1/3} \frac{dn}{dx}$

$$= \frac{2}{3} \left(\frac{\mu_0}{n} \right) \left(\frac{dn}{dx} \right) \quad \dots \textcircled{3} \quad \left\langle \mu_0 = \left(\frac{h^2}{2m} \right) \left(\frac{3n}{\pi} \right)^{2/3} \right\rangle$$

Now from eqn ②;

$$\dot{J}_x = - \frac{n\tau}{m} \cdot \frac{d\mu}{dx} = - \frac{2\tau}{3m} \mu_0 \cdot \left(\frac{dn}{dx} \right) \quad \langle \text{using eqn ③} \rangle$$

$$= - \frac{1}{3} \tau v_F^2 \cdot \left(\frac{dn}{dx} \right)$$

$$\boxed{\dot{J}_x = - D \frac{dn}{dx}} \quad \left\langle \text{where } D = \frac{1}{3} v_F^2 \tau(\mu) \right\rangle$$

→ Which resembles quite well with the classical results; $\boxed{D = \tau \cdot \frac{RT}{m} = \frac{1}{3} v^2 \tau}$.

⑧   The Maxwell-Boltzmann distribution law can be expressed as $n_i = \dfrac{n e^{-\beta \epsilon_i}}{z}$ where $z \to$ partition function.

$$\therefore \ln n_i = \ln n - \ln z - \beta \epsilon_i \quad \text{----} ①$$

At equilibrium, both entropy (S) & the thermodynamic probability attain their maxima. The relation between the two can be written as $\to$ $S = k \ln W \cdots ②$ where 'k' is Boltzmann constant.

We know that $W = \dfrac{n!}{n_0! \, n_1! \cdots} = \dfrac{n!}{\prod n_i!}$

or: $\ln W = \ln n! - \sum \ln n_i!$ [Applying Stirling's approx $= n \ln n - \sum n_i \ln n_i$ as both n & the are very large & $\sum n_i = n$]

Now from eqn ②; $S/k = \ln W = n \ln n - \sum n_i \ln n_i$

$$= n \ln n - \sum n_i (\ln n - \ln z - \beta \epsilon_i)$$

from eqn ①

or; $S = (n k \ln z + k \beta E)$ $\langle \because \sum n_i = n$ & $\underline{\sum n_i \epsilon_i = E} \rangle$

Now differentiating the above eqn w.r.t 'E' at constant volume (V); $\left(\dfrac{\partial S}{\partial E}\right)_V = \dfrac{n k}{z}\left(\dfrac{\partial z}{\partial \beta}\right)\left(\dfrac{\partial \beta}{\partial E}\right)_V + k\beta$

or; $\left(\dfrac{\partial S}{\partial E}\right)_V = -\dfrac{n k}{z} \cdot \dfrac{E z}{n}\left(\dfrac{\partial \beta}{\partial E}\right)_V + k\beta + kE\left(\dfrac{\partial \beta}{\partial E}\right)_V$ $\begin{array}{l} + kE\left(\dfrac{\partial \beta}{\partial E}\right)_V \\ \hline z = \sum e^{-\beta \epsilon_i} \\ = \sum \epsilon_i \cdot \dfrac{n_i z}{n} \\ = -\dfrac{E z}{n} \end{array}$

$= k\beta$

When the energy is purely internal energy(u), then $\left(\dfrac{\partial S}{\partial u}\right)_V = k\beta \quad \cdots ③$

From 1st & 2nd law of thermodynamics we have; $TdS = du + p dv$

$$\therefore \left(\dfrac{\partial S}{\partial u}\right)_V = \dfrac{1}{T} \quad \cdots ④$$

Comparing eqn ③ & ④; $k\beta = \dfrac{1}{T}$

$$\text{or; } \boxed{\beta = 1/kT}$$