STATISTICAL THERMODYNAMICS (Module - 2: Maxwell – Boltzmann Statistics) (M.Sc. Sem – II/ Chemistry, Paper III, Unit – II)

Statistical Thermodynamics



Contents:

- Recapitulation of last lecture
 - Statistical Thermodynamics
 - System, Assembly & Ensembles
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 - Macrostate and Microstate
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 - Thermodynamic Probability
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STATISTICAL THERMODYNAMICS

Classical Thermodynamics deals with the macroscopic matter and describes the behaviour of large no. of molecules in terms of properties like P, V, T.

Quantum Mechanics deals with matter at microscopic level and the state is described by a wave function.

Statistical Mechanics provides the link between the microscopic properties of matter and its bulk/ macroscopic properties.

Statistical Thermodynamics thus acts as a bridge between Microscopic world & Macroscopic world Quantum Mechanics and Classical Thermodynamics



SYSTEM, ASSEMBLY & ENSEMBLES

- System: If there is a collection of particles, each single particle is referred to as System
- Assembly: Collection of systems (particles) as a whole forms Assembly
- Ensemble: Collection of very large number of assemblies which are independent of each other but which have been made macroscopically as identical as possible is known as Ensemble introduced by W. Gibbs



MACROSTATE , MICROSTATE , THERMODYNAMIC PROBABILITY & DEGENERACY

MACROSTATE

The number of ways of obtaining a distribution by just specifying the number of molecules (or phase points) in each energy state (or cell of phase space)

MICROSTATE

The number of possible ways a particular distribution can be achieved if molecules (or phase points) are distinguishable i.e. by specifying to which energy state (or cell of phase space) molecules (or phase points) temporarily belongs

THERMODYNAMIC PROBABILITY

The number of microstates corresponding to a particular macrostate and is represented by W

DEGREE OF DEGENERACY

The number of energy states of an energy level having the same energy, represented by Statistical Weight Factor, g_i

IMPORTANT CONCEPTS & FORMULAS

ESSENTIAL CONDITIONS FOR DISTRIBUTION OF MOLECULAR STATES

 $\Sigma N_i = N$ and $\Sigma N_i \varepsilon_i = E$ (N & E must remain constant)

PRINCIPLE OF EQUAL A PRIORI PROBABILITIES

All possibilities for the distribution of energy are equally probable

THERMODYNAMIC PROBABILITY

 $W = N! / N_1! N_2!... = N! / \Pi N_i!$

STERLING'S APPROXIMATION

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

MOST PROBABLE DISTRIBUTION

 $\delta W(N) / \delta N_i = 0$ or $\delta \ln W(N) / \delta N_i = 0$



PARTICLE STATISTICS



• No. of ways of arranging N distinguishable particles W = N!

PROBABILITY DISTRIBUTIONS

S Mathew

- No. of ways in which n distinguishable particles can be selected from N distinguishable particles is W = N!/(N-n)! n!
- No. of ways of arranging N distinguishable particles into groups without restriction

 Boltzmannons eg: Gas molecules
 W = N!/N₁! N₂!... (Boltzmann distribution)
- No. of ways in which N indistinguishable particles can be arranged in g states (g>>N) with not more than one particle in each state – Fermions (those with half integral spin) eg: Electron W = g!/(g-N)! N! (Fermi – Dirac distribution)
- No. of ways in which N indistinguishable particles can be arranged in g states (g>>N) with no restriction Bosons (those with integral spin) eg: Photons W = (g + N 1)!/(g-1)! N! (Bose-Einstein distribution)

MAXWELL – BOLTZMANN DISTRIBUTION

- Suppose we have a bulk/ macroscopic system with the following conditions:
 - Consist of N distinguishable particles with total energy E at temperature T
 - Isolated system with no interaction between particles
 - No restriction on Occupancy of energy levels
 - Total number of particles and energy must remain conserved $\Sigma N_i = N$ and $\Sigma N_i \varepsilon_i = E$ (N & E must remain constant) $\Sigma \delta N_i = 0$ and $\Sigma \varepsilon_i \delta N_i = 0$



• Such particles are called **Boltzmannons** e.g. System composed of gas

- Most Probable Macrostate ???
 - The one with maximum no. of microstates gives Maximum Thermodynamic Probability (W_{max})
 - $\delta W(N) / \delta N_i = 0$ or $\delta \ln W(N) / \delta N_i = 0$
- Consider the distribution of Total energy E among various energy levels ε₀, ε₁, ε₂...... of N distinguishable particles at temperature T
- Total number of particles N and Total energy E remains constant $\Sigma N_i = N \text{ and } \Sigma N_i \varepsilon_i = E \qquad(1)$
- N₀ particles are present in level with ε₀ energy level, N₁ in level with ε₁ energy, N₂ in level with ε₂ energy,
- No. of ways of achieving :

$$W = \frac{N!}{N_0! N_1! N_2! \dots}$$

Taking logarithm on both sides of eqn. 2 $W = N! / N_0! N_1! N_2!...$ $\ln W = \ln N! - (\ln N_0! + \ln N_1! + \ln N_2! +)$ $= \ln N! - \sum \ln N_!!$(3) According to Stirling's Approximation $\ln \mathcal{N}! = \mathcal{N} \ln \mathcal{N} - \mathcal{N}$(4) $\ln N_i! = N_i \ln N_i - N_i$ $\sum \ln N_i! = \sum N_i \ln N_i - \sum N_i \quad (But \sum N_i = N)$ $=\sum N_i \ln N_i - N$(5) Substituting eqn. 4 & eqn. 5 in eqn. 3, we get $\ln W = N \ln N - N - \sum N_i \ln N_i + N$ $\ln W = N \ln N - N - \sum N_i \ln N_i + N$ S Mathew



- The one for which W is maximum (W_{max})
- Condition for maxima: δW and $\delta \ln W$ will have to be zero $\delta W = \delta \ln W = 0$ (7)
- On differentiating eqn. 6, $\ln W = N \ln N \sum N_i \ln N_i$ results in $\delta \ln W = \delta N \ln N - \delta \sum N_i \ln N_i$

 $\delta \ln W = -\delta \sum N_i \ln N_i \qquad \dots \qquad (8) \quad [\delta N \ln N = 0, \delta(\text{constant}) = 0]$

• Putting the condition of eqn. 7

 $\delta \ln W = -\delta \sum N_{i} \ln N_{i} = \mathbf{0} \qquad (9)$ $= -\left[\sum N_{i} \delta \ln N_{i} + \sum \ln N_{i} \delta N_{i}\right] = \mathbf{0}$ $= -\left[\sum N_{i} \frac{1}{N_{i}} \partial N_{i} + \sum \ln N_{i} \delta N_{i}\right] = \mathbf{0} \quad \text{where} \quad \delta \ln N_{i} = \frac{1}{N_{i}} \partial N_{i}$ $= -\left[\sum \delta N_{i} + \sum \ln N_{i} \delta N_{i}\right] = \mathbf{0} \qquad [\sum \delta N_{i} = \mathbf{0}]$ $= -\left[\sum \ln N_{i} \delta N_{i}\right] = \mathbf{0} \qquad (10)$

- Distribution must satisfy the condition: N & E must remain constant,
 - $\delta N \& \delta E$ must be equal to zero

- Using Lagrange's Method of Undetermined Multipliers
 - multiplying eqn. 11 by α and eqn. 12 by β
 - $\alpha \, \delta N = \Sigma \, \alpha \delta N_i = 0 \qquad(13)$ $\beta \, \delta E = \Sigma \, \beta \, \varepsilon_i \, \delta N_i = 0 \qquad(14)$
 - and adding to eqn. 10,

$$- \left[\sum \ln N_i \delta N_i \right] = 0, \text{ we get}$$

• $\delta N_0, \delta N_1, \delta N_2, \delta N_3, \dots, \delta N_i$ are independent of each other, so each term in summation must be zero $\delta N_i \neq 0$ $\alpha + \beta \epsilon_i - \ln N_i = 0$ (16)

• Removing logarithm from eqn. 17

$$\mathbf{n} \mathbf{N}_{i} = (\alpha + \beta \varepsilon_{i}) \qquad (17)$$

$$\mathbf{N}_{i} = \mathbf{e}^{(\alpha + \beta \varepsilon_{i})} \qquad \text{where } \beta = -1/kT \qquad [\mathbf{k} = \text{Boltzmann constant}]$$

$$\mathbf{N}_{i} = \mathbf{e}^{\alpha} \mathbf{e}^{-\varepsilon_{i}/kT} \qquad (18)$$

For getting General Distribution Law, Degeneracy of energy states has to be incorporated.
 For this a Statistical Weight factor g_i is introduced for each energy level ε_i

$$\mathbf{N}_{\mathbf{i}} = \mathbf{g}_{\mathbf{i}} \mathbf{e}^{\alpha} \mathbf{e}^{-\varepsilon_{\mathbf{i}}/kT}$$

......(19)

This equation is known as Maxwell – Boltzmann Distribution

- **Taking summation over all energy levels from zeroth level** (For all the particles present in the system)

• Dividing eqn. 19 by eqn. 20, we get

$$\frac{N_{i}}{N} = \frac{g_{i} e^{\alpha} e^{-\varepsilon_{i}/kT}}{\sum g_{i} e^{\alpha} e^{-\varepsilon_{i}/kT}}$$

S Mathew

This gives the general form of Maxwell – Boltzmann Distribution Law

$$\frac{N_{i}}{N} = \frac{g_{i} e^{-\varepsilon_{i}/kT}}{\sum g_{i} e^{-\varepsilon_{i}/kT}}$$

- Fraction of total molecules in the *i*th energy level
- The quantity in the denominator is represented by Q and is called Partition Function

$$\mathbf{Q} = \mathbf{\Sigma} \mathbf{g}_{\mathbf{i}} \, \mathbf{e}^{\mathbf{-\varepsilon} \mathbf{i}/\mathbf{k} \mathbf{T}}$$

• It is a great analytical tool in Statistical Thermodynamics