# Statistical Thermodynamics

⇒ Thermodynamic $f^n$ can derivied without knowing the composition of the system irrespective of atoms/ and molecules.

⇒ It is bridge b/w molecular properties of individual particles and thermodynamics properties of a system as a whole.

⇒

## Macrostate :

A macrostate is defined as a state of the system where the distribution of particles over the energy level is specified.

The macrostate includes what are the different energy levels and the number of particles having particular energies. It contains many microstates

## Microstate (possible configuration in various e level/macrostate)

A microstate is defined as a state of the system where all the parameters of the constitutents (particles) are specified.

## Most probable microstate

It is defined as the state which contain larger no of microstate.

## Thermodynamic probability

The no of microstate corresponding to any macro state is called thermodynamic probability (W)

$$W = \frac{N!}{N_1!\,N_2!\cdots N_i!} = \frac{N!}{\Pi_i N_i!}$$

N = total no of mol. in system

$N_i$ = no. of molecules distributed in diff. energy levels.

⇒ ~~Lot~~ tea

S.N A system has four distinguishable particles distributed among two compartment in all possible ways calculate total number of macrostate and microstate.

Ans Let there be four particles p, q, r and s distributed in two different compartments x and y

The distribution of particles are as follows

| | | | | | |
|---|---|---|---|---|---|
| x | 4 | 3 | 2 | 1 | 0 |
| y | 0 | 1 | 2 | 3 | 4 |
| | I | II | III | IV | V |

no of macrostate = 05

microstate in macrostate - I

$$W_1 = \frac{N!}{\Pi_i N_i} = \frac{4!}{4!\,0!} = 1$$

| x | pqrs |
|---|---|
| y | — |

For macrostate - II

$$W_2 = \frac{4!}{3!\,1!} = \frac{4\times3\times2\times1}{3\times2\times1\times1} = 4$$

| x | pqr | pqs | prs | qrs |
|---|---|---|---|---|
| y | s | r | q | p |

For macrostate - III

$$W_3 = \frac{4!}{2!\,2!} = 6$$

| x | pq | pr | ps | qr | qs | rs |
|---|---|---|---|---|---|---|
| y | rs | qs | qr | ps | pr | pq |

For macrostate - IV

$$W_4 = \frac{4!}{1!\,3!} = 4$$

| x | Reverse of II |
|---|---|
| y | |

For macrostate - V

$$W_5 = \frac{4!}{0!\,4!} = 1$$

| x | Reverse of I |
|---|---|
| y | |

Total no. of microstate, $W = W_1 + W_2 + W_3 + W_4 + W_5 = 16$

Most probable macrostate $= \underline{W_3}$ = macrostate - III

⇒ Total number of ways putting N distinguishable object into $l$ distinguishable location without no restriction

$$W = l^N$$

⇒ For N indistinguishable object into $l$ distinguishable location

$$W = \frac{(N+l-1)!}{N!\,(l-1)!}$$

So for the previous system, $W = 2^4 = 16$

If the four particle are indistinguishable, then p, q, r and s all are same and say denoted as A

$$W = \frac{(4+2-1)!}{4!\,(2-1)!}$$

| | | | | | |
|---|---|---|---|---|---|
| x | AAAA | - | AAA | A | AA |
| y | - | AAAA | A | AAA | AA |

$$= \frac{5!}{4!\,1!} = 5$$

Q) Calculate the weight of distribution for
i) two distinguishable object in three boxes
ii) " indistinguishable " " " "

Ans i) $W_{dis} = l^N = 3^2 = 9$

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| x | ab | - | - | a | a | - | b | b | - |
| y | - | ab | - | b | - | a | a | - | b |
| z | - | - | ab | - | b | b | - | a | a |

ii) $W_{indis} = \frac{(N+l-1)!}{N!\,(l-1)!} = \frac{(2+3-1)!}{2!\,(3-1)!}$

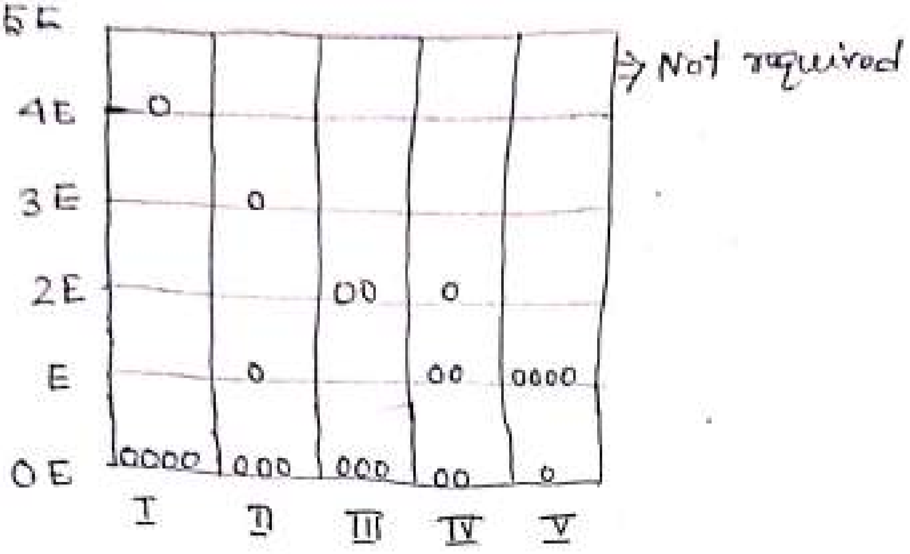
$= \frac{4!}{2!\,2!} = 6$

| | | | | | | |
|---|---|---|---|---|---|---|
| x | aa | - | - | a | a | - |
| y | - | aa | - | a | - | a |
| z | - | - | aa | - | a | a |

N.B. W = Thermodynamic probabilities
= no. of microstates (total)
= no. of ways of distribution
= The weight of distribution

Q// Calculate the no. of macrostate and total no. of microstate of 5 distinguishable particle sharing an energy 4E.

Ans



Five macrostate are possible

For I,

$$W_1 = \frac{5!}{4!0!0!0!1!} = 5$$

$$W_2 = \frac{5!}{3!1!0!1!0!} = \frac{3!\times4\times5}{3!} = 20$$

$$W_3 = \frac{5!}{3!0!2!0!0!} = \frac{3!\times4\times5}{3!\times2} = 10$$

$$W_4 = \frac{5!}{2!2!\times1!\times0!0!} = \frac{2!\times3\times4\times5}{2!\times2} = 30$$

$$W_5 = \frac{5!}{1!4!0!0!0!} = \frac{4!\times5}{4!} = 5$$

Total no. of microstate = $\Sigma W_i = 70$

$$W_{total} = \frac{(N+E-1)!}{(N-1)!E!}$$

N = no. of constitutents

E = quanta of energy in maxlevel

= total energy of system

$$= \frac{(5+4-1)!}{(5-1)!4!} = \frac{8!}{4!4!} = \frac{4!\times5\times6\times7\times8}{4!\times4\times3\times2} = 70$$

Most probable distribution = macrostate IV

Mathematical probability $p = \frac{W_i}{\sum W_i}$

$$\therefore p_1 = \frac{5}{70},\ P_2 = \frac{20}{70},\ P_3 = \frac{10}{70},\ P_4 = \frac{30}{70},\ P_5 = \frac{5}{70}$$

$$= \frac{1}{14} \qquad = \frac{2}{7} \qquad = \frac{1}{7} \qquad = \frac{3}{7} \qquad = \frac{1}{14}$$

### Boltzmann distribution law

for degenerate state

$$\frac{n_i}{n} = \frac{g_i e^{-\beta \epsilon_i}}{\sum_i g_i e^{-\beta \epsilon_i}} \ ; \ \beta = \frac{1}{k_B T}$$

$n_i$ = no of molecules occupy in the ith energy level having energy $\epsilon_i$.

$n$ = total no of molecules of the system

$g_i$ = statistical weight factor/ degree of degeneracy

$k_B$ = Boltzmann constant

Similarly for non-degenerate state, $g_i = 1$

$$\frac{n_i}{n} = \frac{e^{-\epsilon_i / k_B T}}{\sum_i e^{-\epsilon_i / k_B T}}$$

Partition function $f = \sum e^{-\beta \epsilon_i}$

Q) What will be distribution when (i) $T \to 0$ and (ii) $T \to \infty$

Ans
(i) When $T \to 0$, $e^{-\epsilon_i/k_B T} \sim 0$

$$\therefore \frac{n_i}{n} = 0 \Rightarrow n_i = 0$$

i.e. all the molecules will be in the ground state

(ii) When $T \to \infty$, $e^{-\epsilon_i/k_B T} \simeq 1$

$$\frac{n_{i+1}}{n_i} = \frac{e^{-\epsilon_{i+1}/k_B T}}{e^{-\epsilon_i/k_B T}} = e^{-\Delta\epsilon/k_B T} \sim 1$$

$$\Rightarrow n_{i+1} = n_i$$

i.e. all the molecules are equal probable

Q) Show that $n_i > n_{i+1}$

Ans

$$\frac{n_{i+1}}{n_i} = \frac{e^{-\epsilon_{i+1}/k_B T}}{e^{-\epsilon_i/k_B T}} \quad \left[\begin{array}{l} n_{i+1} = n_0 e^{-\epsilon_{i+1}/k_B T} \\ n_i = n_0 e^{-\epsilon_i/k_B T} \end{array}\right.$$

$$= e^{-\frac{1}{k_B T}(\epsilon_{i+1} - \epsilon_i)} = e^{-\Delta\epsilon/k_B T}$$

$$\because \epsilon_{i+1} > \epsilon_i, \text{ so, } e^{-\Delta\epsilon/k_B T} < 1$$

$$\therefore \frac{n_{i+1}}{n_i} < 1 \Rightarrow n_i > n_{i+1}$$

Q1) Show that for a Boltzmann distribution (non-degenerate) the no. of molecules in three successive levels will be in geometric progression if the values of energy in the three levels are in arithmetic progression.

Ans Let $n_1$, $n_2$ and $n_3$ are the no. of molecules occupy in three successive energy levels $\epsilon_1$, $\epsilon_2$ and $\epsilon_3$ respectively.

As energy levels are in arithmetic progression

so, $\epsilon_1 + \epsilon_3 = 2\epsilon_2$

Now, for non-degenerate state

$$\frac{n_i}{n} = \frac{e^{-\epsilon_i/k_BT}}{\sum_i e^{-\epsilon_i/k_BT}}$$

$$n_1 = \frac{n\, e^{-\epsilon_1/k_BT}}{\sum_i e^{-\epsilon_i/k_BT}}, \quad n_2 = \frac{n\, e^{-\epsilon_2/k_BT}}{\sum_i e^{-\epsilon_i/k_BT}}$$

$$n_3 = \frac{n\, e^{-\epsilon_3/k_BT}}{\sum_i e^{-\epsilon_i/k_BT}}$$

Now

$$n_1 \times n_3 = \frac{n^2 e^{-\epsilon_1/k_BT} \cdot e^{-\epsilon_3/k_BT}}{\left(\sum_i e^{-\epsilon_i/k_BT}\right)^2}$$

$$= \frac{n^2 e^{-(\epsilon_1+\epsilon_3)/k_BT}}{\left(\sum_i e^{-\epsilon_i/k_BT}\right)^2}$$

$$= \frac{n^2 e^{-2\epsilon_2/k_BT}}{\left(\sum_i e^{-\epsilon_i/k_BT}\right)^2} = \left(\frac{n e^{-\epsilon_2/k_BT}}{\sum_i e^{-\epsilon_i/k_BT}}\right)^2 = n_2^2$$

$\therefore$ $n_1 \times n_2 = n_2^2$ $\Rightarrow$ geometric progression

## Derivation of relation b/w $S$ and $W$

Since the entropy ($S$) is a measure of thermodynamic randomness of molecular system, and the larger is randomness, larger is the number of configuration.

Therefore, we consider that entropy is a universal fn of configuration (probability). Thus we can write

$$S = f(W) \longrightarrow (i)$$

Suppose $S_1$ and $S_2$ are the entropies, and $W_1$ and $W_2$ are the respective thermodynamic probabilities of two independent system. Then

$$S_1 = f(W_1) \longrightarrow (ii) \qquad S_2 = f(W_2) \longrightarrow (iii)$$

If two systems are combined, then

$$S = S_1 + S_2 \longrightarrow (iv)$$

$$W = W_1 W_2 \longrightarrow (v)$$

$$\therefore S = f(W_1) + f(W_2) \quad \{\text{from (ii), (iii), (iv)}\}$$

$$\Rightarrow f(W) = f(W_1) + f(W_2) \quad \{\text{from (i)}\} \longrightarrow (vi)$$

$$\Rightarrow \frac{df(W)}{dW}\frac{dW}{dW_1} = \frac{df(W_1)}{dW_1} \longrightarrow (vii) \quad \left\{\begin{array}{l}\text{differentiating (vi) w.r.t. } W_1 \\ \text{Keeping } W_2 \text{ const}\end{array}\right.$$

from (v) $\frac{dW}{dW_1} = W_2 \longrightarrow (viii)$

putting (viii) in (vi) we get

$$\frac{df(W)}{dW} \cdot W_2 = \frac{df(W_1)}{dW_1}$$

$$\Rightarrow W_1 W_2 \frac{df(W)}{dW} = W_1 \frac{df(W_1)}{dW_1} \quad \left\{\begin{array}{l}\text{multiplying both} \\ \text{side by } W_1\end{array}\right.$$

$$\Rightarrow W \frac{df(W)}{dW} = W_1 \frac{df(W)}{dW_1} \rightarrow (ix)$$ {putting using eqn (v)}

Similarly, $$\frac{W\, df(W)}{dW} = W_2 \frac{df(W_2)}{dW_2} \rightarrow (x)$$

L.H.S. of eqn (ix) and (x) are same

$$\therefore \quad W_1 \frac{df(W)}{dW_1} = W_2 \frac{df(W_2)}{dW_2}$$

$$\Rightarrow W \frac{df(W)}{dW} = \text{constant}$$

$$\Rightarrow W \frac{df(W)}{dW} = k_B = \text{Boltzmann constant}$$

$$\Rightarrow df(W) = k_B \frac{dW}{W}$$

$$\Rightarrow f(W) = k_B \ln W + C$$ {Integrating both sides)

$$\Rightarrow S = k_B \ln W + C$$ ; C = Integration const.

Boltzmann assume, $C = 0$

$$\therefore \quad S = k_B \ln W$$

⇒ When the system is perfectly ordered then $W = 1$ and

$S = k_B \ln W = 0$

For perfect crystal and at $T \rightarrow 0K$, all the molecules are localised in lattice points, then $W = 1$, $S = 0$

This correspons to third law of thermodynamics

Q) What is partition function

**Ans** Partition function represent by 'f'

$$f = \sum_i g_i e^{-\epsilon_i / k_B T} \quad \text{for degeneracy}$$

$$= \sum_i e^{-\epsilon_i / k_B T} \quad \text{" non- "}$$

The different states having same energy are known as degenerate state and the number of different states corresponding to a given energy is the degeneracy of the state.

**N.B.**

When $T \to \infty$

$$f = \sum g_i e^{-\epsilon_i / k_B T} = g_0 + g_1 + g_2 + \cdots = \sum_i g_i$$

$$= x = \text{total no energy level}$$

⇒ Qualitatively, the partition $f^n$ indicate how the particles are distributed among the various energy states. It is measure of available energy-levels.

## Derivation of Boltzmann Distribution law

Consider a system containing n molecules (very large) having a total energy E. Let there be a given distribution such that $n_0$ molecules resides at energy level $\epsilon_0$, $n_1$ in $\epsilon_1$, $n_2$ in $\epsilon_2$ and so on. The allowed energy levels are fixed by quantum mechanical principles.

Therefore

$$n = n_0 + n_1 + n_2 + \cdots = \sum n_i \quad \cdots (1)$$

$$E = n_0 \epsilon_0 + n_1 \epsilon_1 + n_2 \epsilon_2 + \cdots = \sum n_i \epsilon_i \quad \cdots (2)$$

Thermodynamic probability of a given distribution is

$$W = \frac{n!}{\Pi_i n_i!} = \frac{N!}{\Pi_i N_i!} \quad \cdots\cdots (3)$$

$$\Rightarrow \ln W = \ln n! - \cancel{+} \ln(\Pi_i n_i!)$$

$$= \ln n! - \ln(n_0!\, n_1!\, n_2! \cdots)$$

$$= \ln n! - (\ln n_0 + \ln n_1 + \ln n_2 + \cdots)$$

$$= \ln n! - \sum_i \ln n_i! \quad \cdots\cdots (4)$$

According to stirling approximation

$$\ln N! = N \ln N - N \quad [\because n \text{ is very large by assumptions}]$$

$$\therefore \ln W = (n \ln n - n) - \sum_i (n_i \ln n_i \mp n_i)$$

$$= n \ln n - n - \sum_i n_i \ln n_i + \sum n_i$$

$$= n \ln n - n - \sum_i n_i \ln n_i + n \quad [\because \sum n_i = n = \text{total no. molecules}]$$

$$= n \ln n - \sum_i n_i \ln n_i = I_1 + I_2 \quad \cdots (5)$$

Now, Now, $d \ln W = dI_1 + dI_2 \quad \cdots (6)$

$$dI_1 = d(n \ln n) = dn \cdot \ln n + \frac{n}{n} dn$$

$$= 0 + 0 = 0 \quad \left[\because n = \text{const for a system} \atop \therefore dn = 0\right]$$

$$dI_2 = d\left(\sum_i n_i \ln n_i\right)$$

$$= \sum_i dn_i \ln n_i + \sum \frac{n_i}{n_i} dn_i = \sum_i dn_i \ln n_i + \sum_i dn_i$$

$$= \sum_i dn_i \ln n_i \quad \left[n = \sum n_i = \text{const} ; \therefore \sum_i dn_i = 0\right]$$

$$\therefore d \ln W = \sum_i dn_i \ln n_i$$

At equilibrium, the distribution is maximum, i.e $d \ln W = 0$

$$\therefore \sum_i dn_i \ln n_i = 0 \quad \cdots\cdots (6)$$

Now, $\sum dn_i = 0 \quad \cdots (7) \qquad \sum n_i \varepsilon_i = \overset{\text{remain const}}{E} \Rightarrow \sum n_i d\varepsilon_i = 0 \quad \cdots (8)$

Multiplying eqn by arbitory multipliers $\alpha$ and $\beta$ respectively and adding eqn (6) we get

i.e. $\alpha \times \text{eqn}(7) + \beta \times \text{eqn}(8) + \text{eqn}(6) = 0$

$$\Rightarrow \alpha \sum_i dn_i + \beta \sum_i G_i dn_i + \sum_i \ln n_i \, dn_i = 0$$

$$\Rightarrow \left\{ \sum_i (\alpha + \beta G_i + \ln n_i) \right\} dn_i = 0 \quad \text{---- (9)}$$

Sine, $\alpha$ and $\beta$ are independent, the restriction condition may removed, again $dn_i \neq 0$

$$\therefore \alpha + \beta G_i + \ln n_i = 0$$

$$\Rightarrow n_i = e^{-\alpha} . e^{-\beta G_i} \quad \text{--- (10)}$$

eqn (10) is true for ~~all~~ any energy-level as $n_i$ is independ

Again $n = \sum_i n_i = \sum_i e^{-\alpha} . e^{-\beta G_i}$ {from eqn (10)

$$\Rightarrow n = e^{-\alpha} \sum_i e^{-\beta G_i}$$

$$\Rightarrow e^{-\alpha} = \frac{n}{\sum_i e^{-\beta G_i}} \quad \text{--- (11)}$$

from eqn (10) and eqn (11

$$\therefore n_i = \frac{n e^{-\beta G_i}}{\sum_i e^{-\beta G_i}}$$

$$= \frac{n e^{-G/k_BT}}{f} \quad \left[ \begin{array}{l} \beta = \frac{1}{k_BT} ; k_B = \text{Boltzmann const} \\ f = \text{partition } f^n \end{array} \right]$$

Q) Proove that modulus of distribution ($\beta$) is equal to $1/k_BT$

**Ans** Partition function, $f = \sum_i e^{-\beta G_i}$ ---- (1)

Now, $n_i = \frac{n}{f} e^{-\beta G_i}$ ---- (2)

$\therefore \ln n_i = \ln n - \ln f - \beta G_i$ ---- (3)

we Know, $S = k_B \ln W$

$$\Rightarrow \frac{S}{k_B} = \ln W$$

$$= n\ln n - \sum_i n_i \ln n_i$$

$$= n\ln n - \sum_i n_i (\ln n - \ln f - \beta G_i)$$

$$= n\ln n - \ln n \sum_i n_i + \ln f \sum_i n_i + \beta \sum_i n_i G_i$$

$$= n\ln n - n\ln n + n\ln f + \beta E = n\ln f + \beta E$$

$$\Rightarrow S = nk_B \ln f + k_B \beta E \quad \ldots (4)$$

$$\Rightarrow \left(\frac{\partial S}{\partial E}\right)_V = nk_B\left(\frac{\partial f}{\partial E}\right)_V + k_B\beta + k_B E\left(\frac{\partial \beta}{\partial E}\right)_V$$

$$= nk_B\left(\frac{\partial f}{\partial \beta}\right)\left(\frac{\partial \beta}{\partial E}\right)_V + k_B\beta + k_B E\left(\frac{\partial \beta}{\partial E}\right)_V \quad \ldots (5)$$

from eqn ① $\left(\frac{\partial f}{\partial \beta}\right) = -\sum_i G_i e^{-\beta G_i}$

$$= -\sum_i G_i \cdot e \, \frac{n_i f}{n}$$ {putting $e^{-\beta G_i}$ value from eqn ②}

$$\Rightarrow \frac{\partial f}{\partial \beta} = -\frac{Ef}{n} \quad \ldots (6)$$

putting eqn (6) in eqn (5)

$$\left(\frac{\partial S}{\partial E}\right)_V = nk_B \cdot \frac{-Ef}{n}\left(\frac{\partial \beta}{\partial E}\right)_V + k_B\beta + k_B E\left(\frac{\partial \beta}{\partial E}\right)_V$$

$$\Rightarrow \left(\frac{\partial S}{\partial E}\right)_V = k_B\beta \quad \ldots (7)$$

Assuming energy is purely internal energy, $\left(\frac{\partial S}{\partial U}\right)_V = k_B\beta \quad \ldots (8)$

from 2nd law, $dQ = dU + pdV \Rightarrow TdS = dU + pdV$

$$\Rightarrow T\left(\frac{\partial S}{\partial U}\right)_V = 1 + 0 \Rightarrow \left(\frac{\partial S}{\partial U}\right)_V = \frac{1}{T} \quad \ldots (9)$$

∴ Comparing eqn (8) and (9)

$$k_B\beta = \frac{1}{T} \Rightarrow \beta = \frac{1}{k_B T}$$

Q) What is significance of partition function

Ans $f = \sum_i g_i e^{-\beta \epsilon_i} = \sum_i g_i e^{-\epsilon_i/k_BT}$

'f' describes how the total energy of the system is partition among several energy state at temp T

at absolute zero, $f = g_0$

i.e. f becomes equal to degeneracy of ground state, i.e all molecules come down to ground the state

As T increases, f also increases, so at high temp. all the energy states of the system are accessible to a molecule

Therefore it is no. of energy states that are thermally accessible to a molecule at temp. T.

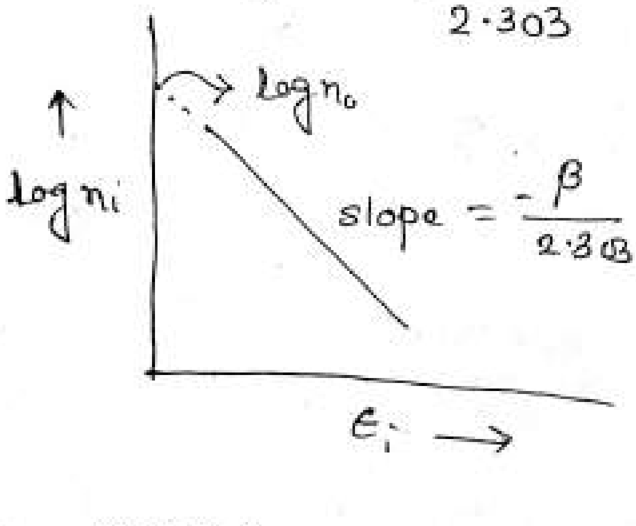
Q) Plot $\log n_i$ vs $\epsilon$ at a particular temp.

Ans $n_i =$ ~~$n_0\beta$~~ $n_0 e^{-\beta\epsilon_i}$

$n_i$ = no. of mol at ith level with energy $\epsilon_i$

$\Rightarrow \log n_i = \log n_0 - \frac{\beta\epsilon_i}{2.303}$

$n_0$ = no. of mol. at g. level



Q) Calculate $\left(\frac{\partial n_i}{\partial \beta}\right)$ and explain its significance

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

$$\Rightarrow \frac{\partial n_i}{\partial \beta} = 0 + e^{\alpha} \cdot e^{-\beta \epsilon_i}(-\epsilon_i)$$

$$= -e^{\alpha} \cdot e^{-\beta \epsilon_i} \cdot \epsilon_i$$

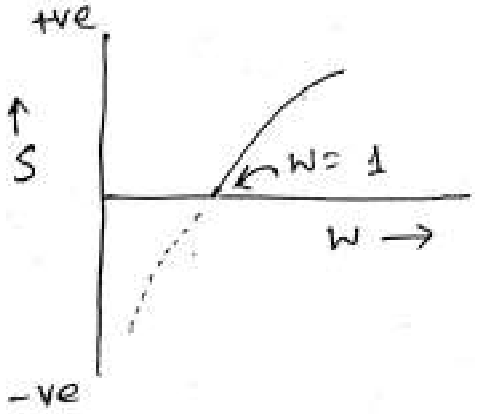
$$= -n_i \epsilon_i$$

$$= -E$$ = - Total energy of the system

Thus magnitude of $\left(\frac{\partial n_i}{\partial \beta}\right)$ is nothing but total energy of the system.

Q// Draw an S vs W graph.

Ans



$S = k_B \ln W$

# Partition function and thermodynamic properties

## Internal energy (U)

$$U = \sum_i n_i \epsilon_i \quad \cdots ①$$

$$n_i = \frac{n}{Q} \sum_i e^{-\beta \epsilon_i} \cdots (2)$$ $Q$ = molecular partition fn

$$\therefore U = \frac{n}{Q} \sum_i \epsilon_i e^{-\beta \epsilon_i} \cdots (3)$$ [combining ① and ②]

Again $$Q = \sum_i e^{-\beta \epsilon_i} = \sum_i e^{-\epsilon_i / k_B T}$$

$$\Rightarrow \left(\frac{\partial Q}{\partial T}\right)_V = \frac{1}{k_B T^2} \cdot \sum_i \epsilon_i e^{-\epsilon_i / k_B T}$$

$$\Rightarrow \sum_i \epsilon_i e^{-\epsilon_i / k_B T} = k_B T^2 \left(\frac{\partial Q}{\partial T}\right)_V \cdots (4)$$

from ③ and ④

$$U = \frac{n}{Q} k_B T^2 \left(\frac{\partial Q}{\partial T}\right)_V = n k_B T^2 \frac{1}{Q} \left(\frac{\partial Q}{\partial T}\right)_V$$

$$\Rightarrow U = n k_B T^2 \left(\frac{\partial \ln Q}{\partial T}\right)_V$$

$$\Rightarrow \langle u \rangle = k_B T^2 \left(\frac{\partial \ln Q}{\partial T}\right)_V$$

## Entropy (S)

We know,

$$S = k_B \ln Q + k_B \beta U$$

$$\Rightarrow S = k_B \ln Q + k_B \cdot \frac{1}{k_B T} U$$

$$= k_B \ln Q + \frac{U}{T}$$

$$= k_B \ln Q + k_B T \left(\frac{\partial \ln Q}{\partial T}\right)_V$$

**Work function (A)**

$$A = U - TS$$
$$= U - T\left(k_B \ln Q - \frac{U}{T}\right)$$
$$= -k_B T \ln Q$$

**Pressure (P)**

$$dA = -PdV - SdT$$

$$\left\{ \begin{aligned} A &= U - TS \Rightarrow dA = dU - TdS - SdT \\ \Rightarrow dA &= dq - dw - TdS - SdT \\ &= TdS - PdV - TdS - SdT \end{aligned} \right.$$

$$\Rightarrow \left(\frac{\partial A}{\partial V}\right)_T = -P$$

$$\therefore P = k_B T \left(\frac{\partial \ln Q}{\partial V}\right)_T$$

**Gibbs free energy (G)**

$$G = H - TS = U + PV - TS = (U - TS) + PV$$
$$\Rightarrow G = A + PV$$
$$= -k_B T \ln Q + \left\{k_B T \left(\frac{\partial \ln Q}{\partial V}\right)_T\right\} V$$
$$= -k_B T \left[\ln Q - \left(\frac{\partial \ln Q}{\partial \ln V}\right)_T\right]$$

**Heat content (H)**

$$H = U + PV$$
$$= k_B T^2 \left(\frac{\partial \ln Q}{\partial T}\right)_V + k_B T V \left(\frac{\partial \ln Q}{\partial V}\right)_T$$
$$= k_B T \left[\left(\frac{\partial \ln Q}{\partial \ln T}\right)_V + \left(\frac{\partial \ln Q}{\partial \ln V}\right)_T\right]$$

**Heat Capacity ($C_V$)**

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V = k_B \left\{\frac{\partial}{\partial T}\left(\frac{T^2 \partial \ln Q}{\partial T}\right)_V\right\}_V$$

$$C_P = \left(\frac{\partial H}{\partial T}\right)_V = k_B \left[\frac{\partial}{\partial T}\left(\frac{T \partial \ln Q}{\partial \ln T}\right)_V + \left(\frac{T \partial \ln Q}{\partial \ln V}\right)_T\right]_V$$

## Molecular Partition function (Q)

$$Q = \sum_{t,r,v,e} g_t g_r g_v g_e e^{-\beta\epsilon} \quad ; \epsilon = \epsilon_t+\epsilon_r+\epsilon_v+\epsilon_e$$

$$= \sum_t g_t e^{-\beta\epsilon_t} \sum_r g_r e^{-\beta\epsilon_r} \sum_v g_v e^{-\beta\epsilon_v} \sum_e g_e e^{-\beta\epsilon_e}$$

$$= q_t q_r q_v q_e$$

Hence Q is pdt of all partition $f^n$

## Translational Partition function ($q_t$)

$$q_t = \sum_t e^{-\beta\epsilon_t} = \sum_{n_x=1}^{\infty} e^{-\beta E_x}$$

$$\epsilon_t = \frac{h^2}{8ml^2}\left(n_x^2+n_y^2+n_z^2\right)$$

$n_x$, $n_y$ and $n_z$ varies b/w 1 to ∞

$$q_t = \sum_{n_x=1}^{\infty}\sum_{n_y=1}^{\infty}\sum_{n_z=1}^{\infty} e^{-\frac{h^2}{8ml^2k_BT}\left(n_x^2+n_y^2+n_z^2\right)}$$

$$= \left\{\sum_{n_x=1}^{\infty} \exp\left(\frac{-n^2h^2}{8ml^2k_BT}\right)\right\}^3$$

$$= \left\{\int_1^{\infty} \exp\left(\frac{-n^2h^2}{8ml^2k_BT}\right)dx\right\}^3 \quad \left[\because \text{they are close to each other}\right.$$

$$= \left\{\int_0^{\infty} \exp\left(\frac{-n^2h^2}{8ml^2k_BT}\right)dn\right\}^3 \quad \Big[$$

$$= \left\{\int_0^{\infty} e^{-ax^2}dx\right\}^3 \quad \left[a = \frac{h^2}{8ml^2k_BT}\right.$$

Applying gamma $f^n$

$$\int_0^\infty e^{-ax^2}dx = \frac{1}{2}\sqrt{\frac{\pi}{a}}$$

$$\left\{ \begin{array}{l} \text{put } x^2 = t \Rightarrow 2x\,dx = dt \\ \Rightarrow dx = \frac{dt}{2x} = \frac{1}{2}t^{-1/2}dt \\ e^{-ax^2}dx = e^{-at}\cdot\frac{1}{2}t^{-1/2}dt \\ = \frac{\Gamma(-1/2+1)}{\frac{1}{2}a^{1/2}} = \frac{1}{2}\sqrt{\frac{\pi}{a}} \end{array} \right.$$

$$\therefore q_t = \left[\frac{1}{2}\sqrt{\frac{\pi\cdot 8m\ell^2 k_BT}{h^2}}\right]^3$$

$$= \left\{\sqrt{2}\,\ell\sqrt{\frac{\pi m k_BT}{h^2}}\right\}^3$$

$$= \left(\frac{2mk_BT}{h^2}\right)^{3/2}\cdot \ell^3 = \left(\frac{2mk_BT}{h^2}\right)^{3/2}\cdot V$$

$$= (\lambda^{-2})^{3/2}\cdot V = \lambda^{-3}\cdot V$$

Total translational partition $f^n$

$$Q_{tr} = \frac{q_t^N}{N!}$$ [distinguishable particles]

## Rotational Partition function ($q_r$)

$$q_r = \sum_{J=0}^{\infty} g_r\, e^{-\beta\epsilon_r}$$

$$= \sum_{J=0}^{\infty}(2J+1)\, e^{-\frac{h^2}{8\pi^2 I k_BT}J(J+1)}$$

$$\left\{ \begin{array}{l} g_r = (2J+1) \\ \epsilon_J = BJ(J+1) \\ = \frac{h^2}{8\pi^2 I}J(J+1) \end{array} \right.$$

Rotation temp. $\theta_R = \frac{h^2}{8\pi^2 I k_B}$

$T \gg \theta_R$ ⇒ classical ⇒ Integration

$T \ll \theta_R$ ⇒ quantum ⇒ Summation

$$\therefore q_r = \int_0^\infty \left\{(2J+1)\exp\cdot\left(-\frac{h^2 J(J+1)}{8\pi^2 I k_BT}\right)\right\}dJ$$

let $J(J+1) = x \Rightarrow (2J+1)\,dJ = dx$ $\left\{ \begin{array}{l} J=0,\ x=0 \\ J=\infty,\ x=\infty \end{array} \right.$

$$\therefore q_r = \int_0^\infty e^{-\frac{\theta_R x}{T}}dx$$

$$\Rightarrow q_r = \left[-\frac{T}{\theta_R} e^{-\frac{\theta_R x}{T}}\right]_0^{\infty}$$

$$= -\frac{T}{\theta_R}\left[e^{-\infty} - e^{0}\right] = \frac{T}{\theta_R}$$

$$\Rightarrow q_r = \frac{8\pi^2 I k_B T}{h^2} \quad [\text{putting } \theta_R]$$

$$= \frac{8\pi^2 I k_B T}{\sigma h^2} \quad \{\sigma = \text{symmetry element}$$

Vibrational Partition function

$$q_v = \sum_{v=0}^{\infty} e^{-\epsilon_v/k_BT}$$

$$\epsilon_v = (v+\tfrac{1}{2})h\omega \qquad \omega = \text{frequency}$$

$$q_v = \sum_{v=0}^{\infty} e^{-(v+\frac{1}{2})\frac{h\omega}{k_BT}}$$

$$= e^{-h\omega/2k_BT} + e^{-\frac{3h\omega}{2k_BT}} + e^{-5h\omega/2k_BT} + \cdots$$

$$= e^{-h\omega/2k_BT}\left[1 + e^{-h\omega/k_BT} + e^{-2h\omega/k_BT} + \cdots\right]$$

$$= x^{-1/2}\left[1 + x + x^2 + \cdots\right] \quad \left\{x = e^{-h\omega/k_BT}\right\}$$

Now $1+x+x^2+\cdots = \frac{1}{1+x}$ [Taylor series]

$$\therefore q_v = \frac{e^{-h\omega/2k_BT}}{1 - e^{-h\omega/k_BT}}$$

$$= \frac{e^{-\theta_v/2T}}{1 - e^{-\theta_v/T}} \quad \left[\theta_v = \frac{h\omega}{k_B} = \text{vib temp.}\right.$$

# Relation b/w Partition function and equilibrium constant

For any rea$^n$ at eq$^m$

$$\sum_i \nu_i \mu_i = 0 \cdots ① \quad \left[\begin{array}{l} \nu_i = \text{coefficient of rea}^n \\ = +ve \Rightarrow \text{pdt} \\ = -ve \Rightarrow \text{reactant} \end{array}\right.$$

Now $A = U - TS = U + G - H$

$$= U + G - U - PV = G - PV$$

$$\Rightarrow dA = dG - PdV - VdP$$

$$= -SdT + VdP + \sum_i \mu_i dn_i - PdV - VdP$$

$$= -SdT - PdV + \sum_i \mu_i dn_i$$

$$\Rightarrow \left(\frac{\partial A}{\partial n_i}\right)_{V,T,n_{i\neq j}} = \mu_i \quad \cdots (2)$$

putting eq$^n$ ② in eq$^n$ (1) we get

$$\sum \nu_i \left(\frac{\partial A}{\partial n_i}\right)_{V,T,n_{i\neq j}} = 0 \quad --- (3)$$

~~Now $A = -k_BT \frac{\partial \ln Q}{\partial n_i}$~~

Now $A = -k_BT \ln Q$

$$\Rightarrow \left(\frac{\partial A}{\partial n_i}\right)_{V,T,n_{i\neq j}} = -k_BT\left(\frac{\partial \ln Q}{\partial n_i}\right)_{V,T,n_{i\neq j}} \quad --- (4)$$

Again $Q = \prod_i \frac{q_i^{n_i}}{n_i!}$

$$\Rightarrow \ln Q = \ln \prod_i \frac{q_i^{n_i}}{n_i!} = \ln\left[\frac{q_1^{n_1}}{n_1!}\cdot\frac{q_2^{n_1}}{n_2!}\cdots\right]$$

$$= \ln\left(\frac{q_1^{n_1}}{n_1!}\right) + \ln\left(\frac{q_2^{n_1}}{n_2!}\right) + \cdots$$

$$= \sum \ln \frac{q_i^{n_i}}{n_i!}$$

$$= \sum n_i \ln q_i - \sum \ln n_i!$$

$$= \sum n_i \ln q_i - \sum n_i \ln n_i - \sum n_i$$ [using stirling approximation ✓

$$\Rightarrow \frac{\partial \ln Q}{\partial n_i} = \ln q_i - \ln N_i - n_i \frac{1}{n_i} + 1$$

$$= \ln q_i - \ln n_i$$

$$\left\{ \frac{d}{dn_i}\left(\sum n_i\right) = \frac{dn_i}{dn_i} + \frac{dn_j}{dn_i} + \frac{dn_k}{dn_i} \ldots = 1 + 0 + 0 + \ldots = 1 \right.$$

$$\Rightarrow \frac{\partial \ln Q}{\partial n_i} = \ln \frac{q_i}{n_i} \quad \ldots\ldots (5)$$

Putting eqn (5) in eqn (4)

$$\frac{\partial A}{\partial n_i} = -k_B T \ln \frac{q_i}{n_i} \quad \ldots\ldots (6)$$

Again putting (6) in (3) we get

$$\sum \nu_i \,(-k_B T) \ln \frac{q_i}{n_i} = 0$$

$$\Rightarrow \sum \ln \left(\frac{q_i}{n_i}\right)^{\nu_i} = 0$$

$$\Rightarrow \ln \prod_i \left(\frac{q_i}{n_i}\right)^{\nu_i} = 0$$

$$\Rightarrow \prod_i \left(\frac{q_i}{n_i}\right)^{\nu_i} = 1$$

$$\left\{ C_i = \frac{n_i}{n_A} \cdot V \right.$$

$$\Rightarrow \prod_i q_i^{\nu_i} = \prod_i n_i^{\nu_i}$$

$$\Rightarrow \prod_i \left(\frac{q_i}{n_A V}\right)^{\nu_i} = \prod_i \left(\frac{n_i}{n_A V}\right)^{\nu_i}$$ [Dividing both sides by $n_A V$

$$\Rightarrow \prod_i \left(\frac{q_i}{n_A V}\right)^{\nu_i} = \prod_i C_i^{\nu_i}$$

R.H.S is nothing but eqm const $K_c$

$$\therefore K_c = \prod_i \left(\frac{q_i}{n_A V}\right)^{\nu_i}$$

## Nernst Heat theorem

A study of the enthalpy changes and entropy changes at very low temp. for some galvanic cell reacⁿ remain revealed an interesting fact. At extremely low temp., $\Delta G$ and $\Delta H$ tends to become equal.

$$\Delta G = \Delta H - T\Delta S$$

$$\Delta G = \Delta H + T\left(\frac{\partial \Delta G}{\partial T}\right)_P$$ [Applying Gibbs-Helmholtz eqⁿ

at $\lim_{T \to 0}$, $T\left(\frac{\partial \Delta G}{\partial T}\right)_P \sim 0$, then $\Delta G = \Delta H$

at 0K $T\left(\frac{\partial \Delta G}{\partial T}\right)_P$ will be zero, wheather $\left(\frac{\partial \Delta G}{\partial T}\right)_P$ is finite or zero

Nernst, made the bold postulate that for a process in a condensed system $\left(\frac{\partial \Delta G}{\partial T}\right)_P$ will be zero in the vicinity of absolute zero (0K)

then $\lim_{T \to 0} \frac{\partial \Delta H}{\partial T} \sim 0$

$$\Delta G = \Delta H + T\frac{\partial \Delta G}{\partial T}$$

$$\Rightarrow \Delta G = \Delta H$$

$$\Rightarrow \frac{\partial \Delta G}{\partial T} = \frac{\partial \Delta H}{\partial T}$$

$$\Rightarrow 0 = \frac{\partial \Delta H}{\partial T}$$

## Variation of $\Delta G$ and $\Delta H$ with T

It is easy to see that if $\Delta G$ increases with temp in a process $\Delta H$ will diminish and vice versa

$$\Delta G = \Delta H + T\left(\frac{\partial \Delta G}{\partial T}\right)_P$$

$$\Rightarrow \frac{\partial \Delta G}{\partial T} = \frac{\partial \Delta H}{\partial T} + T\frac{\partial^2 \Delta G}{\partial T} + \frac{\partial \Delta G}{\partial T}$$

$$\Rightarrow -\frac{\partial \Delta H}{\partial T} = T\frac{\partial^2 \Delta G}{\partial T} \longrightarrow (1)$$

Therefore two terms $\frac{\partial \Delta H}{\partial T}$ and $\frac{\partial^2 \Delta G}{\partial T}$ evidently have opposite signs

Since, by Nernst postulate $\Delta G$ converges to a limiting value at low T, so both 1st and 2nd derivative of $\Delta G$ must have same sign i.e. $\frac{\partial \Delta G}{\partial T}$ & $\frac{\partial^2 \Delta G}{\partial T}$ bear same sign and

Hence from eqⁿ (1) $\frac{\partial \Delta H}{\partial T}$ and $\frac{\partial \Delta G}{\partial T}$ must have opposite sign

Therefore $\Delta G$ would increases with temp. if $\Delta H$ diminishes and vice versa

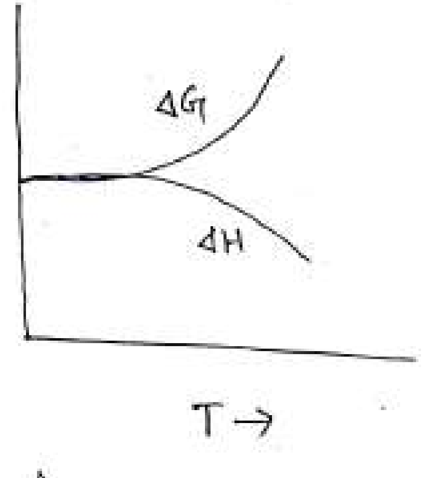
So, two postulates of Nernst for a condensed system are

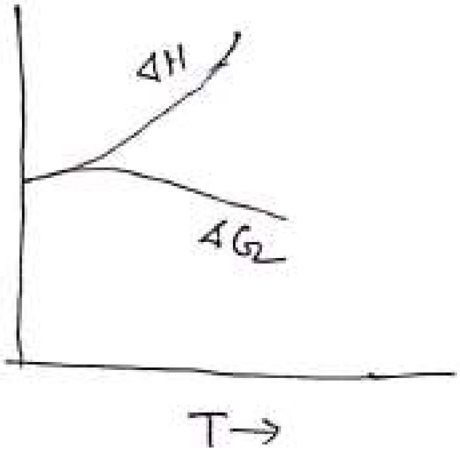
$$\left.\begin{aligned}\lim_{T\to 0}\left(\frac{\partial \Delta G}{\partial T}\right) &= 0\\ \lim_{T\to 0}\left(\frac{\partial \Delta H}{\partial T}\right) &= 0\end{aligned}\right\}\text{ Nernst Heat theorem}$$

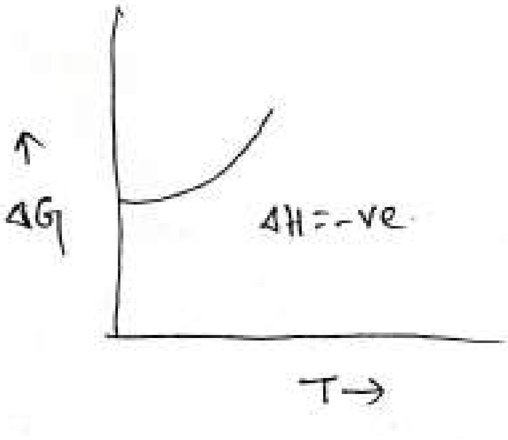
## Graphical Presentation of $\Delta G$ and $\Delta H$ with T

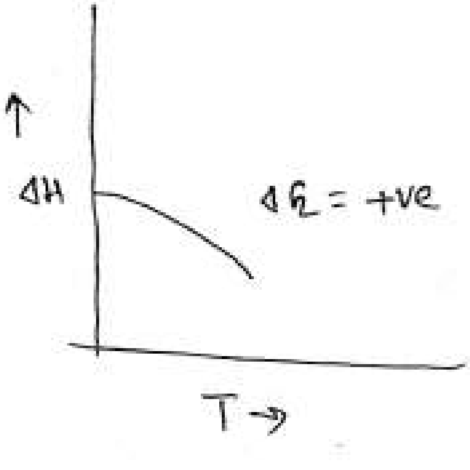
It is already known that with lowering of temp, the magnitude of $\Delta G$/ $\Delta H$ may increases/ decreases, but at extremely low temp $\Delta G$/ $\Delta H$ would be constant and equal

Nernst further suggested that non only $\Delta G$ and $\Delta H$ are equal at the absolute zero, but they approach equality in this temp. range asymtotically.









# Entropy and the Third law of Thermodynamics

Solid (0K, P) → Solid (T, P)

entropy Chang in given by

$$dS = \frac{dq}{T} = \frac{C_p dT}{T}$$

$$\Rightarrow \int_0^T dS = \int_0^T \frac{C_p dT}{T}$$

$$\Rightarrow \Delta S = S_T - S_0 = \int_0^T \frac{C_p dT}{T} \quad \ldots (1)$$

from heat theorem $\lim_{T\to 0}\left(\frac{\partial \Delta H}{\partial T}\right) = 0$, or $\lim_{T\to 0} \Delta C_p = 0$

i.e. heat capacities of all substance (reactant/ product) at absolute zero must be the same.

This is also corroborate by the experiment. Hence at low temp $C_p/T$ is zero or finite quantity.

Since $C_p$ is +ve and $\frac{C_p}{T}$ is finit quantity, therefor integral of eqn(1) is +ve, thus entropy can only increases with temp.

Thus at 0K the entropy has its smallest possible algebraic value $S_0$; the entropy at any higher temp. is greater that $S_0$ i.e. $S_T > S_0$, in other words, the entropy at any temp must be greater that its entropy at absolute zero.

Max-Plank suggested that the value of $S_0$ is zero for every pure, perfectly crystalline substance. This is third law

"The entropy of a pure, perfectly crystalline substance is zero at the absolute zero temp."

Therefore

$$S_T = \int_0^T \frac{C_p dT}{T}$$

$S_T$ = third law entropy / entropy of solid at temp T and Pr. P.

⇒ Third law :- Every system has a finite positive entropy but a the absolute zero of temp the entropy may bec zero and does so become in the case of P crystalline substances (Lewis and Randall)

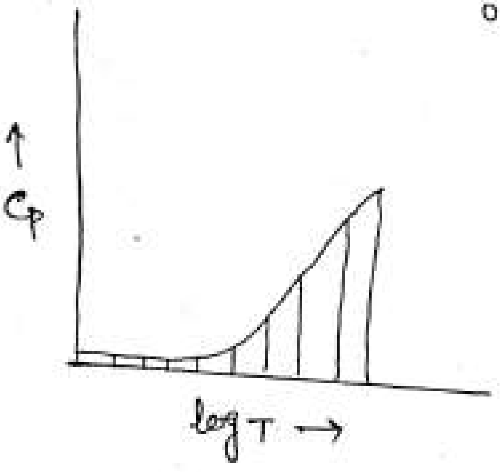
⇒ Other statement :- At any pressure, the entropy of every crystal solid in thermodynamic eq^m at absolute zero is zero

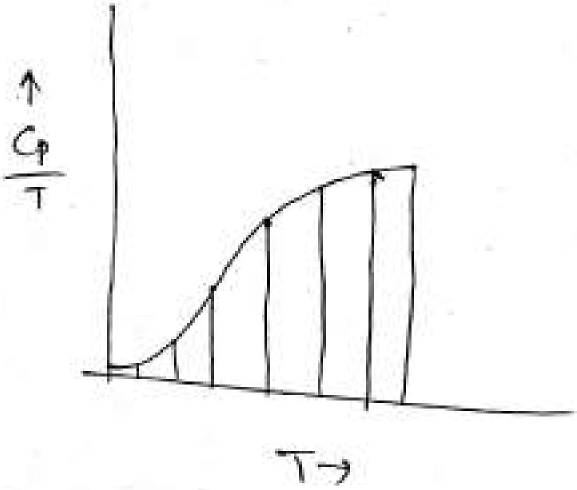
⇒ Max-Plank :- Minimum entropy may be assigned a zero value for a perfectly crystalline substance.

## Experimental determination of entropy

$$S_T = \int_0^T \frac{C_p\, dT}{T}$$

$$= \int_0^T C_p\, d\ln T = 2.303 \int_0^T C_p\, d\log T$$





The area under the both curve is the value of integral (S

To evaluate the value of $S_T$, heat capacity should be known over the range of temp. from absolute zero to the temp of interest. Ordinarily measurement of Cp have to be made up to a lower temp that lies in range 10 to 15K. Bel this temp the Cp of solid is determined from Debye 'T³ la accurately ($C_p = aT^3$)

Q) Comment on the expression $S = k_B \ln W$

Ans For perfect crystalline solid substance at $\lim_{T \to 0}$, all molecules are localised in the lattice points, then $W = 1$

$\therefore S = k_B \ln 1 = 0$

This corresponds to the 3rd law of thermodynamics.

## Absolute entropy

The entropy change of substance taken from 0K to the given temp T K

$$\Delta S_{abs} = S_T - S_0 = \int_0^T C_p \, d \ln T$$

$$= \int_0^{T'} C_p \, d \ln T + \int_{T'}^{T} C_p \, d \ln T \qquad \{ 0 < T' < 15 K$$

## Residual entropy

Every perfect crystalline substance have zero entropy at 0K. Residul entropy is the ~~def~~ entropy of crystal which it posses at 0K. It is the difference b/w calculated and experimental entropy.

$$S_{res} = S_{cal} - S_{exp} = S_0$$

A Common exple is CO, has small $\mu$ value, In solid state some allign themselves in to perfect crystal and fews not packed like perfect crystal

| | | | | | |
|---|---|---|---|---|---|
| CO | CO | CO | CO | OC | CO |
| CO | CO | CO | CO | CO | CO |
| CO | CO | CO | CO | CO | OC |

Perfect crystal

For $N_A$ molecules

$W = 2^{N_A}$ arrangments

$$S_{res} = k_B \ln 2^{N_A} = N_A k_B \ln 2$$

$$= R \ln 2 = 8.314 \times \ln 2$$

$= 5.76$ ~~J/m~~ J/K/mol

**Q//** Entropy of a solid is zero at 0 K – Justify or critisize

**Ans** True for perfectly crystalline substance (eg. CO) ⇒ Not justified

**Q//** Deduce a relation b/w $G$ and $q_m$ for an ideal gas

**Ans**

$$G = A + PV = A + nRT$$

$$= -k_BT\ln Q + nRT = -k_BT\ln\frac{q^N}{N!} + nRT$$

$$= -k_BT\ln q^N + k_BT\ln N! + nRT$$

$$= -Nk_BT\ln q + k_BT(N\ln N - N) + nRT$$

$$= -RT\ln q + RT\ln N - Nk_BT + nRT$$

$$= -RT\ln q_m + RT\ln N_m - nRT + nRT$$ [introducing mole term

$$= -RT\ln\left(\frac{q_m}{N_m}\right).$$