UNIT-5

INTRODUCTION TO
STATISTICAL THERMODYNAMICS

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UNIT-5 INTRODUCTION TO STATISTICAL THERMODYNAMICS

STRUCTURE:

5.1 Introduction:

Do you know the laws of thermodynamics? You might have learned about the four laws of thermodynamics and various thermodynamic parameters like enthalpy, internal energy, entropy Gibbs free energy etc. Actually, thermodynamics is an experimental science which is concerned with the bulk or macroscopic properties of a system of interest without making any reference to the contributions of individual constituent, molecule, ion or atom. Statistical mechanics aims to derive the bulk (observable) properties of mater using the laws of mechanics applied on the constituent particles. However in statistical thermodynamics we deal with system which changes with time in the direction to equilibrium state. The purpose of statistical thermodynamics is to understand the behavior of the large assemblies of (relatively) simple systems such as molecules in a gas, atoms in crystal in terms of the behavior of its constituents.

Quantum mechanics provides the information about the energy states or levels of a molecular system while the statistical mechanics gives the possible arrangements of the molecules in various energy states or levels. Therefore, study of statistical thermodynamics presumes not only classical thermodynamics but also quantum mechanics and calculus (differential and integral).

In the first section we will introduces the three types of statistics and the basic differences between classical thermodynamics & statistical thermodynamics. In the next sections we will discuss about ensembles, microstates & macrostares, thermodynamic probability and distribution of particles which will help us to describe the behavior of a system of large number of particles elegantly. Then you will learn to establish a relationship between entropy and thermodynamic probability which bridges the thermodynamics and statistical view-point. In the next section, we will derive the Boltzmann distribution law for the equilibrium state (i.e., most probable distribution). This introduces a very important parameter known as Partition Function, f. Then we will derive few thermodynamic parameters in terms of f. You will learn to derive the partition function for few simple systems in the next unit.

5.2 Objectives:

After studying this unit you will be able to-

→ Explain the terms- ensembles, microstates & macrostares, thermodynamic probability and partition function;

→ Distinguish between various types of statistics

→ Compute the therodynamic probability for different types of distributions

→ Derive the relationship between entropy and thermodynamic probability

$\rightarrow$ Derive the Boltzmann distribution law for most probable distribution

$\rightarrow$ Express few thermodynamic parameters in terms of f

5.3 Statistics in Thermodynamics:

5.3.1 Classical Thermodynamics and Statistical Thermodynamics:

Classical thermodynamics is concerned with systems composed of large numbers molecules, atoms, etc. So any property of the system is a macroscopic one. The method of averaging the bahaviour of a large number of individuals is called Statistical method. For example, the kinetic energy of a gaseous system at a particular temperature is a statistical average of the kinetic energies of the individual molecules. Statistical thermodynamics is based on the principle that the thermodynamic properties are the averages of molecular properties, and based on statistical methods, it sets up a scheme for calculating these averages. Therefore, the branch of science dealing with the calculation of macroscopic thermodynamic properties (such as Pressure, Entropy, Internal energy, Gibb's free energy etc.) of systems from the microscopic properties of individual molecules by statistical methods is known as Statistical thermodynamics. Hence, Statistical thermodynamics provide a link between microscopic properties of matter (i.e. quantum mechanics) and its bulk properties (i.e. classical thermodynamics). So the foremost concept to understand in this unit is the differences between classical thermodynamics and statistical thermodynamics which are listed in *table 5.1*.

Classical thermodynamics	Statistical thermodynamics
Deal with Macroscopic properties of large number of molecules	Computation of Macroscopic properties of bulk matter from the data of microscopic properties of individual particles
Study the change of thermodynamic parameters (i.e. ΔE, ΔH, ΔU, ΔG etc.) i.e. Study of energy transfer in macroscopic level	Try to find out the absolute values of the thermodynamic parameters (i.e. E, H, U, G etc.)
Based on the thermodynamics laws	Based on probabilistic methods (an average method)

Table 5.1 *Difference between Classical and Statistical Thermodynamics*

5.3.2 Types of Distribution or Statistics: There are three types of statistics depending on different physical situations in nature.

1. **Maxwell-Boltzmann (or M-B) Distribution:** In M-B statistics the particles are assumed to be distinguishable and any number of particles may occupy the same energy level.

2. **Bose-Einstein (or B-E) Statistics:** In B-E statistics the particles are assumed to be indistinguishable and any number of particles may occupy the same energy level. This statistics is obeyed by particles having integral ($I= 1, 2, 3, 4$ etc) spins. E.g. ^{4}He, N_2, H_2, D_2, photons, etc. The B-E statistics is applicable to those particles whose wave functions are symmetric in nature.

3. **Fermi-Dirac (F-D) Statistics**: In F-D statistics the particles are assumed to be indistinguishable but only one particle may occupy in a given energy level. This statistics is obeyed by particles having half-integral ($I=1/2, 3/2, 5/2, 7/2$ etc) spins. E.g. ^{3}He, NO, protons, electrons etc. The F-D statistics is applicable to those particles whose wave functions are antisymmetric in nature.

The differences among the three types of statistics are summarizes in *table 5.2*.

M-B Statistics	B-E Statistics	F-D Statistics
The laws of **classical mechanics** are applicable according to which individual molecules/atoms have definite positions and momenta.	The laws of **quantum mechanics** are applicable according to which individual molecules/atoms have only quantized values of energy.	The laws of **quantum mechanics** are applicable.
Particles are **distinguishable**	Particles are **indistinguishable**	Particles are **indistinguishable**
Any number of particles may occupy the same energy level.	Any number of particles may occupy the same energy level.	Only one particle may occupy in a given energy level.
Does not depend on the **internal structure** of the particles.	This statistics is obeyed by particles having **integral nuclear spin** whose wave functions are **symmetric** in nature.	This statistics is obeyed by particles having **half-integral spin** whose wave functions are **antisymmetric** in nature.
The particles obeying the M-B statistics are called **maxwellons or boltzmannons**.	The particles obeying the B-E statistics are called **bosons**.	The particles obeying the F-D statistics are called **Fermions**.

Table 5.2 *Difference of M-B, B-E and F-D Statistics*

5.4 Ensemble:

A collection of a large number of systems which are identical with the system under consideration in a number of aspects (such as Volume, number of particles etc.) is called an ensemble of system. Ensembles are of three types depending upon the thermodynamic variables kept constant.

> **Microcanonical ensemble:** An ensemble of systems in which each system (member) has the same value of number of particle (N), volume (V) and energy (E) is called a microcanonical ensemble. In classical thermodynamic sense, each system in microcanonical ensemble is like an isolated system. Hence, we can imagine a microcanonical ensemble in which each system (member) is separated by rigid, impermeable, adiabatic walls so that neither energy nor material particles can flow from one system to the other.
> **Canonical ensemble**: If all the members (systems) of an ensemble have the same value of N, V and T, then it is called a canonical ensemble. It can be set up by imagining rigid but conducting walls separating the different systems through which energy can pass but not the particles. Due to the conducting walls, each member of the ensemble has the same temperature, but may not have the same energy. Thus each system in a canonical ensemble is like a closed system in the thermodynamic sense.
> **Grand canonical ensemble**: In a grand canonical ensemble, for each system, V, T and μ (chemical potential) for each component is same. In thermodynamic sense, each member of a grand canonical ensemble is an open system such that matter can flow between the systems and the composition of each member may fluctuate.

Self Assessment Questions:

SAQ-1. Identify the Maxwellons, Bosons and Fermions from the following

    (i)   Electron   (ii)   Protons   (iii) ^4_2He

    (iv) ^2D (v)   a gas at high temperature

SAQ-2. If all the members of an ensemble have the same value of N, V and T, then it is called

    (Tick the correct option)

    (i) Microcanonical ensemble (ii) Canonical ensemble (iii) grand canonical ensemble

SAQ-3. In MB statistics, which of the following statements is correct?

    (i) Particles are identical   (ii) Particles are distinguishable

    (iii) Particles are indistinguishable   (iv) Particles are identical but indistinguishable

SAQ-4. Any number of particles can be accommodated in an energy state for

    (i)   MB statistics only.   (ii)BE statistics only

    (iii)   FD statistics only   (iv) Both MB and BE statistics

5.5 Macrostate, Microstate, Thermodynamic Probability:

In thermodynamics, a system is characterized by specific values of density, pressure, temperature and other measurable quantities. The specified values determine the state of the system as whole which is called a macrostate. However, for the same density, temperature, and so on, the particles of the system can be distributed in various energy levels by different ways. Each given distribution of particle is called a microstate of the system. The thermodynamic probability (denoted by *W*) is equal to the number of micro-states which realize a given macrostate.

Alternatively, each physically distinct ways of assigning the particles/molecules in different available energy levels is called thermodynamic probability (*W*).

5.6 Distributions of Particles:

The number of particles in a given energy level is called occupation number (n_i). A set of occupation numbers represents an instantaneous distribution of a macrostate.

To describe a distribution of the particles over their possible energy states, we specify the states, $\mathcal{E}_1, \mathcal{E}_2, \mathcal{E}_3 \ldots\ldots, \mathcal{E}_i, \ldots\ldots \mathcal{E}_r$; beginning with the lowest state, $\mathcal{E}_1$ first and ending with the highest state $\mathcal{E}_r$. We then arbitrarily assign n_1 particles to state $\mathcal{E}_1$, n_2 to $\mathcal{E}_2$ and so on, i.e.

Energy state No.→	1	2	3	…………...	i	…………...	r
Energy →	$\mathcal{E}_1$	$\mathcal{E}_2$	$\mathcal{E}_3$	…………...	$\mathcal{E}_i$	…………...	$\mathcal{E}_r$
Number of particles →	n_1	n_2	n_3	…………...	n_i	…………...	n_r

Thermodynamic probability (*W*) is equal to the number of ways of observing a distribution with say n_1 atoms in $\mathcal{E}_1$, n_2 in $\mathcal{E}_2$ . . . n_i in $\mathcal{E}_i$ and so on. We are concern for the distribution with highest value of *W*, called most probable distribution. However, to complete the enumeration we must add the restrictions-

(i) $\displaystyle\sum_{i=1}^{i=r} n_i = N = $ total number of particle is constant; and

(ii) $\displaystyle\sum_{i=1}^{i=r} n_i \varepsilon_i = E = $ total energy of the system is constant.

5.6.1 Distribution of Maxwell-Boltzmann particles: Maxwellons are distinguishable particles. Although any number of maxwellons can occupy in any energy level, sometimes we may forced few restrictions during distribution. There may be five cases for the distribution of maxwellons. Each situation is illustrated by simple example(s) which leads to a general formula for thermodynamic probability.

Case I: No restriction, i.e. any number of particles may occupy the same energy level.

Illustration-1: Find the nos. of ways of distributing 2 particles in 2 energy levels.

Solution: There are three distributions *viz* (1, 1), (2, 0) and (0, 2) as follows-

Distribution-I   Distribution-II   Distribution-III

However, since the particles are distinguishable (say A & B) the distribution-I can be achieved in two ways as follows-

Distribution-I   Distribution-II   Distribution-III

$W_I = 2$ $W_{II} = 1$ $W_{III} = 1$

Hence, the total numbers of ways = 4

Illustration-2: In how many ways may N identical, distinguishable objects be placed in M different containers with no limitation on the number per container?

Solution: Because no limit exists, each object can be placed in any of the M containers. Therefore,

$$W = M^N \dots\dots\dots\dots\dots (E\text{-}5.1)$$

In general, the total numbers of ways of distributing N particles in M energy levels is given by $(M)^N$.

Case II: Restriction is given that only one particle may occupy in an energy level.

Illustration-3: Find the nos. of ways of distributing 2 particles in 3 energy levels such that only one particle can occupy in any energy level.

Solution:

Distribution-I   Distribution-II   Distribution-III

$W_I = 2$ $W_{II} = 2$ $W_{III} = 2$

Hence, the total numbers of ways = 6

Illustration-4: In how many ways may N identical, distinguishable objects be placed in M different containers with a limit of one object per container?

Solution: The limitation of one object per container requires $N \leq M$. The first object may be placed in any of M available containers, the second in $(M-1)$ available containers, and so on. Hence the number of ways for this case becomes

$$W = M (M-1) (M-2) \ldots\ldots\ldots (M-N+1)$$

Or $W = \dfrac{M!}{(M-N)!}$

In general, the total numbers of ways of distributing N particles in M energy levels such that only one particle can occupy in any energy level is given by –

$$^M P_N = \dfrac{M!}{(M-N)!} \ldots\ldots\ldots\ldots\ldots..(E\text{-}5.2)$$

Case-III: The distribution is given.

Illustration-5: Find the nos. of ways of distributing 3 particles in 2 energy levels for the distribution (2, 1).

Solution: Let the particles be A, B and C (distinguishable)
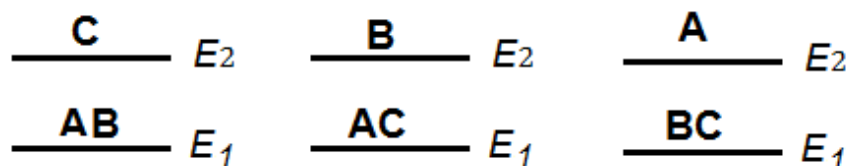
Hence, the total numbers of ways = 3

Illustration-6: In how many ways may N identical, distinguishable objects be placed in M different containers such that the ith container holds exactly n_i objects?

Solution: The total number of permutations for N objects is $N!$ However, within each container, permutations are irrelevant as we are concerned only with their number rather than

their identity. Hence, the number of permutations, $N!$, overcounts the number of ways by the number of permutations, $n_i!$, for each container. Therefore, the number of ways is-

$$W = \frac{N!}{n_1!.n_2!.n_3!........n_i!......} = \frac{N!}{\prod n_i!}$$

In general, the total numbers of ways of distributing N particles in M energy levels with the distribution (n_1, n_2, n_3, ……… n_i, …….) is given by –

$$W = \frac{N!}{n_1!.n_2!.n_3!........n_i!......} = \frac{N!}{\prod n_i!} \qquad\ldots\ldots\ldots\ldots\ldots\ldots\ldots..(E\text{-}5.3)$$

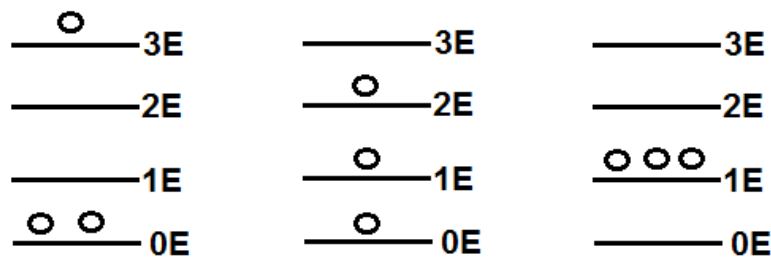Remember that, $\sum n_i = n_1 + n_2 + n_3 + ... + n_i + ... = N$

Illustration-7: Find the nos. of ways of distributing 10 particles in 5 energy levels for the distribution (4, 3, 0, 2, 1).

Solution: $W = \dfrac{10!}{4!.3!.0!.2!.1!}$

Case-IV: Condition Given (Total energy is given)

Illustration-8. Find the nos. of ways of distributing 3 particles (distinguishable) having total energy of 3E.

Solution:

Distribution-I   Distribution-II   Distribution-III

$$W_I = \frac{3!}{2!.0!.0!.1!} = 3 \qquad W_{II} = \frac{3!}{1!.1!.1!.0!} = 6 \qquad W_{III} = \frac{3!}{0!.3!.0!.0!} = 1$$

Hence, the total numbers of ways $W = W_I + W_{II} + W_{III} = 3 + 6 + 1 = 10$

Here, distribution-II is the most probable distribution.

Probabilty for distribution-I, $P_I = 3/10$

Similarly, $P_{II} = 6/10$ (Maximum value) and $P_{III} = 1/10$

Hence the total probability, $P = P_I + P_{II} + P_{III} = 1$

(**Do Yourself**: Draw all possible microstates for the above Distribution-I & II.)

Case-V: Condition Given; distribution and degeneracies of each energy level are given.

In general, the total numbers of ways of distributing N distinguishable particles having the distribution (n_1, n_2, n_3, ……… n_i, …….) in various energy levels ($\mathcal{E}_1$, $\mathcal{E}_2$, $\mathcal{E}_3$, ……… $\mathcal{E}_i$, …….) with degeneracy (g_1, g_2, g_3, ……… g_i, …….) is given by- {using equation (*E-5.1* &*E-5.3*)}

$$W = N!.\frac{(g_1)^{n_1}}{n_1!}.\frac{(g_2)^{n_2}}{n_2!}.\frac{(g_3)^{n_3}}{n_3!}\text{...........} = N!\prod\frac{(g_i)^{n_i}}{n_i!}\text{...............}(E\text{-}5.4)$$

Equation (*E-5.4*) and (*E-5.3*) are the two forms of Maxwell-Boltzmann's distribution with and without having degeneracy respectively.

5.6.2 Distribution of Bosons: Bosons are **i**ndistinguishable particles, any number of particles may occupy the same energy level. Here, we may have two cases depending upon with and without having degeneracy.

Case-I: Without degeneracy of the energy levels.

Illustration-9: Find the nos. of ways of distributing 2 indistinguishable particles in 2 energy levels.
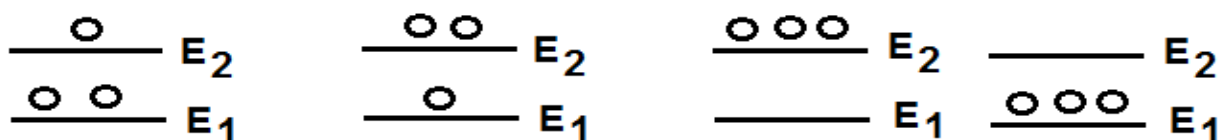
Solution: There are three distributions *viz* (1, 1), (2, 0) and (0, 2) as follows-
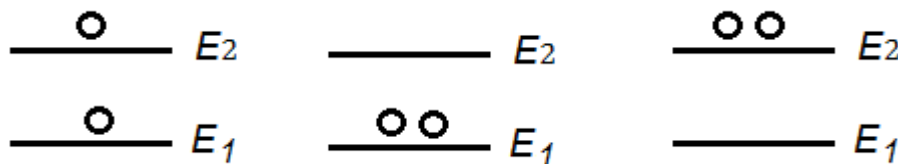
Since the particles are indistinguishable hence, the total numbers of ways $W = 3$

Illustration-10: Find the nos. of ways of distributing 3 indistinguishable particles in 2 energy levels.

Solution: There are four distributions *viz* (2, 1), (1, 2), (0, 3) and (3, 0) as follows-

Since the particles are indistinguishable hence, the total numbers of ways $W = 4$

Illustration-11: In how many ways may N identical, indistinguishable objects be placed in M different containers with no limitation on the number per container?

Solution: This fully unconstrained case (indistinguishable objects, no limitation) mandates a totally different approach .We begin by initially assuming distinguishable objects labeled 1, 2, 3. . . N. Let us now arrange these N objects in a row, with the M containers identified and separated by (*M-1*) partitions. As an example, the distribution

$$1, 2, 3 \mid 4, 5 \mid 6 \mid . . .\mid N - 1, N$$

specifies that objects 1, 2, and 3 are in the first container, objects 4 and 5 are in the second container, object 6 is in the third container, and so on. Now, regardless of their actual arrangement, the maximum number of rearrangements among the N objects and $M-1$ partitions is $(N + M - 1)!$. However, interchanging the partitions produces no new arrangements; thus, we have overcounted by a factor of $(M - 1)!$. Similarly, because the N objects are actually indistinguishable, we have again overcounted by a factor of $N!$. Therefore, the number of ways for this case becomes

$$W = \frac{(N + M - 1)!}{N!.(M - 1)!}$$

In general, the total numbers of ways of distributing N indistinguishable particles in M energy levels is given by $W = \dfrac{(N + M - 1)!}{N!.(M - 1)!}$ …………………………. (***E-5.5***)

Illustration-12: Find the nos. of ways of distributing 20 particles having integral nuclear spin in 15 energy levels.

Solution: $W = \dfrac{(20 + 15 - 1)!}{20!.(15 - 1)!}$

Case II: If degeneracy is given:

In general, the total numbers of ways of distributing N particles having the distribution (n_1, n_2, n_3, ……… n_i, …….) in various energy levels ($\mathcal{E}_1$, $\mathcal{E}_2$, $\mathcal{E}_3$, ……… $\mathcal{E}_i$, …….) with degeneracy (g_1, g_2, g_3, ……… g_i, …….) is given by-

$$W = \prod \frac{(n_i + g_i - 1)!}{n_i!.(g_i - 1)!} \quad \text{…………………………. (***E-5.6***)}$$

Note: For the ith energy level having degeneracy g_i, occupying n_i indistinguishable particles,

$$W_i = \frac{(n_i + g_i - 1)!}{n_i!.(g_i - 1)!}$$

5.6.3 **Distribution of Fermions:** Fermions are indistinguishable particle, only one particle may occupy in a given energy level. We may have two cases depending upon with and without having degeneracy.

Case-I: Without degeneracy of the energy levels

Illustration-13: Find the nos. of ways of distributing 2 Fermions in 3 energy level*s*.

Solution: There are three distributions *viz* (1, 1, 0), (1, 0, 1) and (0, 0, 1) as follows-
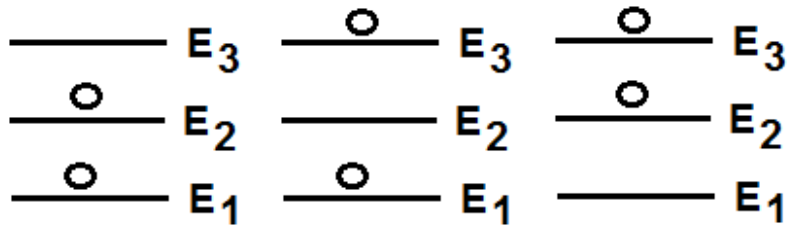
Since the particles are indistinguishable hence, the total numbers of ways $W = 3$

Illustration-14: In how many ways may N identical, indistinguishable objects be placed in M different containers with a limit of one object per container?

Solution: The limitation of one object per container requires $N \le M$. The first object may be placed in any of M available containers, the second in $(M-1)$ available containers, and so on. Hence the number of ways becomes

$$W_1 = M\,(M-1)\,(M-2)\,\ldots\ldots\ldots\,(M-N+1) = \frac{M!}{(M-N)!}$$

For indistinguishable objects, however, any rearrangement among the N objects is unrecognizable. Hence, W_1 overcounts the number of ways for indistinguishable objects by a factor of $N!$. Therefore, $W = \dfrac{M!}{N!.(M-N)!}$

In general, the total numbers of ways of distributing N indistinguishable particles in M energy levels such that only one particle can occupy in an energy level is given by-

$$W = {}^M C_N = \frac{M!}{N!.(M-N)!} \ldots\ldots\ldots\ldots\ldots (\textit{E-5.7})$$

Here, it should be noted that, $M \ge N$. If $M = N$, then $W = 1$.

Illustration-15: Find the nos. of ways of distributing 10 particles, whose wave functions are antisymmetric in nature, in 15 energy levels.

Solution: $W = {}^{15}C_{10} = \dfrac{15!}{10!.(15-10)!}$

Case II: If degeneracy is given:

In general, the total numbers of ways of distributing N Fermions having the distribution (n_1, n_2, n_3, ……… n_i, …….) in various energy levels ($\mathcal{E}_1$, $\mathcal{E}_2$, $\mathcal{E}_3$, ……… $\mathcal{E}_i$, …….) with degeneracy (g_1, g_2, g_3, ……… g_i, …….) is given by-

$$W = \prod \frac{g_i!}{n_i!.(g_i - n_i)!} \dots\dots\dots\dots\dots\dots (\textbf{\textit{E-5.8}})$$

Note: For the ith energy level having degeneracy g_i, occupying n_i indistinguishable particles,

$$W_i = \frac{g_i!}{n_i!.(g_i - n_i)!}$$

Here, it should be noted that, $g_i \geq n_i$. If, $g_i = n_i$, then, $W = 1$.

Note: if you have not given any characteristics [distinguishable/indistinguishable (wave function, nuclear spins)] of the particles, then always assume them as distinguishable.

Self Assessment Oestions:

SAQ-5. In how many ways two indistinguishable balls may be placed in 3 containers

   (i)   Without any restrictions
   (ii)   ball can Only one be in one box
   (iii)   The balls are distinguishable

SAQ-6. Define Thermodynamic Probability. For three distinguishable particles in three boxes

   (i)   Write & draw all possible distributions
   (ii)   Calculate thermodynamic probability for each distribution
   (iii)   Find out the most probable distribution

5.7 Relationship between Entropy and Thermodynamic Probability:

From the second law of thermodynamics, we have come across a very important state function, called the entropy S, which is the measure of disorder in a system. We also know that, a thermally isolated system in its equilibrium state has maximum value of entropy. According to statistical mechanics too, for such a system in equilibrium is the most probable one in the sense that it corresponds to maximum thermodynamic probability, W. Therefore, both entropy and thermodynamic probability of a system are maximum in the equilibrium state. Thus we can expect a functional relationship between entropy (S) and the thermodynamic probability (W) which can be expressed as-

$$S = f(W) \dots\dots\dots\dots\dots\dots (\textbf{\textit{E-5.9}})$$

Let us consider a system with total entropy S and total probability W, which is obtained by combining two non-interacting systems with entropy S_1 and S_2 and the respective thermodynamic probabilities w_1 and w_2.

Since, entropy is an additive property and thermodynamic probability is a multiplicative property, we have-

$$S = S_1 + S_2 \ldots\ldots\ldots\ldots\ldots\ldots (E\text{-}5.10)$$

$$W = w_1.w_2 \ldots\ldots\ldots\ldots\ldots\ldots (E\text{-}5.11)$$

Combining the above equations, we get-

$$f(W) = S_1 + S_2$$

or $\qquad f(W) = f(w_1.w_2) = f(w_1) + f(w_2) \ldots\ldots\ldots\ldots\ldots (E\text{-}5.12)$

Differentiating equation ($E\text{-}5.11$), we have

$$dW = w_1.dw_2 + w_2.dw_1$$

If w_1 is constant, then $dw_1 = 0$, we have

$$dw_2 = \frac{dW}{w_1} \ldots\ldots\ldots\ldots\ldots\ldots (E\text{-}5.13)$$

Similarly, if w_2 is constant, then $dw_2 = 0$, we have

$$dw_1 = \frac{dW}{w_2} \ldots\ldots\ldots\ldots\ldots\ldots (E\text{-}5.14)$$

Differentiating equation ($E\text{-}5.12$) w.r.t. w_2, keeping w_1 constant, we have

$$\frac{d\{f(W)\}}{dw_2} = 0 + \frac{d\{f(w_2)\}}{dw_2}$$

$$\frac{d\{f(W)\}}{dW}.w_1 = \frac{d\{f(w_2)\}}{dw_2} \ldots\ldots\ldots\ldots\ldots (E\text{-}5.15)$$

Now differentiating equation ($E\text{-}5.15$) w.r.t. w_1, we get,-

$$\frac{d\{f(W)\}}{dW}.\frac{dw_1}{dw_1} + w_1.\frac{d}{dw_1}\left[\frac{d\{f(W)\}}{dW}\right] = 0$$

$$\Rightarrow \frac{d\{f(W)\}}{dW} + w_1.w_2\left[\frac{d^2\{f(W)\}}{dW^2}\right] = 0$$

$$\Rightarrow f'(W) + W.f''(W) = 0$$

$$\Rightarrow \frac{f''(W)}{f'(W)} = -\frac{1}{W}$$

Where prime ($'$) denotes differentiation w.r.t. W. On integration we have-

$$\Rightarrow \ln f'(W) = -\ln W + \ln C$$

Where, C is a constant. We can write it as-

$$\Rightarrow f'(W) = \frac{C}{W}$$

Integrating again, w.r.t. W, we obtain-

$$\Rightarrow f(W) = C\ln W + W_0$$

Using equation (*E-5.9*) we get,-

$$S = C\ln W + W_0$$

From the third law of thermodynamics, we know that the entropy of a system in the fully ordered state ($W=1$) is zero. Therefore $W_0 = 0$, and the entropy is related to the thermodynamic probability by the expression-

$$S = C\ln W \dots\dots\dots\dots (\textit{E-5.16})$$

This is the famous Boltzmann relationship between entropy and thermodynamic probability. This equation provides a bridge between macroscopic (thermodynamics) and microscopic (Statistical mechanics) view-point. The constant C is identified with the Boltzmann constant k_B ($=1.38\times10^{-23}JK^{-1}$).

Identification of the Constant C

Let us consider a vessel which is divided into two parts by mean of a partition, one portion of volume V_1 and the total volume V_2 (*Figure-5.1*). If one molecule of ideal gas is introduce in the vessel, then the thermodynamic probability of finding the molecule the in the portion with volume V_1 is equal to $\frac{V_1}{V_2}$. Now, if we there are two molecules in the vessel, then the thermodynamic probability will be, $\left[\frac{V_1}{V_2}\right]^2$. Similarly, if we have one mole ideal gas

molecules, then the probability, $w_1 = \left[\dfrac{V_1}{V_2}\right]^N$. Now, if we remove the partition, then probability of finding one mole molecules in the entire volume V_2 is $w_2 = 1$.
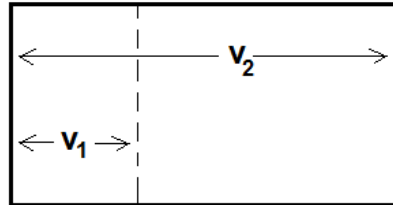

Figure-5.1

Using equation (***E-5.16***), we have-

$$\Delta S = S_2 - S_1 = C \ln \frac{w_2}{w_1}$$

$$\Delta S = C \ln \left[\frac{V_2}{V_1}\right]^N \dots\dots\dots\dots \text{(E-5.17)}$$

Again, the expression for the change of entropy of one mole of a perfect gas on isothermal expansion from volume V_1 to V_2 is -

$$\Delta S = R \ln \frac{V_2}{V_1} = Nk_B \ln \frac{V_2}{V_1} = k_B \ln \left[\frac{V_2}{V_1}\right]^N \dots\dots\dots\dots \text{(E-5.18)}$$

Where R is the gas constant and k_B is the Boltzmann constant k_B (=1.38x10^{-23}JK^{-1}). Comparing equation (***E-5.17***) and (***E-5.18***), we get, $C = k_B$. Hence, the entropy and thermodynamic probability are related as-

$$S = K \ln W \dots\dots\dots\dots\dots\dots\dots \text{(E-5.19)}$$

5.8 Stirling Approximation:

In the study of statistical mechanics, we usually consider a system consisting of very large number of particles. If the number is represented by N, the calculation of *lnN*! becomes very laborious. Hence a simple approximation is used for the value of *lnN*! which is called **Stirling Approximation.**

$$ln\ N! = N\ lnN - N \dots\dots\dots\dots \text{(E-5.20)}$$

5.8.1 Derivation of Stirling Formula:

We know that,

$$N! = N \cdot (N\text{-}1) \cdot (N\text{-}2) \cdot (N\text{-}3)\ldots\ldots\ldots\ldots 3 \cdot 2 \cdot 1$$

or, $N! = 1 \cdot 2 \cdot 3 \ldots\ldots\ldots\ldots(N\text{-}2) \cdot (N\text{-}1) \cdot N$

$\therefore$ $lnN! = ln1 + ln2 + ln3 + \ldots\ldots\ldots\ldots + ln(N\text{-}2) + ln(N\text{-}1) + lnN = \displaystyle\sum_{x=1}^{N} \ln x$

In the above summation, except for the first few terms whose values are small, as x increases and attains large values, the increase in the value of lnx with the increase in the value of x by unity is very small. Hence the summation can be approximately treated as continuous and replaced by integration.

$$\ln N! = \int_{x=1}^{x=N} \ln x \, dx$$

$$\ln N! = \left[x \ln x\right]_{1}^{N} - \int_{x=1}^{x=N} x \cdot \frac{1}{x} \, dx = N \ln N - N$$

Hence for large values of N

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

This is the Stirling formula.

5.9 The Maxwell-Boltzmann distribution law:

Consider a system composed of N distinguishable, non-interacting particles. Let out of these N particles $n_1, n_2, n_3, \ldots\ldots n_i \ldots$ particles are to be distributed in energy levels $E_1, E_2, \ldots, E_i, \ldots\ldots$ respectively and these energy levels have $g_1, g_2, \ldots, g_i, \ldots\ldots\ldots$ number of quantum states correspondingly. i.e.,

Energy state No.→	1	2	3	…………	i	…………	r
Energy →	$\mathcal{E}_1$	$\mathcal{E}_2$	$\mathcal{E}_3$	…………	$\mathcal{E}_i$	…………	$\mathcal{E}_r$
Degeneracy→	g_1	g_2	g_3	…………	g_i	…………	g_r
Number of particles →	n_1	n_2	n_3	…………	n_i	…………	n_r

Since the total energy E and total number of particles N are constant for the system, we can write

$$\sum_{i=1}^{i=r} n_i = N \; ; \ldots\ldots\ldots\ldots (\boldsymbol{E\text{-}5.21})$$

and, $$\sum_{i=1}^{i=r} n_i \varepsilon_i = E \ \dots\dots\dots\dots(E\text{-}5.22)$$

The number of ways in which the groups of particles $n_1, n_2, n_3, \dots\dots n_i\dots$ could be chosen from N particles is-

$$W_1 = \frac{N!}{n_1!.n_2!.n_3!\dots\dots.n_i!\dots\dots} = \frac{N!}{\prod_{i=1}^{i=r} n_i!} \ \dots\dots\dots (E\text{-}5.23)$$

Now, n_i particles can be distributed in g_i states in $(g_i)^{n_i}$ ways. Considering all the values of i, total number of arrangement would be-

$$W_2 = \prod_{i=1}^{i=r} (g_i)^{n_i} \ \dots\dots\dots\dots. (E\text{-}5.24)$$

Therefore, the total number of ways W by which all the N particles could be distributed among the quantum states is-

$$W = W_1 W_2 = \frac{N!}{\prod_{i=1}^{i=r} n_i!} \prod_{i=1}^{i=r} (g_i)^{ni} = N! \prod \frac{(g_i)^{n_i}}{n_i!} \ \dots\dots\dots\dots (E\text{-}5.4)$$

This is the Maxwell-Boltzmann distribution law for N distinguishable particles. However, we are interested in finding a distribution that has the maximum value of W.

Now taking the natural logarithm on both sides of equation ($E\text{-}5.4$) we get,

$$\ln W = \ln N! + \sum_{i=1}^{i=r} n_i \ln g_i - \sum_{i=1}^{i=r} \ln n_i! \ \dots\dots\dots\dots (E\text{-}5.25)$$

Applying Stirling approximation (i.e., $ln\ x! = x\ ln\ x - x$, where, x is very large), we get

$$\ln W = N \ln N - N + \sum_{i=1}^{i=r} n_i \ln g_i - \sum_{i=1}^{i=r} (n_i \ln n_i - n_i)$$

$\therefore \qquad \ln W = N \ln N - N + \sum_{i=1}^{i=r} n_i \ln g_i - \sum_{i=1}^{i=r} (n_i \ln n_i) + N$

$\therefore \qquad \ln W = N \ln N + \sum_{i=1}^{i=r} n_i \ln g_i - \sum_{i=1}^{i=r} (n_i \ln n_i) \ \dots\dots\dots\dots\dots (E\text{-}5.26)$

Now differentiating both sides we get, (Note that, N and g_i are constant)

$$d(\ln W) = 0 + \sum_{i=1}^{i=r} n_i d(\ln g_i) + \sum_{i=1}^{i=r} (\ln g_i).dn_i - \sum_{i=1}^{i=r} n_i d(\ln n_i) - \sum_{i=1}^{i=r} (\ln n_i)dn_i$$

$$\therefore \quad d(\ln W) = 0 + 0 + \sum_{i=1}^{i=r} (\ln g_i).dn_i - \sum_{i=1}^{i=r} n_i . \frac{1}{n_i} .dn_i - \sum_{i=1}^{i=r} (\ln n_i)dn_i$$

$$\therefore \quad d(\ln W) = 0 + 0 + \sum_{i=1}^{i=r} (\ln g_i).dn_i - 0 - \sum_{i=1}^{i=r} (\ln n_i)dn_i$$

$$\therefore \quad d(\ln W) = \sum_{i=1}^{i=r} (\ln g_i).dn_i - \sum_{i=1}^{i=r} (\ln n_i)dn_i \dots\dots\dots\dots\dots(E\text{-}5.27)$$

For the most probable distribution, $d(\ lnW_{max}) = 0$; Therefore-

$$d(\ln W) = \sum_{i=1}^{i=r} (\ln g_i).dn_i - \sum_{i=1}^{i=r} (\ln n_i)dn_i = 0$$

$$\therefore \quad \sum_{i=1}^{i=r} (\ln \frac{g_i}{n_i}).dn_i = 0 \dots\dots\dots\dots\dots(E\text{-}5.28)$$

Since the system is in equilibrium, total number of particle and the total energy of the system are constant. So, from equation (*E-5.21*) & (*E-5.22*) are now differentiated to account for the imposed constraints during the optimization process. The results are

$$dN = \sum_{i=1}^{i=r} dn_i = 0 \dots\dots\dots\dots\dots\dots (E\text{-}5.29)$$

$$dE = \sum_{i=1}^{i=r} \varepsilon_i dn_i = 0 \dots\dots\dots\dots\dots\dots (E\text{-}5.30)$$

Multiplying equation (*E-5.29*) by α and (*E-5.30*) by β and then subtracting from equation (*E-5.28*), to guarantee independent values of n_i. This is called Lagrange's method. Thus, we get-

$$\sum_{i=1}^{i=r} \left[\ln \frac{g_i}{n_i} - \alpha - \beta\varepsilon_i \right].dn_i = 0 \dots\dots\dots\dots\dots (E\text{-}5.31)$$

where, the unknowns α and β are the so-called Lagrange multipliers, and the entire expression is set equal to zero to identify the most probable macrostate.

Since dn_i's are independent of one another, the above equation holds only if,

$$\left[\ln \frac{g_i}{n_i} - \alpha - \beta\varepsilon_i \right] = 0$$

$$\therefore \quad \ln \frac{g_i}{n_i} = \alpha + \beta \varepsilon_i$$

$$\therefore \quad n_i = \frac{g_i}{e^{\alpha + \beta \varepsilon_i}}$$

$$\therefore \quad n_i = g_i \, e^{-\alpha - \beta \varepsilon_i} \quad \text{……………..} \ (E\text{-}5.32)$$

Equation (**E-5.32**) is the Boltzmann distribution law for most probable distribution for a macrostate. It gives the occupation numbers of the molecular energy levels for the most probable distribution in terms of energies ε_i, the degeneracy g_i and the Lagrange's undetermined multipliers α & β.

5.9.1 Evaluation of the Lagrange's undetermined Multipliers:

Evaluation of α:

According to Boltzmann law,- $n_i = g_i \, e^{-\alpha - \beta \varepsilon_i}$ .... (**E-5.32**)

$$\therefore \quad \sum_{i=1}^{i=r} n_i = \sum_{i=1}^{i=r} g_i \, e^{-\alpha} \cdot e^{-\beta \varepsilon_i}$$

Since, $\sum_{i=1}^{i=r} n_i = N$, we can write $e^{-\alpha} = \dfrac{N}{\sum\limits_{i=1}^{i=r} g_i \cdot e^{-\beta \varepsilon_i}} = \dfrac{N}{f}$ ……………(**E-5.33**)

Where, the term $f = \sum\limits_{i=1}^{i=r} g_i \cdot e^{-\beta \varepsilon_i}$ is an important quantity in statistical mechanics, known as partition function. When molecules are considered, it is called molecular partition function.

Evaluation of β:

Combining equation (**E-5.32**) and (**E-5.33**), we get-

$$n_i = \frac{N g_i \, e^{-\beta \varepsilon_i}}{f}$$

$$\frac{n_i}{N} = \frac{g_i \, e^{-\beta \varepsilon_i}}{f} \quad \text{……………….} \ (E\text{-}5.34)$$

This equation gives the fraction of molecules in the ith energy level with energy ε_i.

The Maxwell-Boltzmann distribution law for N distinguishable particles is-

$$W = N! \prod \frac{(g_i)^{n_i}}{n_i!} \quad \ldots\ldots\ldots\ldots(\textbf{\textit{E-5.4}})$$

Now taking the natural logarithm on both sides and applying Stirling approximation, we get,

$$\ln W = \ln N! + \sum_{i=1}^{i=r} n_i \ln g_i - \sum_{i=1}^{i=r} \ln n_i!$$

$$\ln W = N \ln N - N + \sum_{i=1}^{i=r} n_i \ln g_i - \sum_{i=1}^{i=r} (n_i \ln n_i - n_i)$$

$$\therefore \quad \ln W = N \ln N - N + \sum_{i=1}^{i=r} n_i \ln g_i - \sum_{i=1}^{i=r} (n_i \ln n_i) + N$$

$$\therefore \quad \ln W = N \ln N + \sum_{i=1}^{i=r} n_i \ln g_i - \sum_{i=1}^{i=r} (n_i \ln n_i)$$

$$\therefore \quad \ln W = N \ln N - \sum_{i=1}^{i=r} n_i \ln \frac{n_i}{g_i} \quad \ldots\ldots\ldots\ldots\ldots\ldots \textbf{(E-5.26)}$$

Putting the value of $\dfrac{n_i}{g_i}$ from equation (**E-5.34**), we get-

$$\ln W = N \ln N - \sum_{i=1}^{i=r} n_i (\ln N - \beta \varepsilon_i - \ln f)$$

$$\therefore \quad \ln W = N \ln N - N \ln N + \beta E + N \ln f = \beta E + N \ln f \quad \ldots\ldots\ldots..(\textbf{\textit{E-5.35}})$$

Since, $S = k \ln W$, putting the value of *lnW*, we get-

$$S = k\beta E + Nk \ln f \quad \ldots\ldots\ldots\ldots\ldots \textbf{(E-5.36)}$$

Now differentiating equation (**E-5.36**) w.r.t. *E* at constant *V,* we get-

$$\left(\frac{\partial S}{\partial E}\right)_V = k\beta + kE\left(\frac{\partial \beta}{\partial E}\right)_V + Nk \frac{\partial \ln f}{\partial f} \cdot \frac{\partial f}{\partial \beta} \left(\frac{\partial \beta}{\partial E}\right)_V \quad \ldots\ldots\ldots\ldots \textbf{(E-5.37)}$$

Since, $f = \sum_{i=1}^{i=r} g_i \cdot e^{-\beta \varepsilon_i}$

$$\therefore \quad \frac{\partial f}{\partial \beta} = -\sum_{i=1}^{i=r} g_i . \varepsilon_i \cdot e^{-\beta \varepsilon_i} = -\sum_{i=1}^{i=r} \varepsilon_i . \frac{n_i f}{N} = -\frac{Ef}{N} \quad \ldots\ldots\ldots\ldots\ldots\ldots \textbf{(E-5.38)}$$

From equation (**E-5.37**) and (**E-5.38**) we get-

$$\therefore \quad \left(\frac{\partial S}{\partial E}\right)_V = k\beta \quad \dots\dots\dots\dots\dots\dots \text{ (}\textbf{\textit{E-5.39}}\text{)}$$

From the 1st and 2nd law of thermodynamics,

$$dq = dE + pdV = TdS$$

$$\therefore \quad \left(\frac{\partial S}{\partial E}\right)_V = \frac{1}{T} \quad \dots\dots\dots\dots\dots\dots \text{ (}\textbf{\textit{E-5.40}}\text{)}$$

Comparing equation (**E-5.39**) and (**E-5.40**) we get-

$$\beta = \frac{1}{kT} \quad \dots\dots\dots\dots\dots\dots \text{ (}\textbf{\textit{E-5.41}}\text{)}$$

Thus, the Maxwell-Boltzmann distribution law becomes as-

$$n_i = \frac{Ng_i e^{-\frac{\varepsilon_i}{kT}}}{f} = \frac{Ng_i e^{-\frac{\varepsilon_i}{kT}}}{\sum g_i e^{-\frac{\varepsilon_i}{kT}}} \quad \dots\dots\dots\dots\dots \text{ (}\textbf{\textit{E-5.42}}\text{)}$$

5.9.2 <u>Maxwell-Boltzmann distribution law and the population ratio:</u>

The equation (**E-5.42**) is helpful in calculating the ratio of the populations, i.e., the ratio of the number of particles in any two energy levels ε_i and ε_j. Thus,

$$\frac{n_i}{n_j} = \frac{g_i}{g_j} \cdot e^{-\frac{(\varepsilon_i - \varepsilon_j)}{kT}}$$

Or, $$\frac{n_i}{n_j} = \frac{g_i}{g_j} \cdot e^{\frac{(\varepsilon_j - \varepsilon_i)}{kT}} \quad \dots\dots\dots\dots\dots \text{ (}\textbf{\textit{E-5.43}}\text{)}$$

Since, $\beta = \frac{1}{kT}$ is positive and if $\varepsilon_j > \varepsilon_i$, then $n_i > n_j$; i.e., the lower energy level is more populated than the higher energy level. When T increases (i.e. β decreases), the population in the higher energy levels goes on increasing.

Self Assessment Questions

SAQ-7. Calculate the ratio of population at (i) $25°C$ & (ii) $250°C$ between ground and 1st excited energy levels of a molecule separated by 10 *KJmol^{-1}*.

SAQ-8. If n_i is the number of identical and indistinguishable particles in the 'i' th energy state with degeneracy g_i then M-, B-E and F-D statistics will gives identical results if

   (i) $n_i = g_i$ (ii) $n_i << g_i$ (iii) $n_i >> g_i$ (iv) independent on the ratio $\dfrac{n_i}{g_i}$

SAQ- 9. The ratio of the molecules in energy levels depends on
   (i)   their energy separation (ΔE) only   (ii)   Temperature of the system only
   (iii)   both ΔE and T   (iv)   does not depends on ΔE and T

5.10 Partition Function:

According to Boltzmann law,-

$$n_i = g_i\, e^{-\alpha - \beta \varepsilon_i} = g_i\, e^{-\alpha} \cdot e^{-\beta \varepsilon_i} \quad .... \textbf{\textit{(E-5.32)}}$$

$$\therefore \qquad \sum n_i = N = \sum g_i\, e^{-\alpha} \cdot e^{-\beta \varepsilon_i}$$

$$\therefore \qquad \frac{n_i}{N} = \frac{g_i\, e^{-\beta \varepsilon_i}}{\sum g_i \cdot e^{-\beta \varepsilon_i}} \quad .... \textbf{\textit{(E-5.44)}}$$

We know that the term β $\left(\beta = \dfrac{1}{kT}\right)$ is a measure of temperature of the system, whereas the energy levels (ε_i's) are the characteristics of the system itself. Therefore the quantity $\sum g_i \cdot e^{-\beta \varepsilon_i}$ appearing in the above equation is a characteristic of the system. This is called the partition function which is an important quantity in statistical mechanics denoted by f. Therefore, the equation (ii) can be written as,-

$$\frac{n_i}{N} = \frac{g_i\, e^{-\beta \varepsilon_i}}{f} \quad .... (\textbf{\textit{E-5.34}})$$

Significance of Partition Function:

   (i)   Let us consider the ith state be the ground state so that $\varepsilon_i = 0$; where $n_i = n_0$ and let $g_0 = 1$. Then the Boltzmann law i.e., equation (**E-5.34**) becomes

$$\frac{n_0}{N} = \frac{1}{f}$$

$$\therefore \qquad f = \frac{N}{n_0}$$

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Therefore, the partition function can be defined as the ratio of the total number of particles to the number of particles in the ground level.

(ii)   Partition function indicates the mode of distribution of particles in various energy levels.

(iii)   'f' is a dimensionless quantity.

(iv)   The lowest value of 'f' is 1, at absolute zero when all the particles occupy in the ground state. As the temperature is raised, the particles will be populated in the higher energy levels and the value of 'f' increases accordingly. Therefore 'f' is a measure of the escaping tendency of the molecules from the ground state.

(v)   The higher is the value of 'f', the closer is the spacings of energy levels.

(vi)   When T = 0K, $f = 1$, i.e., only the ground level is populated; and when $T \rightarrow \infty$, then $f \rightarrow \infty$. Thus, partition function gives an indication of the average number of energy levels that are accessible to a molecule/particle at the temperature of the system.

5.10.1 Relation between Partition Function and Thermodynamic Functions:

Here, we will derive the relations between the molecular/particle partition function, f and the different thermodynamic functions.

(i)   **_Internal energy, E:_**
        The internal energy is given by

$$E = \sum_i n_i \varepsilon_i$$

Putting the value of n_i from the Boltzmann law, $\dfrac{n_i}{N} = \dfrac{g_i e^{-\beta \varepsilon_i}}{f}$ we get,

$$E = \sum_i \frac{N g_i \varepsilon_i e^{-\beta \varepsilon_i}}{f} = \frac{N}{f} \sum_i g_i \varepsilon_i e^{-\frac{\varepsilon_i}{kT}} \ldots\ldots\ldots(E\text{-}5.45)$$

Now, differentiating the expression partition function w.r.t. T, we get,

$$f = \sum g_i \cdot e^{-\frac{\varepsilon_i}{kT}}$$

$$\left(\frac{\partial f}{\partial T}\right)_V = \frac{1}{kT^2} \sum g_i \cdot \varepsilon_i \, e^{-\frac{\varepsilon_i}{kT}} \ldots\ldots\ldots\ldots\ldots(E\text{-}5.46)$$

From equation (**E-5.45**) and (**E-5.46**) we have

$$E = \frac{N}{f} kT^2 \left(\frac{\partial f}{\partial T}\right)_V = NkT^2 \left(\frac{\partial \ln f}{\partial T}\right)_V \ldots\ldots\ldots\ldots(E\text{-}5.47)$$

(ii)   **_Enthalpy, H:_**
        Similar to internal energy, the expression for enthalpy is given as-

$$H = \frac{N}{f}kT^2\left(\frac{\partial f}{\partial T}\right)_P = NkT^2\left(\frac{\partial \ln f}{\partial T}\right)_P \ \ldots\ldots\ldots(E\text{-}5.48)$$

Alternatively, enthalpy is given by, $H = E + PV$; so, substituting the value of E from equation (E-5.47), we get

$$H = NkT^2\left(\frac{\partial \ln f}{\partial T}\right)_V + PV \ \ldots\ldots\ldots\ldots\ldots\ldots(E\text{-}5.48a)$$

(iii) *Heat capacity at constant volume (C_V):*

By definition, $C_V = \left(\dfrac{\partial E}{\partial T}\right)_V$, therefore substituting the value of E we get,

$$C_V = \frac{\partial}{\partial T}\left[NkT^2\left(\frac{\partial \ln f}{\partial T}\right)\right]_V \ \ldots\ldots\ldots(E\text{-}5.49)$$

(iv) *Heat capacity at constant pressure (C_P):*

By definition, $C_P = \left(\dfrac{\partial H}{\partial T}\right)_P$, therefore substituting the value of E we get,

$$C_P = \frac{\partial}{\partial T}\left[NkT^2\left(\frac{\partial \ln f}{\partial T}\right)\right]_P \ \ldots\ldots\ldots(E\text{-}5.50)$$

(v) *Entropy, S*

The Maxwell-Boltzmann distribution law for N distinguishable particles is-

$$W = N!\prod\frac{(g_i)^{n_i}}{n_i!} \ \ldots\ldots\ldots\ldots(E\text{-}5.4)$$

Now taking the natural logarithm on both sides and applying Stirling approximation, we get,

$$\ln W = \ln N! + \sum_{i=1}^{i=r} n_i \ln g_i - \sum_{i=1}^{i=r} \ln n_i!$$

$$\ln W = N \ln N - N + \sum_{i=1}^{i=r} n_i \ln g_i - \sum_{i=1}^{i=r} (n_i \ln n_i - n_i)$$

$$\therefore \quad \ln W = N \ln N - N + \sum_{i=1}^{i=r} n_i \ln g_i - \sum_{i=1}^{i=r} (n_i \ln n_i) + N$$

$$\therefore \quad \ln W = N \ln N + \sum_{i=1}^{i=r} n_i \ln g_i - \sum_{i=1}^{i=r} (n_i \ln n_i)$$

$$\therefore \quad \ln W = N \ln N - \sum_{i=1}^{i=r} n_i \ln \frac{n_i}{g_i} \ \ldots\ldots\ldots\ldots\ldots(E\text{-}5.26)$$

Putting the value of $\dfrac{n_i}{g_i} = \dfrac{N e^{-\beta \varepsilon_i}}{f}$ from equation (**E-5.34**), we get-

$$\ln W = N \ln N - \sum_{i=1}^{i=r} n_i (\ln N - \beta \varepsilon_i - \ln f)$$

$$\ln W = N \ln N - N \ln N + \beta E + N \ln f = \beta E + N \ln f \ \ldots\ldots\ldots..(\ E\text{-}5.35)$$

Since, $S = k \ln W$, putting the value of lnW, we get-

$$S = k\beta E + Nk \ln f \ \ldots\ldots\ldots\ldots\ (E\text{-}5.36)$$

Putting the value of E from (**E-5.47**), we get-

$$S = k \frac{1}{kT} \left[NkT^2 \left(\frac{\partial \ln f}{\partial T} \right)_V \right] + Nk \ln f$$

$$S = \left[NkT \left(\frac{\partial \ln f}{\partial T} \right)_V \right] + Nk \ln f \ \ldots\ldots\ldots..\ (E\text{-}5.51)$$

Alternate derivation for S:

By definition, $dS = \dfrac{C_V}{T} dT$; now, integrating both sides between suitable limits, we get

$$\int_{S=S_0}^{S=S} dS = \int_0^T \frac{C_V}{T} dT$$

$$\therefore \qquad S - S_0 = \int_0^T \frac{C_V}{T} dT$$

Using the value of C_V from (…… (**E-5.49**), we get

$$S - S_0 = \int_0^T \frac{1}{T} \cdot \frac{\partial}{\partial T} \left[NkT^2 \left(\frac{\partial \ln f}{\partial T} \right) \right]_V dT = \int_0^T \frac{1}{T} \left[NkT^2 \left(\frac{\partial^2 \ln f}{\partial^2 T} \right)_V + 2NkT \left(\frac{\partial \ln f}{\partial T} \right)_V \right] dT$$

$$= Nk \int_0^T T \left(\frac{\partial^2 \ln f}{\partial^2 T} \right)_V dT + 2Nk \int_0^T \left(\frac{\partial \ln f}{\partial T} \right)_V dT$$

Partial integration provides

$$S - S_0 = NkT \left(\frac{\partial \ln f}{\partial T} \right)_V - Nk \int_0^T \left(\frac{\partial \ln f}{\partial T} \right)_V dT + 2Nk \int_0^T \left(\frac{\partial \ln f}{\partial T} \right)_V dT$$

$$= NkT\left(\frac{\partial \ln f}{\partial T}\right)_V + Nk\int_0^T \left(\frac{\partial \ln f}{\partial T}\right)_V dT$$

$$= NkT\left(\frac{\partial \ln f}{\partial T}\right)_V + Nk\left[\ln f\right]_0^T$$

$$S - S_0 = NkT\left(\frac{\partial \ln f}{\partial T}\right)_V + Nk\ln f - Nk(\ln f)_{T=0}$$

$$S - S_0 = \frac{E}{T} + Nk\ln f - Nk(\ln f)_{T=0}$$

In this expression, comparing the temperature-independence term with the constant S_0, that is the entropy at T=0K

$$S_0 = Nk(\ln f)_{T=0}$$

Therefore, we get

$$S = \frac{E}{T} + Nk\ln f$$

or, $$S = NkT\left(\frac{\partial \ln f}{\partial T}\right)_V + Nk\ln f \ldots\ldots\ldots\ldots\ldots (\boldsymbol{E\text{-}5.51})$$

(vi)   _Helmholtz free energy, A:_

Helmholtz free energy or work function (A) is given by,

$$A = E - TS$$

Substituting the value of S, we get

$$A = E - T\left[\frac{E}{T} + Nk\ln f\right] = -NkT\ln f \ldots\ldots\ldots\ldots (\boldsymbol{E\text{-}5.52})$$

(vii)   _Gibbs free energy, G:_

Gibbs free energy (H) is given by,

$$G = H - TS = E + PV - TS = (E - TS) + PV = A + PV$$

Substituting the value of A, we get

$$G = -NkT\ln f + PV \ldots\ldots\ldots\ldots (\boldsymbol{E\text{-}5.53})$$

(viii)   _Pressure, P:_

Pressure is expressed as, $P = -\left(\dfrac{\partial A}{\partial V}\right)_T$. Since, $A = -NkT \ln f$; therefore differentiating the value of A, we get

$$P = NkT\left(\dfrac{\partial \ln f}{\partial V}\right)_T \ldots\ldots\ldots\ldots\ldots \textbf{\textit{(E-5.54)}}$$

Self Assessment Questions

SAQ-10. The unit of molecular partition function is-

(i) $KJmol^{-1}$ (ii) s^{-1} (iii) dimensionless   (iv) cm^{-1}

SAQ-11. Derive the relationship between Chemical potential (μ) and partition function.

5.11 SUMMARY:

❖ The total numbers of ways of distributing N distinguishable particles having the distribution (n_1, n_2, n_3, ... n_i, ...) in various energy levels ($\mathcal{E}_1$, $\mathcal{E}_2$, $\mathcal{E}_3$, ... $\mathcal{E}_i$, ...) with degeneracy (g_1, g_2, g_3, ... g_i, ...) is given by-

$$W = N!\prod \dfrac{(g_i)^{n_i}}{n_i!}.$$

❖ Entropy and thermodynamic probability is connected by the Boltzmann equation $S = k_B \ln W$

This relation bridges the gap between thermodynamic and statistical view-point.

❖ The Maxwell-Boltzmann (Classical) distribution equation is-

$$n_i = g_i\, e^{-\alpha - \beta\varepsilon_i} = g_i\, e^{-\alpha} \cdot e^{-\frac{\varepsilon_i}{kT}}$$

❖ The ratio of the populations in any two energy levels ε_i and ε_j is given by

$$\dfrac{n_i}{n_j} = \dfrac{g_i}{g_j} \cdot e^{-\frac{(\varepsilon_i - \varepsilon_j)}{kT}}$$

❖ The term $f = \sum\limits_{i=1} g_i \cdot e^{-\beta\varepsilon_i}$ is an important quantity in statistical mechanics, known as partition function.

❖ Various thermodynamic functions are related to the partition function, f as follows

$$E = \dfrac{N}{f}kT^2\left(\dfrac{\partial f}{\partial T}\right)_V = NkT^2\left(\dfrac{\partial \ln f}{\partial T}\right)_V$$

$$H = NkT^2 \left(\frac{\partial \ln f}{\partial T} \right)_V + PV$$

$$C_V = \frac{\partial}{\partial T} \left[NkT^2 \left(\frac{\partial \ln f}{\partial T} \right) \right]_V$$

$$C_P = \frac{\partial}{\partial T} \left[NkT^2 \left(\frac{\partial \ln f}{\partial T} \right) \right]_P$$

$$S = \left[NkT \left(\frac{\partial \ln f}{\partial T} \right)_V \right] + Nk \ln f$$

$$A = -NkT \ln f$$

$$G = -NkT \ln f + PV$$

$$P = NkT \left(\frac{\partial \ln f}{\partial V} \right)_T$$

5.12   Suggested Readings/References:

1.   *Statistical Thermodynamics* by *M. C. Gupta*, New Age International, 2007

2.   *Physical Chemistry (Vol-II)* by Dr. S. Pahari, New Central Book Agency(P) Ltd., 2000

3.   **https://youtu.be/MkqQ6DrmaFc?list=PL0xcyW6_Yz ZMYgoGc_rNnP5RBAAFy6f_7**

4.   **https://youtu.be/dTjjT90Fq70?list=PL0xcyW6_YzZ MYgoGc_rNnP5RBAAFy6f_7**

5.13 Hints to the SAQ/CYP:

SAQ-1. Maxwellons- (v);   Bosons- (iii), (iv);   Fermions- (i), (ii)

SAQ-2. (ii)

SAQ-3. (ii)

SAQ-4. (iv)

SAQ-5. (a) Here, N = 2, M = 3; $\therefore W = \dfrac{(N + M - 1)!}{N!.(M - 1)!} = 6$

(b) Here N = 2, M = 3; $\therefore W = \dfrac{M!}{N!.(M - N)!} = 3$

(c) Here N = 2, M = 3; $\therefore W = M^N = 9$

[Do Yourself: Draw all possible microstates for (a), (b) & (c)]

SAQ-6. (i) and (ii) The all possible arrangements for three distinguishable particles (Let, A, B & C) are listed below.

Macrostates	Energy Levels	← Microstates→						Nos. of microstates $W = \dfrac{N!}{n_1!.n_2!.n_3!}$
(1, 1, 1)	$E_3\rightarrow$	C	B	C	A	B	A	$W = \dfrac{3!}{1!.1!.1!} = 6$
	$E_2\rightarrow$	B	C	A	C	A	B	
	$E1\rightarrow$	A	A	B	B	C	C	
(2, 1, 0)	$E_3\rightarrow$	-		-		-		$W = \dfrac{3!}{2!.1!.0!} = 3$
	$E_2\rightarrow$	C		B		A		

	E$_1$→	AB	AC	BC	
(2, 0, 1)	E$_3$→ E$_2$→ E$_1$→	C - AB	B - AC	A - BC	$W = \dfrac{3!}{2!.0!.1!} = 3$
(1, 2, 0)	E$_3$→ E$_2$→ E$_1$→	- AB C	- AC B	- BC A	$W = \dfrac{3!}{1!.2!.0!} = 3$
(1, 0, 2)	E$_3$→ E$_2$→ E$_1$→	AB - C	AC - B	BC - A	$W = \dfrac{3!}{1!.0!.2!} = 3$
(0, 2, 1)	E$_3$→ E$_2$→ E$_1$→	C AB -	B AC -	A BC -	$W = \dfrac{3!}{0!.2!.1!} = 3$
(0, 1, 2)	E$_3$→ E$_2$→ E$_1$→	AB C -	AC B -	BC A -	$W = \dfrac{3!}{0!.1!.2!} = 3$
(3, 0, 0)	E$_3$→ E$_2$→ E$_1$→	--- --- ABC			$W = \dfrac{3!}{3!.0!.0!} = 1$
(0, 3, 0)	E$_3$→ E$_2$→ E$_1$→	--- ABC ---			$W = \dfrac{3!}{0!.3!.0!} = 1$
(0, 0, 3)	E$_3$→ E$_2$→ E$_1$→	ABC --- ---			$W = \dfrac{3!}{0!.0!.3!} = 1$

(iii) The distribution (1, 1, 1) has the maximum value of thermodynamic probability which is the most probable distribution.

SAQ-7. Since degeneracy is not given, assume both energy levels be non-degenerate. Thus,

$$\frac{n_1}{n_0} = e^{-\frac{\Delta\varepsilon_{0,1}}{kT}}$$

(i)   At 25°C

$$\frac{\Delta\varepsilon_{0,1}}{kT} = \frac{\Delta\varepsilon_{0,1}}{RT} \frac{10000\,Jmol^{-1}}{8.314\,JK^{-1}mol^{-1} \times 298K} = 4.036$$

$$\frac{n_1}{n_0} = e^{-4.037} = 0.01766$$

(i.e., only 1.766% is populated in the 1st excited state)

(ii)   At 250°C ; $\dfrac{n_1}{n_0} = e^{-.4037} = 0.6679$

(i.e., 66.79% is populated in the 1st excited state!)

SAQ-8. (ii)

SAQ-9. (iii)

SAQ-10. (iii)

SAQ-11. From thermodynamics, the chemical potential, μ_i of any component is given by-

$$\mu_i = \left(\dfrac{\partial A}{\partial n_i} \right)_{V,T,n_j}$$

Since, from equation (*E-5.52*), $A = -kT \ln f$

$$\mu_i = -kT \left(\dfrac{\partial \ln f}{\partial n_i} \right)_{V,T,n_j}$$

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