

Statistical Thermodynamics

Date: / /

* Statistical Thermodynamics :-

Statistical thermodynamics has been applied successfully to relate the microscopic properties of the individual molecules (M.I, dipole moment, etc) with macroscopic properties (molar heat capacity, polarization, etc) of a system having a large number of molecules, it can be used for systems at equilibrium as well as away from equilibrium.

* Distinction between quantum mechanics, statistical mechanics & statistical thermodynamics

Statistical mechanics acts as a bridge between thermodynamics & quantum mechanics. Quantum mechanics provides information about the energy of the molecular systems & statistical mechanics tell us about the possible arrangements of the energy among various molecules of the systems & introduces the concept of probability and partition function. Statistical thermodynamics deals with the relationship between the probability partition function & thermodynamic properties.

* Probability Theorem

The following are the important probability theorems which are used in statistical thermodynamics.

1] The number of ways in which N distinguishable particles can be arranged in order is $N!$

2] The number of different ways in which n indistinguishable particles can be arranged in g distinguishable states with not more than one particle in each state is $g!$

$$n! (g-n)!$$

3] The number of ways in which n particles can be selected from N distinguishable particles irrespective of the order of selection is equal to

$$N!$$

$$(N-n)!n!$$

* Phase space

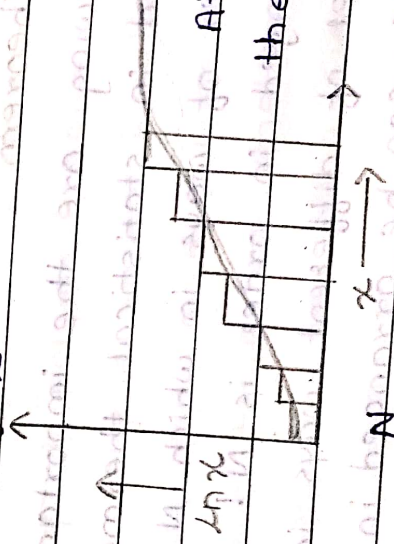
To specify the state of q as from the molecular point of view, we shall the position & momentum of each of its molecules. A six dimensional space in which $dx, dy, dz, dp_x, dp_y, dp_z$ is an element of volume & position of a point in this space will be described by a set of six co-ordinates x, y, z, p_x, p_y, p_z , this six dimensional space is called phase space & an element of volume in space is termed as cell.

* Stirling Approximation -

$$\ln N! = \ln 1 + \ln 2 + \ln 3 + \ln 4 + \dots + \ln N$$

$$= \sum_{i=1}^N \ln x_i$$

This summation can be evaluated by plotting graph $\ln x$ vs x



$$\ln N! = \int_1^N \ln x \, dx$$

$$= [x \ln x]_1^N - [x]_1^N$$

$$= N \ln N - N + 1$$

$\approx N \ln N - N$ as N is very very large

$$\ln N! = N \ln N - N$$

This is Stirling approximation & this is required for all statistical mechanics.

* Configuration

Different equivalent ways of obtaining a state is known as configuration of the system.

For example -

Consider two coins x & y . The state of showing one Head (H) & one tail (T) can be obtained in two ways:

- a) Coin x shows a tail & coin y a head
- b) coin x shows a head & coin y a tail

Thus, these are two ways of arriving at the same state of 1H & 1T, so the no. of configuration is 2.

* Ensembles

It is a collection of a very large number of assemblies which are independent of each other but which have been made as macroscopically as identical as possible.

Types of Ensembles -

- 1) Uniform ensembles
- 2) Microcanonical ensemble
- 3) Canonical ensemble
- 4) Grandcanonical ensemble

① Uniform Ensemble -

In a uniform ensembles, the density in phase space is constant.

$$\lim_{\Delta V \rightarrow 0} \frac{1}{\Delta V} = \lim_{N \rightarrow \infty} \frac{\Delta N}{N} = \text{constant}$$

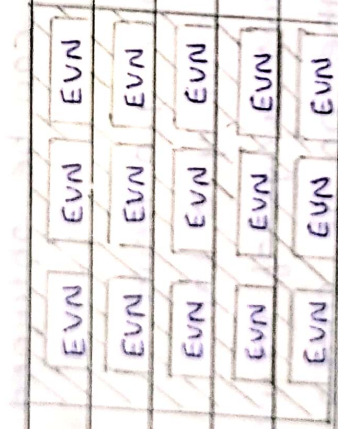
Where,

ΔN = No. of systems in an element of volume ΔV

N = Total no. of system in an ensemble.

② Microcanonical Ensemble -

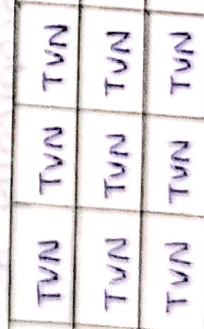
It is collection of large no. of essentially independent assembly each of which posses the same energy E , volume V & no. of system N .



In fig shows that, this ensembles in which individual assemblies are separated by rigid & well insulated walls is that E, V & N for particular assembly are not affected by the presence of other assemblies. It is isolated system.

③ Canonical ensemble -

It is a collection of large no. of independent of assemblies having the same T, V & N .



In fig. shows that, canonical ensembles in which individual assemblies are separated by rigid impermeable & conductivity wall. It is closed system.

④ Grandcanonical ensemble -

It is collection of large no. of independent of assemblies having the same temp T , volume V & chemical potential μ .

In fig shows that grand canonical ensemble in which the individual assemblies are separated by rigid permeable & conducting walls, each of this assemblies can exchange both energy and particles with one another. It is open system.

Use of ensembles - There are infinite no. of ensembles, the four types are discussed above which are particularly useful for two main reasons.

- ① Firstly all four types corresponds approximately to the type of thermodynamic measurements which are frequently met in practice.
- ② Secondly, We have considered four types in which the values of thermodynamic quantities are not very sensitive to the methods of measurements.

* Boltzmann - Plank's equation

According to Boltzmann entropy is a function of probability of thermodynamic state.

$S \propto \ln W$
 $S = F(W)$

where,

$S =$ entropy

$W =$ Probability of a particular state
As we know that, energy is additive property and probability is the multiplicative property

$S = S_1 + S_2$

and $W = W_1 \times W_2$

$F(W) = F(W_1 \times W_2)$

Suppose there are two types of arrangement i.e.

A & B. entropy is S_A & S_B

Probability is W_A & W_B

$$S_A \propto W_A$$

$$\text{and } S_B \propto W_B$$

on combining eqⁿ (1), (2) & (3)

$$S = S_1 + S_2 = F(W_1 \times W_2) \quad \text{--- (4)}$$

$$S = F(W_1) + F(W_2) = F(W_1 \times W_2) \quad \text{--- (5)}$$

on diff this eqⁿ w.r.t. W_1 & constant W_2

$$W_2 F'_1(W_1 \times W_2) = F'_1(W_1) \quad \text{--- (6)}$$

again diff w.r.t. W_2 & keep W_1 constant, we get

$$W_1 W_2 F''(W_1 \times W_2) + F'_1(W_1 \times W_2) = 0$$

$$\text{OR } W F''(W) + F'(W) = 0$$

by putting $P = F'(W)$ & $dP/dW = F''(W)$ in above eqⁿ

$$W dP + P = 0 \quad \text{--- (7)}$$

$$\text{OR } W dP + P dW = 0$$

$$\text{OR } d(PW) = 0 \quad \text{--- (8)}$$

by integrating this eqⁿ, we get

$$WP = C$$

where, C is constant

$$\text{OR } W \frac{d}{dW} [F(W)] = C \quad \text{--- } [\because P = F'(W) = \frac{d}{dW} [F(W)]$$

$$\text{OR } dF(W) = \frac{C dW}{W} \quad \text{--- (9)}$$

integrating the expression

$$F(W) = C \ln W + C_1$$

where,

$C_1 = \text{constant of integration}$

k constant which has the same value as Boltzmann constant
eqⁿ (10) is known as Boltzmann equation

Planck showed that,
 $c = 0$

$$S = k \ln W \quad [S = F(\omega)]$$

This eqⁿ is known as Boltzmann-Planck equation.

* Maxwell - Boltzmann Distribution law

Consider a system of constant energy E composed of n identical particles at temp T & possessing characteristics as:

1. Particles do not attract or repel each other.
2. Each particle is distinguishable from other
3. No restriction on assigning various energy level to the particles is being imposed.

Now, we shall consider the distribution of the total energy E among the various energy level say E_1, E_2, E_3 of the n particles.

As we know that, each particle is exist in a no. of allowable energy levels in a such way that n -particle is present in level with energy E_1, n_2 in level with E_2 & so on ...

Irrespective of this distribution the total no. of particles & the energy of the system remain constant.

$$\left. \begin{aligned} \text{Total number of particles } N &= \sum n_i \\ \text{Total energy } E &= \sum n_i E_i \end{aligned} \right\} \text{--- (1)}$$

such summation are to be carried over all energy levels.

$$W = \frac{n!}{n_1! n_2! \dots}$$

$$n_0! n_1! n_2! \dots$$

$$dn = \sum_{i=0}^{\infty} dn_i \quad (9)$$

$$dn = \alpha dn_i \quad (9)$$

$$dE = \sum_{i=0}^{\infty} E_i dn_i$$

$$dE = \beta E_i dn_i \quad (10)$$

Multiplying eqⁿ (9) and (10) by two arbitrary constants α & β respectively & adding eqⁿ (8) We get

$$\sum (\ln n_i + 1 + \alpha + \beta E_i) dn_i = 0$$

but

$$1 + \alpha = \alpha$$

$$\sum (\ln n_i + \alpha + \beta E_i) dn_i = 0 \quad (11)$$

As the variables dn_1, dn_2, dn_3, \dots are independent on each other, then each term in the summation must be zero

$$\ln n_i + \alpha + \beta E_i = 0 \quad (dn_i \neq 0)$$

$$\ln n_i = -(\alpha + \beta E_i)$$

$$n_i = e^{-(\alpha + \beta E_i)} \quad (12)$$

This eqⁿ is known as Boltzmann distribution law.

eqⁿ (12) can be put as

$$n_i = e^{-\alpha} \cdot e^{-E_i/KT} \quad (13)$$

where $\beta = \frac{1}{KT}$

It is possible that, there may be a number of a quantum levels of almost identical energies & for this a statistical weight factor g_i is introduced for level E_i ,

$$n_i = g_i e^{-\alpha} \cdot e^{-E_i/KT} \quad (14)$$

$$\sum n_i = \sum g_i e^{-\alpha} e^{-E_i/KT}$$

$$n = \sum g_i e^{-\alpha} e^{-E_i/KT} \quad (15)$$

dividing eqⁿ (14) & (15)

$$\frac{n_i}{n} = \frac{g_i \cdot e^{-\alpha} \cdot e^{-E_i/KT}}{\sum g_i \cdot e^{-\alpha} \cdot e^{-E_i/KT}}$$

This eqⁿ is general Maxwell-Boltzmann distribution law.

* Partition function

Partition function is the dimensions factor. It is defined as "the sum of probability factor for different energy states." It is denoted by Q .

$$Q = \sum g_i e^{-E_i/KT}$$

Where,

g_i = statistical weight factor

E_i = energy of quantum states in excess of lowest possible value

T = Temp in Kelvin

K = Boltzmann constant

Significance -

- ① Partition function is dimensionless property, its name summarises in convenient mathematical form, the energy of the system of molecule is partitioned among the molecule levels.
- ② The value of partition function depends upon the molecular weight, temp, molecular volume, internuclear distances.
- ③ Partition function provides the linking between microscopic properties of individual molecules (i.e. moment of inertia, dipole moment, etc) with the macroscopic properties of molecules (i.e. molar heat capacity, entropy, polarization)
- ④ Partition funⁿ value increases with temp, as the temp is raised, then there are more no. of molecules in zero

energy levels, so partition function increases at highest temperature.

Types of partition function

There are four types of partition functions.

- ① Translational partition function
- ② Rotational partition function
- ③ Vibrational partition function
- ④ Electronic partition function

Suppose the various mole of system posses types of energy like translational, vibrational, rotational, electronics, so on

Total energy E is given by,

$$E = E_r + E_t + E_v + E_e + E_0 \quad \text{--- (1)}$$

Where,

E_0 = zero point energy

Also the value of statistical weight factor g_i , is

$$g_i = g_t \times g_r \times g_v \times g_e \times g_0$$

$$Q = \sum g_i e^{-E_i/KT} \times \sum g_r e^{-E_r/KT} \times \sum g_v e^{-E_v/KT} \times \sum g_e e^{E_e/KT}$$

$$Q = Q_t \times Q_r \times Q_v \times Q_e \times Q_0 \quad \text{--- (2)}$$

From this it follows that, the net partition funⁿ is equal to be the product of the separate partition funⁿ in respect of different types of energy independently associated with the molecules.

① Translational partition function

The partition function Q_t for a translational motion in one direction is given by.

$$Q_t(x) = \sum g_t \cdot e^{-E_t/KT} \quad \text{--- (1)}$$

Where,

E_t = translational energy of a molecule in x direction

K = Boltzmann constant

As the statistical weight of each level is unity

$$Q_t(x) = \sum_{g_t=1} e^{-E_t/KT} \quad \text{--- (2)}$$

We have translational energy given as

$$E_t = \frac{n^2 h^2}{8ma^2} \quad \text{--- (3)}$$

using value of E_t in eqⁿ (2) we get

$$Q_t(x) = \sum e^{-n^2 h^2 / 8ma^2 KT}$$

The energy level are so closely spaced that the variation of energy may be take to be continuous & summation is replaced by integration

$$Q_t(x) = \int_0^{\infty} e^{-n^2 h^2 / 8ma^2 KT} dn$$

but

$$a = \frac{h^2}{8ma^2 KT}$$

We have

$$Q_t(x) = \int_0^{\infty} e^{-n^2 a} dn$$

$$Q_t(x) = \frac{1}{2} \sqrt{\pi/a}$$

$$\text{but } a = \frac{h^2}{8ma^2 KT}$$

$$Q_t(x) = \frac{1}{2} \sqrt{\frac{\pi \times 8ma^2 KT}{h^2}}$$

$$Q_t(x) = \frac{(2\pi mKT)^{1/2}}{h} a$$

This is translational partition function for a molecules in three directions x, y, z at right angles to

each other is given by

$$Q_t = Q_t(x) \times Q_t(y) \times Q_t(z)$$

$$Q_t = \frac{a(2\pi mKT)^{1/2}}{h} dx \times \frac{a(2\pi mKT)^{1/2}}{h} dy \times \frac{a(2\pi mKT)^{1/2}}{h} dz$$

$$Q_t = \frac{(2\pi mKT)^{3/2}}{h^3} V$$

Where,

V = volume accessible to a molecule

② Rotational partition function

The partition function for rotational energy of a diatomic molecule is given by

$$Q_r = \sum g_r e^{-E_r/KT} \quad \dots (1)$$

From quantum mechanical principle, the rotational energy (E_r) for diatomic molecule in J^{th} state is given by

$$E_r = \frac{J(J+1) h^2}{8\pi^2 I} \quad \dots (2)$$

Where, I = moment of inertia

J = Rotational quantum no. $J = 0, 1, 2, \dots$ &

As we know that the rotational energy at the J^{th} level is degenerated in $(2J+1)$ ways.

The value of statistical weight factor is given by

$$g_r = (2J+1) \quad \dots (3)$$

From eqⁿ (1), (2), & (3) we get

$$Q_r = \sum (2J+1) e^{-J(J+1)h^2/8\pi^2 IKT} \quad \dots (4)$$

As the levels are closely packed hence the summation is replaced by integration

$$Q_r = \sum_{J=0}^{\infty} (2J+1) e^{-J(J+1)h^2/8\pi^2IKT} \dots \text{--- (5)}$$

but

$$\beta = \frac{h^2}{8\pi^2IKT}$$

$$Q_r = \sum_{J=0}^{\infty} (2J+1) e^{-J(J+1)\beta} dJ \dots \text{--- (6)}$$

Again,

Put $x = J(J+1)$ which on diff gives
 $dx = (2J+1) dJ$

$$Q_r = \int_0^{\infty} e^{-\beta x} dx \dots \text{--- (7)}$$

$$Q_r = \frac{1}{\beta} \dots \text{--- (8)}$$

We know value of β , put in eqⁿ (8) we get

$$Q_r = \frac{8\pi^2IKT}{h^2}$$

This is only true for heteronuclear molecule
 No. HCl, etc

But in the case of homonuclear molecules
 like H₂, N₂, etc

Only half of rotational term will be present

$$Q_r (\text{ortho}) = \frac{8\pi^2IKT}{2h^2}$$

& $Q_r (\text{para}) = \frac{8\pi^2IKT}{2h^2}$

In order to overcome complications, a symmetry
 no. σ is introduced

$$Q_r = \frac{8\pi^2IKT}{\sigma h^2}$$

The value of σ is for symmetrical diatomic is two
 & is unity for unsymmetrical molecule

The rotational partition function for a polyatomic molecule is

$$Q_r = \frac{1}{\sigma} \left[\frac{8\pi^2 (I_{aA} \times I_{bB} \times \dots)^{1/n}}{h^2} kT \right]^{n/2}$$

Where,

I_{aA}, I_{bB}, I_{cC} are the moment of inertia of various atoms of the molecules and σ is the symmetric number.

③ Vibrational partition function

The partition function for vibrational energy of a diatomic molecule is given by

$$Q_v = \sum g_v \cdot e^{-E_v/kT} \dots \text{--- (1)}$$

As the statistical weight factor of each vibrational level is unity ($\therefore g_v = 1$)

$$Q_v = \sum e^{-E_v/kT} \dots \text{--- (2)}$$

According to wave mechanics, The vibrational energy of a harmonic oscillator is

$$E_v = \left(v + \frac{1}{2} \right) h\nu \dots \text{--- (3)}$$

Where, ν is the vibrational quantum no. & its value is 0, 1, 2, 3, ...

& ν is classical frequency & is given by

$$\nu = \frac{1}{2\pi} \sqrt{\frac{F}{\mu}}$$

Where, F = Force constant
 μ = reduced mass

The vibrational energy in lower level can be calculated by putting value $v=0$ in eqⁿ (3)

The zero point energy can be taken as

$$E_0 = \frac{1}{2} h\nu \quad \dots (4)$$

Thus,

the vibrational energy E_v corresponding lowest energy state is given by

$$E_v - E_0 = E_v = (v + \frac{1}{2}) h\nu - \frac{1}{2} h\nu$$

$$E_v = v h\nu + \frac{1}{2} h\nu - \frac{1}{2} h\nu$$

$$E_v = v h\nu \quad \dots (5)$$

but,

$$\nu = c/\lambda = c\omega \quad (\because 1/\lambda = \omega)$$

hence, the above eqⁿ becomes

$$E_v = v h c \omega \quad \dots (6)$$

where

c = velocity of light

ω = equilibrium frequency

From eqⁿ (2) & (6)

$$Q_v = \sum_{v=0}^{\infty} e^{-v h c \omega / K T}$$

$$Q_v = \sum_{v=0}^{\infty} e^{-v x} \quad \dots (x = h c \omega / K T) \quad \dots (7)$$

$$Q_v = 1 + e^{-x} + e^{-2x} + e^{-3x} + \dots \quad \dots (8)$$

$$Q_v = (1 - e^{-x})^{-1}$$

$$Q_v = \frac{1}{1 - e^{-x}}$$

$$Q_v = \frac{1}{1 - e^{-h c \omega / K T}} \quad \dots (9)$$

$$Q_v = \frac{1}{(1 - e^{-Q_v / T})} \quad \dots (10)$$

Where, Q_v = characteristic vibrational dimension

chlorine atom is the ground state

i.e. for $J = 3/2$
for $J = 1/2$

therefore electronic partition function for atomic chlorine at ordinary temp is

$$Q_e = (2 \times 3/2 + 1) e^{-E_0/KT} + (2 \times 1/2 + 1) e^{-E_1/KT}$$

$$Q_e = 4 + 2 e^{-E_1/KT}$$

where

E_1 = electronic level of upper level.

* Relationship between partition function & thermodynamic properties -

a) Internal energy

The internal energy of a molecular system is given by

$$E = n_0 E_0 + n_1 E_1 + n_2 E_2 + \dots + n_i E_i \quad \text{--- (1)}$$

where,

$n_0, n_1, n_2, \dots, n_i$ are no. of molecules in system and the $E_0, E_1, E_2, \dots, E_i$ are energies

We have

$$E = \sum n_i E_i \quad \text{--- (2)}$$

here $n_i = \frac{N}{Q} g_i e^{-E_i/KT}$ --- (2)

eqn (2) becomes,

$$E = \frac{N}{Q} \sum g_i E_i e^{-E_i/KT} \quad \text{--- (3)}$$

but,

$$Q = \sum g_i e^{-E_i/KT} \quad \text{--- (4)}$$

$$Q = g_0 e^{-E_0/KT} + g_1 e^{-E_1/KT} + g_2 e^{-E_2/KT} + \dots + g_i e^{-E_i/KT} \quad \text{--- (5)}$$

diff eqⁿ (1) w.r.t T at constant volume

$$\left(\frac{dQ}{dT}\right)_V = \left(\frac{E_i}{RT^2}\right) \left[\sum g_i e^{E_i/RT}\right] \quad (2)$$

$$\sum g_i e^{E_i/RT} = \frac{KT^2}{E_i} \left(\frac{dQ}{dT}\right)_V \quad (7)$$

From eqⁿ (3) & (4)

$$E = \frac{N_A k_B}{\Phi} \left(\frac{dQ}{dT}\right)_V$$

$$E = RT^2 \left(\frac{1}{\Phi} \frac{dQ}{dT}\right)_V$$

$$E = RT^2 \left(\frac{d \ln Q}{dT}\right)_V \quad (3)$$

This equation gives the internal energy in terms of partition function

b) Heat capacity -

We have

$$E = RT^2 \left(\frac{d \ln Q}{dT}\right)_V \quad (1)$$

diff eqⁿ (1) w.r.t. temp at constant volume

$$\left(\frac{dE}{dT}\right)_V = \frac{d}{dT} \left[RT^2 \left(\frac{d \ln Q}{dT}\right)_V \right]$$

$$= RT^2 \left(\frac{d^2 \ln Q}{dT^2}\right)_V + \left(\frac{d \ln Q}{dT}\right)_V 2RT$$

$$= RT^2 \left(\frac{d^2 \ln Q}{dT^2}\right)_V + 2RT \left(\frac{d \ln Q}{dT}\right)_V$$

but $\left[\left(\frac{dE}{dT}\right)_V = C_V\right]$

$$C_V = RT^2 \left(\frac{d^2 \ln Q}{dT^2}\right)_V + 2RT \left(\frac{d \ln Q}{dT}\right)_V \quad (2)$$

$$C_p - C_v = R$$

$$C_p = R + C_v$$

$$C_p = RT^2 \left(\frac{d^2 \ln \Phi}{dT^2} \right) + 2RT \left(\frac{d \ln \Phi}{dT} \right) + R$$

gas. eqn ② gives molar heat capacity of an ideal gas.

* Entropy and partition function

① For distinguishable particles

statistical probability is

$$W = \frac{N!}{\sum n_i!} \sum g_i^{n_i} \quad \text{--- (1)}$$

taking logarithm

$$\ln W = \ln N! - \sum \ln n_i! + \sum n_i \ln g_i \quad \text{--- (2)}$$

using Stirling approximation

$$\ln W = N \ln N - N - \sum n_i \ln n_i + \sum n_i + \sum n_i \ln g_i$$

$$\ln W = N \ln N - \sum n_i \ln n_i + \sum n_i \ln g_i \quad \text{--- (3)}$$

We have,

$$n_i = \frac{N}{\Omega} g_i e^{-E_i/KT} \quad \text{--- (4)}$$

taking log

$$\ln n_i = \ln \frac{N}{\Omega} + \ln g_i - \frac{E_i}{KT} \quad \text{--- (5)}$$

We get multiply eqn ⑤ by $\sum n_i$ & using eqn ⑤ in eqn ③

$$\ln W = N \ln N - \sum n_i \ln \frac{N}{\Omega} - \sum n_i \ln g_i + \sum \frac{n_i E_i}{KT} + \sum n_i \ln g_i$$

$$\ln W = N \ln N - \sum n_i \ln N + \sum n_i \ln \Omega + \sum \frac{n_i E_i}{KT} + \sum n_i \ln g_i \quad \text{--- (6)}$$

Here, $\sum n_i = N$ and $E = \sum E_i n_i$

$$\ln W = N \ln Q + \frac{E}{kT} \quad \text{--- (7)}$$

We know that entropy is given by

$$S = k \ln W \quad \text{--- (8)}$$

From eqⁿ (7) and (8)

$$S = Nk \ln Q + \frac{EK}{TK}$$

$$S = kN \ln Q + \frac{E}{T}$$

$$S = R \ln Q + \frac{RT^2}{T} \left(\frac{d \ln Q}{dT} \right)_V$$

$$S = R \ln Q + RT \left(\frac{d \ln Q}{dT} \right)_V$$

② For indistinguishable particles

$$W = \frac{1}{N!} \left[\sum_i g_i n_i \right] \quad \text{--- (1)}$$

Taking log on both sides, we get

$$\ln W = \ln \left(\frac{1}{N!} \right) + \ln \left[\sum_i g_i n_i \right]$$

$$\ln W = \ln N! - \sum_i \ln n_i! + \sum_i n_i \ln g_i + (-\ln N!)$$

(A) *यह एक संयोजन है* $\ln N! \approx N \ln N$

According to Stirling approximation

$$\ln N! \approx N \ln N$$

$$\sum_i \ln n_i! \approx \sum_i n_i \ln n_i - \sum_i n_i$$

$$\ln W = N \ln N - N - \sum_i n_i \ln n_i + \sum_i n_i + \sum_i n_i \ln g_i - N \ln N + N$$

$$S = -N \ln \left(\frac{N}{Q} g_i e^{-\epsilon_i / kT} \right) + N + N \ln g_i$$

$$= N \ln Q + \frac{\sum_i n_i \epsilon_i}{kT} - N \ln N + N$$

$$\ln W = N \ln \Omega + \frac{E}{kT} = N \ln N + N$$

but $S = k \ln W$

$$= k (N \ln \Omega + \frac{E}{kT} = N \ln N + N)$$

$$= kN \ln \Omega + \frac{KE}{kT} - kN \ln N + Nk$$

$$= R \ln \Omega + \frac{E}{T} - R \ln N + R$$

$$(\text{Calc}) = R \ln \frac{\Omega}{N} + \frac{RT^2}{T} \left(\frac{d \ln \Omega}{dT} \right)_V + \frac{R}{T}$$

$$= R \ln \frac{\Omega}{N} + RT \left(\frac{d \ln \Omega}{dT} \right)_V + R$$

$$= R \ln \frac{\Omega}{N} + R + RT \left(\frac{d \ln \Omega}{dT} \right)_V$$

$$S = R \left(\ln \frac{\Omega}{N} + 1 \right) + RT \left(\frac{d \ln \Omega}{dT} \right)_V$$

This is equation for entropy for indistinguishable particles.

* Partition function and Work function

① Helmholtz free energy (A)

We know,

$$A = E - TS$$

$$A = RT^2 \left(\frac{d \ln \Omega}{dT} \right)_V - RT \ln \Omega - RT^2 \left(\frac{d \ln \Omega}{dT} \right)_V$$

$$A = -RT \ln \Omega \Rightarrow$$

For distinguishable particle

$$A = RT^2 \left(\frac{d \ln \Omega}{dT} \right)_V - RT \ln \frac{\Omega}{N} - RT^2 \left(\frac{d \ln \Omega}{dT} \right)_V$$

$$A = N - RT \ln \frac{\Omega}{N} - RT$$

$$A = -RT \left(\ln \frac{\Omega}{N} + 1 \right)$$

\Rightarrow For indistinguishable particle

② Gibbs free energy (G)

$$G = H - TS$$

but

$$H = E + PV$$

$$G = E + PV - TS$$

$$G = E - TS + PV$$

$$G = A + PV \quad [\because A = E - TS]$$

For distinguishable particles

$$G = -RT \ln \Phi + RT \quad [\because PV = RT]$$

$$G = RT (1 - \ln \Phi)$$

For indistinguishable particles:

$$G = -RT \ln \Phi - RT + RT$$

$$G = -RT \ln \frac{\Phi}{N}$$

③ Partition function and pressure

$$ds = \frac{dq_{rev}}{T}$$

$$Tds = dq_{rev} = dE + PdV$$

$$[Tds = dE + PdV]$$

$$A = E - TS$$

diff this eqⁿ

$$dA = dE - Tds - SdT$$

$$dA = dE - dE - PdV - SdT$$

$$dA = -PdV - SdT$$

At constant temp, diff w.r.t V

$$\left(\frac{dA}{dV} \right)_T = -P \quad \text{--- (1)}$$

$$P = - \left(\frac{dA}{dV} \right)_T$$

We have

$$A = -RT \ln Q$$

diff this eqn w.r.t. V at constant T

$$\left(\frac{dA}{dV} \right)_T = -RT \left(\frac{d \ln Q}{dV} \right)_T \quad \text{--- (2)}$$

We have

$$P = - \left(\frac{dA}{dV} \right)_T$$

From eqn (1) & (2)

$$-P = -RT \left(\frac{d \ln Q}{dV} \right)_T$$

$$P = RT \left(\frac{d \ln Q}{dV} \right)_T$$

Application of monatomic

* Sackur Tetraode equation for monatomic gas

The molar entropy of an ideal monatomic gas is given by

$$S = R \ln Q + RT \left(\frac{d \ln Q}{dT} \right)_V + R \quad \text{--- (1)}$$

$$S = R \left[\ln Q + T \left(\frac{d \ln Q}{dT} \right)_V + 1 \right] \quad \text{--- (2)}$$

We have translational contribution to entropy is

$$Q_T = \left[\left(\frac{2\pi m k T}{h^3} \right)^{3/2} \times V \right] \quad \text{--- (3)}$$

Taking log

$$\ln Q_T = \frac{3}{2} \ln T + \ln \left(\frac{2\pi m k}{h^3} \right)^{3/2} \times V \quad \text{--- (4)}$$

diff this eqn w.r.t. temp at constant volume

$$\left[\frac{d \ln Q_T}{dT} \right]_V = \frac{3}{2T} + 0 \quad \text{--- (5)}$$

Use this in eqn (2) we get

$$S = R \left[\ln \frac{Q_L}{N} + T \frac{3}{2T} + 1 \right]$$

$$S = R \left[\ln \frac{Q_L}{N} + \frac{5}{2} \right] \quad \dots \textcircled{2}$$

$$S = R \left[\ln \left(\frac{2\pi m k T}{N h^3} \right)^{3/2} \times v + \frac{5}{2} \right] \quad \dots \textcircled{7}$$

$$S = R \left[\ln \left(\frac{2\pi m k T}{N h^3 P} \right)^{3/2} R T + \frac{5}{2} \right] \quad \dots \textcircled{8}$$

$PV = RT$

eqn (7) & (8) are the alternative forms of Sack Tetrode eqn this eqn (8) is simplified as

$$S = R \left\{ \frac{3}{2} \ln m + \frac{5}{2} \ln R - \ln P + \ln R + \frac{2\pi K}{h^2} \right\}^{3/2} + \frac{5}{2}$$

$$S = \frac{3}{2} R \ln m + \frac{5}{2} R \ln T + R \ln R - R \ln P - R \ln N + \frac{5}{2} R + R \ln (2\pi K h^3)^{3/2}$$

$$S = \frac{3}{2} R \ln m + \frac{5}{2} R \ln T - R \log P + C_1 \quad \dots \textcircled{9}$$

$$\left[C_1 = R \ln R - R \ln N + \frac{5}{2} R + R \ln \left(\frac{2\pi K}{h^3} \right)^{3/2} \right]$$

at 1 atm pressure $\therefore R \ln P = 0$

The value of C_1 can be calculated by putting the values of R, N, K & h & its value is -0.5055 eqn (9) becomes

$$S = R \left[\frac{3}{2} \log m + \frac{5}{2} \log T - \log P - 0.5055 \right]$$

* Equilibrium constant



$$K = \frac{Q_C \cdot Q_D}{Q_A \cdot Q_B}$$

(m = molality)

$$a = \gamma m$$

$$\mu_A = \mu_A^0 + RT \ln a_A$$

$$\mu_B = \mu_B^0 + RT \ln a_B$$

$$\mu_C = \mu_C^0 + RT \ln a_C$$

$$\mu_D = \mu_D^0 + RT \ln a_D$$

Now,

$$(\mu_C + \mu_D) - (\mu_A + \mu_B) = (\mu_C^0 + RT \ln a_C + \mu_D^0 + RT \ln a_D) - (\mu_A^0 + RT \ln a_A + \mu_B^0 + RT \ln a_B)$$

$$= \mu_C^0 + \mu_D^0 - \mu_A^0 - \mu_B^0 + RT \ln a_C + RT \ln a_D - RT \ln a_A - RT \ln a_B$$

$$\Delta G = (\mu_C^0 + \mu_D^0) - (\mu_A^0 + \mu_B^0) + RT \left(\ln \frac{a_C \cdot a_D}{a_A \cdot a_B} \right)$$

$$\text{But, } \Delta G = \Delta G^0 + RT \ln \frac{a_C \cdot a_D}{a_A \cdot a_B}$$

Under equilibrium condition $\Delta G = 0$

$$0 = \Delta G^0 + RT \ln \frac{a_C \cdot a_D}{a_A \cdot a_B}$$

$$\Delta G^0 = -RT \ln \frac{a_C \cdot a_D}{a_A \cdot a_B}$$

$$\Delta G^0 = -RT \ln K$$

but we have

$$\Delta G = -RT \ln \frac{Q}{N} \quad (\text{For liq \& gases})$$

$$-RT \ln \frac{Q}{N} = -RT \ln K$$

$$\frac{Q}{N} = K$$

$Q_A \& Q_B \Rightarrow$ Partition function for reactant
 $Q_C \& Q_D \Rightarrow$ Partition function for product.