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CHEMICAL SCIENCES

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Subunit 8: Statistical Thermodynamics:**Key Terminologies**

Basic Terms: Statistical mechanics [2.8.1], Maxwell-Boltzmann Statistics [2.8.2], Boltzons [2.8.2], Microstate & Macrostate [2.8.3], Ensemble [2.8.4], Canonical Ensemble [2.8.4], Microcanonical Ensemble [2.8.4], Grand canonical Ensemble [2.8.4], Thermodynamic Probability [2.8.5], Entropy relation with Thermodynamic Probability [2.8.6], Boltzmann's Statistics [2.8.9], Boltzmann's Distribution Law [2.8.10], Partition Function [2.8.11]

Standard Terms: Stirling's Approximation [2.8.7], Postulates of Statistical mechanics [2.8.8], Total Molecular Partition Function [2.8.12], Translational Partition Function [2.8.20], Rotational Partition Function [2.8.21], Vibrational Partition Function [2.8.22], Electronic Partition Function [2.8.23], Nuclear Partition Function [2.8.24]

Advanced Terms: Bose-Einstein Statistics [2.8.2], Fermi-Dirac Statistics [2.8.2], Bosons [2.8.2], Fermions [2.8.2], Sucker-Tetrode Equation [2.8.25]

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Key conceptual Points:

2.8.1. **Statistical mechanics** is the branch of science by which we can calculate the macroscopic properties of a system through aggregation of micro-properties such as molecular weight, molecular geometry, or structure, intra- or inter-molecular forces of individual molecules composing microscopic system. In other words, the statistical mechanics provides the much-needed bridge between the mechanics and thermodynamics, that could explain how the resultant properties of the bulk matter have been built up by the system from its microscopic properties.

2.8.2. Three statistical methods are developed so far, viz.,

a. **Maxwell-Boltzmann's Statistics:** According to this statistical theory,

- (i) all particles or molecules of the system are assumed to be distinguishable
- (ii) no limitation on their number in an energy state is placed

Such particles are called **Maxwellions** or **Boltzons** and are hypothetical in nature. Real particles are actually indistinguishable. The number of ways of arranging 'N' distinguishable particles among energy levels of a system such that 'n_i' particles are placed in any energy level 'i' having degeneracy 'g_i' is given by

$$W = N! \prod_i (g_i^{n_i} / n_i!)$$

Maxwell-Boltzmann's method constitutes what we say classical statistical mechanics.

b. **Bose-Einstein Statistics:** It is employed for the distribution of composite particles made from even number of fundamental particles, viz., protons, neutrons, electrons called **Bosons**, e.g., deuterium nuclei, helium nuclei etc.

- (i) they are symmetrical, indistinguishable and have integral spin
- (ii) there is no limitation put on the number of particles to be placed in an energy state
- (iii) only those quantum states are accessible which are symmetric with respect to the particles interchange, i.e., applicable on those particles only whose wave functions don't change sign on interchanging the positions of any two particles in the system

The number of ways of arrangement of 'N' indistinguishable particles in 'g' energy states with no restriction on the occupation of a state is given by

$$W = (N + g - 1)! / N!(g - 1)!$$

c. **Fermi-Dirac Statistics:** It is used for the distribution of fundamental particles like protons, electrons, neutrons along with composite particles made from an odd number of such particles. Such particles are called Fermions, e.g., molecules or atoms having odd number of neutrons and protons in their nuclei.

- (i) these particles have half-integral spin and asymmetric nature
- (ii) no more than one particle can be present in a single state
- (iii) only those quantum states are accessible to the particles which are antisymmetric with respect to particle interchange

The number of ways of placing 'N' indistinguishable particles in 'g' distinguishable energy states [$g \geq N$] with no more than one particle in a state is given by

$$W = \frac{g!}{(g - N)!N!}$$

2.8.3. Microstate and Macrostate: Macrostate signifies the thermodynamic state of the system and is characterized by specifying the values of macroscopic properties or thermodynamic variables such as pressure, temperature and composition or set of three parameters other than previous ones, energy, volume and number of molecules.

Whereas microstate can be defined as the number of energy states or quantum levels with same energy and constituting a level is called degeneracy, denoted by 'g'. In general microstate of a system is described by specification of energy state of each particle along with their identity if any.

2.8.4. Ensemble: An ensemble is a representative set of microscopic states corresponding to a specified microstate. Conceptually, an ensemble is defined as collection of a very large number (even infinite) of macroscopically distinguishable systems identical to a given thermodynamic system, and which have same number of molecules and volume.

Types of Ensemble:

- (i) **Canonical Ensemble:** Canonical ensemble is an assembly of systems with fixed composition (n), Volume (V) and temperature (T) of each of the systems present. The whole ensemble is an isothermal, isolated super system of total energy E having separated systems by rigid, impermeable, and diathermal (good conductor) walls. Hence, in this case, only heat energy not matter can be exchanged from system to system.
- (ii) **Microcanonical Ensemble:** Microcanonical ensemble is an assembly of systems with fixed composition (n), Volume (V) and energy (E) of each of systems present. Each system is individually isolated by rigid, impermeable and well-insulated walls so that both the matter and the energy cannot be exchanged between systems. Neither system can contract nor expand.
- (iii) **Grand Canonical Ensemble:** this ensemble is an open iso-thermal system specified by fixed volume (V), chemical potential (μ) and temperature (T) of each system present. Each of the system both thermal and material contact with its surroundings, i.e., there can be exchanged of both matter and energy as systems are separated by rigid, permeable and diathermal walls. Due to exchange of matter between systems, the composition (n) would change but chemical potential remains unaltered.

2.8.5. Thermodynamic Probability: The thermodynamic probability of a macro-state may be defined as the number of equally probable microstates that corresponds to a given macro-state 'm'. It is represented by W_m or simply W , that stands for Wahrscheinlichkeit means probability in German. Thermodynamic probability (W) of a macro-state depends upon the number of particles arranging and their distinguishable or indistinguishable nature.

The thermodynamic probability of a specified or given state of a system is defined as the total number of possible ways or microscopic arrangements of all the particles composing the system. In other words, it is given by the number of total possible microstates in which the specified thermodynamic state of the system can be realized. **Each such possible arrangements or distribution is called complexions of the system.** For a system, the thermodynamic probability is denoted by Ω and is equal to the sum over all thermodynamic probability of macro-states, hence,

$$\Omega = \sum_m W$$

Ω has value between 1 and ∞ . The thermodynamic probability differs from the mathematical probability as the latter varies between 0 and 1. Ω denotes the total number of possible complexions of the system. It is also called total configurational weight of the system.

Case I: When each of energy level is non-degenerate

$$W = N! / \prod_i n_i!$$

Where, \prod_i represents the product over all energy states from zero to i-th level.

Case II: When energy levels are degenerate

$$W = N! / \prod_i (g_i^{n_i} / n_i!)$$

Where, g_i = degeneracy of i-th level

2.8.6. Relation between Entropy and Thermodynamic probability:

$$S = k_B \ln \Omega$$

2.8.7. Stirling's approximation: Stirling's approximation is of great utility in statistics.

$\ln n! = n \ln n - n$, if n is very large quantity as compared to unity.

$$n! = \sqrt{2\pi n} (n/e)^n \quad [\text{neglecting the higher terms}]$$

$$\ln n = \ln (n/e)^n = n \ln n - n, \text{ so } n = \ln(n^n/n!)$$

2.8.8. Postulates of statistical mechanics:

First postulate: All possible microstates (classical or quantum mechanical) of an isolated system (or assembly) are equally probable. This postulate is called a principle of equal 'priori' probability. The priori probability $[P_i]$ of quantum microstate 'i' depends upon the energy of state, i.e., $P_i = f(E_i)$.

$$P_i = 1/\Omega$$

Second postulate: It states that sufficiently long and measurable time-average of every physical observable (i.e., measurable macroscopic property) is equal to the ensemble-average (i.e., the average value of that property in the ensemble).

$$E_i = \langle E_i \rangle = \sum_i P_i E_i = \int \Psi^* E_i \Psi d\tau$$

2.8.9. Boltzmann's Statistics: The basis of Boltzmann's statistics is the assumption that there are more energy states available than the molecules of a system so that there is low probability of two molecules being in the same energy state. Under this assumption the molecules can be treated as distinguishable from one another.

$$\ln W = N \ln N - \sum_{i=0} n_i \ln \left(\frac{n_i}{g_i} \right)$$

$$n_i = g_i e^{-(\alpha + \beta \epsilon_i)}$$

$$n_i/n_j = g_i/g_j e^{-\beta(\epsilon_i - \epsilon_j)}$$

where, n_i, n_j = number of molecules at i-th and j-th energy level respectively, g_i, g_j = multiplicity of those levels, ϵ_i, ϵ_j = Energy of i-th and j-th level, β = constant.

2.8.10. Boltzmann's Distribution Law: $n_i/n_j = e^{-(\epsilon_i - \epsilon_j)/kT}$

K = Boltzmann Constant

2.8.11. Partition Function: The partition function is the link between the microscopic system and the thermodynamic properties of macroscopic system.

$$N = n_0 \sum_i g_i e^{-\epsilon_i/kT}$$

$$Q = \sum_i g_i e^{-\epsilon_i/kT}$$

$$Q = N/n_0$$

Where, k = Boltzmann's constant,

2.8.12. Total Molecular Partition Function: The total molecular partition function of the system is the product of the molecular partition functions corresponding to different types of energies like translational energy (tr), rotational energy (rot), vibrational energy (vib), electronic energy (el), nuclear energy (nuc) associated with molecule of the system. Assuming Born-Oppenheimer approximation that various types of energies are independent of each other, which is true at relatively high temperatures, the energy of a molecule in excess of zero-point energy is given by the sum of above-mentioned energies.

$$\epsilon_{\text{total}} = \epsilon_{\text{el}} + \epsilon_{\text{tr}} + \epsilon_{\text{rot}} + \epsilon_{\text{vib}} + \epsilon_{\text{nuc}}$$

Also, total statistical weight or quantum weight or multiplicity or degeneracy of various energy levels is given by,

$$g_{\text{total}} = g_{\text{el}} \times g_{\text{tr}} \times g_{\text{rot}} \times g_{\text{vib}} \times g_{\text{nuc}}$$

Now, total molecular partition function is

$$Q_{\text{total}} = \sum g e^{-\epsilon/kT} = \sum g_{\text{el}} \exp(-E_{\text{el}}/k_B T) \times \sum g_{\text{tr}} \exp(-E_{\text{tr}}/k_B T) \times \sum g_{\text{rot}} \exp(-E_{\text{rot}}/k_B T) \times \sum g_{\text{vib}} \exp(-E_{\text{vib}}/k_B T) \times \sum g_{\text{nuc}} \exp(-E_{\text{nuc}}/k_B T) = Q_{\text{el}} \times Q_{\text{tr}} \times Q_{\text{rot}} \times Q_{\text{vib}} \times Q_{\text{nuc}}$$

2.8.13. Internal Energy in terms of Q:

$$U = RT^2 \left[\frac{\partial \ln Q}{\partial T} \right]_V$$

2.8.14. Heat Capacity in terms of Q:

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

2.8.15. Entropy of a system in terms of Q:

Case I: For independent localized system:

$$S = R \ln Q + RT \left[\frac{\partial \ln Q}{\partial T} \right]_V$$

Case II: For non-localized systems like ideal gas:

$$S = R \left[\ln \frac{Q}{N} + T \left[\frac{\partial \ln Q}{\partial T} \right]_V + 1 \right]$$

2.8.16. Helmholtz free energy in terms of Q:

Case I: For independent localized system:

$$A = -RT \ln Q$$

Case II: For non-localized systems like ideal gas:

$$A = -k_B T [\ln(Q^N/N!)]$$

Where, N = Avogadro's number, k_B = Boltzmann's Const.

2.8.17. Pressure of an ideal gas in terms of Q:

$$P = RT \left[\frac{\partial \ln Q}{\partial V} \right]_T$$

2.8.18. Gibbs free energy in terms of Q:

Case I: For independent localized system:

$$G = -RT \ln Q + RTV \left[\frac{\partial \ln Q}{\partial V} \right]_T$$

Case II: For non-localized systems like ideal gas:

$$G = -k_B T \ln(Q^N/N!) + RTV \left[\frac{\partial \ln Q}{\partial V} \right]_T$$

Where, N = Avogadro's Number, k_B = Boltzmann's Constant.

2.8.19. Enthalpy of a system in terms of Q:

$$H = RT^2 \left[\frac{\partial \ln Q}{\partial T} \right]_V + RTV \left[\frac{\partial \ln Q}{\partial V} \right]_T$$

2.8.20. Expression for Translational Partition Function $[Q_{tr}]$:

$$Q_{tr} = \left(\frac{2\pi m k_B T}{h^2} \right)^{3/2} \times nRT/P$$

Where, m = average mass of the particle, k_B = Boltzmann's Constant, h = Planck's constant, n = quantum number; and rest have their usual meanings.

2.8.21. Expression for Rotational Partition Function $[Q_{rot}]$:

Case I: When nuclear spin effect ignored

$$Q_{rot} = 8\pi^2 I k_B T / \sigma h^2$$

Case II: when nuclear spin effect considered

$$Q_{rot} = (2i + 1)(2i' + 1) 8\pi^2 I k_B T / \sigma h^2$$

2.8.22. Expression for Vibrational partition Function $[Q_{vib}]$:

$$Q_{vib} = 1 / (1 - e^{-\theta_v/T})$$

Where, $\theta_v = -h\nu/k_B$

2.8.23. Expression for Electronic Partition Function $[Q_{el}]$:

$$Q_{el} = \sum_0^\infty g e^{-\frac{\epsilon}{kT}}$$

where $g = g_{el}$, $\epsilon = \epsilon_{el}$ only

2.8.24. Expression for Nuclear Partition Function [Q_{nuc}]:

$$Q_{\text{nuc}} = \sum_0^{\infty} g e^{-\frac{\varepsilon}{kT}}$$

where $g = g_{\text{nuc}}$, $\varepsilon = \varepsilon_{\text{nuc}}$ only

2.8.25. Sucker-Tetrode Equation:

$$S_m^0 = R[-1.1541 + (3/2)\ln A_r + (5/2)\ln(T/K) - \ln(P/P^0)]$$

Where, A_r = relative atomic mass, K = Boltzmann's Constant for 1 mol.



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Previous Year Solution

Q. The populations of proton spins in the highest energy level of a sample in magnetic fields of 1.5 T and 7.0 T are N' and N , respectively. The value of $\ln(N'/N)$ is (γ , h , k , T are gyromagnetic ratio of the proton, Planck's constant, Boltzmann constant, and temperature of the sample, respectively; assume that the partition functions for both systems can be approximated as 1)

- (a) $5.5\gamma h/kT$ (b) $(3/14)\gamma h/kT$ (c) $(14/3)\gamma h/kT$ (d) $8.5\gamma h/kT$ [NET 2019 June]

Ans. Total number of population in excited state is $N' = (1/q)\exp(\gamma h B'/2k_B T)$

Total number of population in ground state is $N = (1/q)\exp(\gamma h B/2k_B T)$

Given, partition function $Q = 1$ for both the cases.

Then, population ratio $N'/N = \exp[\gamma h (B - B')/2k_B T]$

Given in the problem, $B = 7$ T and $B' = 1.5$ T,

Now putting the value and taking \ln in both sides, we get,

$$\ln(N'/N) = 5.5\gamma h/2k_B T$$

Correct answer is **Option (a).** [Key point 2.8.10]

Q. The difference between standard molar entropies of two mono-atomic gases (A) and (B) ($S_{m,A}^0 - S_{m,B}^0$) at a given temperature is (given that the molar mass of A is twice the molar mass of B)

- (a) $(3/2)R\ln 2$ (b) $R\ln 2$ (c) $(5/2)R\ln 2$ (d) $(7/2)R\ln 2$ [NET 2019 June]

Ans. From Sackur Tetrode equation, the molar entropy for mono-atomic gas A is

$$S_{m,A}^0 = R[-1.1541 + (5/2)\ln T + (3/2)\ln M_A - \ln(P/P_0)] \dots\dots\dots(i)$$

The molar entropy for mono-atomic gas B is

$$S_{m,B}^0 = R[-1.1541 + (5/2)\ln T + (3/2)\ln M_B - \ln(P/P_0)] \dots\dots\dots(ii)$$

The difference between two standard molar entropy is, (i) – (ii),

$$S_{m,A}^0 - S_{m,B}^0 = (3/2)R \{\ln M_A - \ln M_B\} = (3/2)R\ln 2$$

Correct answer is **Option (a).** [Key point 2.8.25]

Q. The translational partition function for Ar confined to a volume of 1L at 300K, having thermal wavelength of 1.60×10^{-11} m, is closest to

- (a) 24.4×10^{29} (b) 2.44×10^{29} (c) 0.244×10^{29} (d) 244×10^{29} [NET 2018 Dec]

Ans. $\lambda = 1.6 \times 10^{-11}$ m, $C_{tr} = V/\lambda^3 = 1\text{L}/(1.6 \times 10^{-11} \text{ m})^3 = 10^{-3} \text{ m}^3 / 0.244 \times 10^{-33} \text{ m}^3 = 2.44 \times 10^{29}$

Correct answer is **Option (b).** [Key point 2.8.20]

Q. Translational partition function of a D_2 molecule confined in a 100 cm^3 vessel at 25°C is ($h = 6.626 \times 10^{-34} \text{ Js}$, $k = 1.381 \times 10^{-23} \text{ JK}^{-1}$)

- (a) 3.8×10^{22} (b) 5.8×10^{24} (c) 7.8×10^{26} (d) 9.8×10^{28} [NET 2018 June]

Ans. $Q_{tr} = V/\lambda^3 = h/\sqrt{2[mk_B T]} = (6.626 \times 10^{-34} \text{ Js})/\sqrt{2 \times 3.14 \times 4 \times 1.66 \times 10^{-27} \text{ kg} \times 1.38 \times 10^{-23} \text{ JK}^{-1} \times 298 \text{ K}}$

$= 5.05 \times 10^{-11} \text{ m}$

$Q_{tr} = (100 \times 10^{-6} \text{ m}^3)/(5.05 \times 10^{-11} \text{ m})^3 = 7.8 \times 10^{26}$

Correct answer is **Option (c).** [Key Point 2.8.20]

Q. Four distinguishable molecules are distributed in energy levels E_1 and E_2 with degeneracy of 2 and 3, respectively. Number of microstates, with 3 molecules in energy level E_1 and one in energy level E_2 , is (a) 4 (b) 12 (c) 96 (d) 192 [NET 2017 Dec]

Ans.

Q. For distinguishable particles, thermodynamic probability will be

$W = N! \prod_i (g_i^{n_i}/n_i!)$

Now from current problem, we have,

$W = 4!(g_0^{n_0}/n_0!)(g_1^{n_1}/n_1!) = 4! \times (2^3/3!) \times (3^1/1!) = 96.$

Correct answer is **Option (c).** [Key point 2.8.5]

Q. Partition function of a one-dimensional oscillator having equi-spaced energy levels with energy spacing equal to $k_B T$ and zero ground state energy is

- (a) e (b) $1/(e - 1)$ (c) $e/(e - 1)$ (d) $1/(e + 1)$ [NET 2016 Dec]

Ans. Since, zero point energy = 0, so $\Delta E = k_B T$

Partition function $Q = 1/(1 - e^{-\Delta E/kT}) = 1/(1 - e^{-kT/kT}) = 1/1 - e^{-1} = e/e - 1$

Correct answer is **Option (c).** [Key Point 2.8.11]