STATISTICAL THERMODYNAMICS (Module - 4: Partition Function - Basic Concepts) (M.Sc. Sem – II/ Chemistry, Paper III, Unit – II)

Statistical Thermodynamics

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Recapitulation

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 ith energy level
- The quantity in the denominator is represented by Q and is called Partition Function

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

• It is a great analytical tool in Statistical Thermodynamics. It facilitates in calculation of all thermodynamic quantities

Partition Function

It is defined as

$$\mathbf{Q} = \sum_{0}^{\infty} \mathbf{g}_{\mathbf{i}} \, \boldsymbol{e}^{-\boldsymbol{\varepsilon}_{i}/kT}$$

- ε_i is the energy of the quantum state in excess of the lowest possible value
- g_i is the statistical weight factor or is equal to the degree of degeneracy i.e., no. of quantum states having same energy ε_i
- k is the Boltzmann constant & is equal to ratio of Gas constant R to the Avogadro's no. N (k = R/N)
- T is the temperature in Kelvin scale
- Summation is all over the energy levels 0 to infinity

Partition Function

- Typically written as Z, German word Zustandssumme, "Sum over States" as given by Max Planck
- The term Partition Function (Q) is due to Charles Darwin & Ralph Fowler
- **Definition** :

$$\mathbf{Q} = \sum_{0}^{\infty} \mathbf{g}_{\mathbf{i}} \, \boldsymbol{e}^{-\varepsilon_{i}/kT}$$

- Sum of the probability factors for different energy states
- The way in which the energy of a system is partitioned or distributed among molecules constituting the system

Physical Significance of Partition Function

- As the name implies, it summarizes in mathematical form How the energy of a system is partitioned or distributed among the molecules inhabited
- It is a dimensionless quantity and gives the number of thermally assessable states
- Its value depends on molecular weight, molecular volume, molecular motion, temperature, inter-nuclear distances, intermolecular forces, etc.
- Thus provides the most convenient way of linking microscopic properties of individual molecules (moment of inertia, dipole moments, discrete energy levels,...) with the macroscopic properties (entropy, polarization, molar heat,..)

- **Physical Significance of Partition Function**
- According to Maxwell Boltzmann law: $N_i \propto g_i e^{-\varepsilon_i/kT}$
- Population of ith level as compared to zeroth level

$$\frac{N_i}{N_0} = \frac{g_i e^{-\varepsilon_i/kT}}{g_0 e^{-\varepsilon_0/kT}} \quad \varepsilon_0 = 0 \quad \frac{N_i}{N_0} = \frac{g_i}{g_0} e^{-\varepsilon_i/kT}$$

- When $\varepsilon_0 = 0$, $g_0 = 1$; then $N_i = N_0 g_i e^{-\varepsilon_i/kT}$
- Taking summation, we get

 $\sum N_i = N_0 \sum g_i e^{-\varepsilon_i/kT}$ [where $\sum N_i = N$] $N = N_0 \sum g_i e^{-\varepsilon_i/kT}$ [where $\sum \mathbf{g}_i e^{-\varepsilon_i/kT} = \mathbf{Q}$]

Partition function may be defined as -

or

The ratio of the total number of particles to that in zero level

 $N = N_0 \mathbf{Q}$

Partition function is defined as –

- $\mathbf{Q} = \sum g_i e^{-\varepsilon_i/kT}$ and also $\mathbf{Q} = \frac{N}{N_0}$
- At absolute zero, $\varepsilon_i/kT = \infty$ [where $e^{-\infty} = 0$], except for $\varepsilon_0 = 0$ [where $e^0 = 1$] and $\mathbf{Q} = g_0$ i.e., the partition function is equal to the degeneracy of the ground state. If for $\varepsilon_0 = 0$, $g_0 = 1$: $\mathbf{Q} = 1$
- Also, all the particles will occupy the zeroth level at 0 K, $N_0 = N$ then $N \to N_0$ and $Q \to 1$ as $T \to 0$ $\lim_{T \to 0} Q \to 1$
- The value of partition function increases with temperature
 - As temperature increases more molecules will occupy higher energy and value of **Q** increases
 - When T is very high, the term $\varepsilon_i/kT = 0$, $\lim_{T \to \infty} Q \to \infty$

Relation of Molar and Molecular Partition Function

- Molecular partition function (Q)
 - Partition function associated with a molecule
- Molar partition function (Z)
 - When a system is composed of a large no. of entities each containing one mole of the substance i.e., each entity is a mole not a molecule
 - For distinguishable particles (ex as in crystals)

 $Z = Q^N$

- For indistinguishable particles (ex - as in gases)

$$Z = \frac{1}{N!} Q^{N}$$

 When the energy value at ground state is taken as zero, we can denote the partition function as Q⁰

Boltzmann – Planck Relation: Relation between S and W

- According to Boltzmann, entropy (S) is defined as a function of probability of thermodynamic states (W)
 i.e., S = f(W)
- Consider two states having entropy S_A and S_B and probabilities W_A and W_B respectively, such that $S_A = f(W_A)$ and $S_B = f(W_B)$ (2)
- Entropy is additive or extensive property $S = S_A + S_B$ (3)
- Probability is multiplicative

rty
$$S = S_A + S_B$$
(3)
 $S = f(W_A) + f(W_B)$ (4)
 $W = W_A \times W_B$ (5)
 $f(W) = f(W_A \times W_B)$ (6)

 $S = k \ln v$

• Combining eqn. (4), (6) and (1)

 $f(W_A) + f(W_B) = f(W_A \times W_B).....(7)$ • We know the only function which satisfies the above condition is natural logarithm, hence $f(W) \propto \ln W$ Or $f(W) = k \ln W + c$ (8) [where k = Boltzmann constant] • Thus, we can write $S = k \ln W + c$ (9)

Planck showed that value of c = 0, hence
 Boltzmann – Planck equation

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Molecular Energy & Partition Function

Molecular Energy is the sum of contributions from its different modes of motion - **translational (t)**, **rotational (r)** and **vibrational (v)**. The **electronic (e) transition** contribution can also be included, such that **total energy** is given by :

$\mathbf{\varepsilon_i} = \mathbf{\varepsilon_t} + \mathbf{\varepsilon_r} + \mathbf{\varepsilon_v} + \mathbf{\varepsilon_e}$

The separation of these terms is only approximate because the modes are not completely independent but in most cases is satisfactory

Given that the energy is a sum of independent contributions, Partition function factorizes into a product of its contributions

Modes of Motion & Degrees of Freedom

Total degrees of freedom for molecule consisting of N atoms is 3N

Translational degrees of freedom for any molecule is 3

Rotational degrees of freedom for linear molecule is 2 for non-linear molecule is 3

Vibrational degrees of freedom for linear molecule is 3N - 5 for non-linear molecule is 3N - 6



Molecular Partition Function

Molecular Energy is the **sum** of translational (t), rotational (r), vibrational (v) and electronic (e) components, such that **total energy:**

$$\varepsilon_i = \varepsilon_t + \varepsilon_r + \varepsilon_v + \varepsilon_e$$

Statistical weight factor is the **product** of translational (t), rotational (r), vibrational (v) and electronic (e) components, such that **total statistical weight factor**:

Partition function will factorize into a product of its components

Partition Function is given by $\mathbf{Q} = \Sigma \mathbf{g}_i \, \mathbf{e}^{-\boldsymbol{\varepsilon} \mathbf{i}/\mathbf{k}\mathbf{T}}$

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Substituting value of g_i and ε_i :

$$\mathbf{Q} = \sum \left(\mathbf{g}_{t} \times \mathbf{g}_{r} \times \mathbf{g}_{r} \times \mathbf{g}_{v} \times \mathbf{g}_{e} \right) \mathbf{e}^{-\left[\mathbf{\varepsilon}_{t} + \mathbf{\varepsilon}_{r} + \mathbf{\varepsilon}_{v} + \mathbf{\varepsilon}_{e} \right] / \mathbf{k}T$$

 $\mathbf{Q} = \Sigma \mathbf{g}_{\mathbf{t}} \mathbf{e}^{-\boldsymbol{\varepsilon}_{\mathbf{t}}/\mathbf{k}T} \mathbf{x} \Sigma \mathbf{g}_{\mathbf{r}} \mathbf{e}^{-\boldsymbol{\varepsilon}_{\mathbf{r}}/\mathbf{k}T} \mathbf{x} \Sigma \mathbf{g}_{\mathbf{v}} \mathbf{e}^{-\boldsymbol{\varepsilon}_{\mathbf{v}/\mathbf{k}T}} \mathbf{x} \Sigma \mathbf{g}_{\mathbf{e}} \mathbf{e}^{-\boldsymbol{\varepsilon}_{\mathbf{e}}/\mathbf{k}T} \dots \dots \dots (5)$

Expressions for allowed energy levels and their degeneracy

- Translational energy: $\mathcal{E}_t = n^2 h^2 / 8m l_x^2$; $g_t = 1$ where $n = 1, 2, 3, \dots$
- Rotational energy: $\mathcal{E}_r = J (J+1)h^2/8\pi^2 I$; $g_r = 2J + I$ where J = Rotational quantum no. = 0,1,2,3.....; I = μr^2
- Vibrational energy: E_v = (v + ½) hv; g_v = 1 where v = Vibrational quantum no. = 0,1,2,3,....
 Electronic energy: Δε_e = hc v; g_r = 2J +1 (ground state) where J = Resultant angular momentum quantum no.