Example 4.2

Calculate the number of ways of distributing four molecules in four energy levels so as there are 2 molecules in the level ϵ_0, 1 molecules in the ϵ_1 level, 1 molecule in ϵ_2 level and zero molecule in the ϵ_3 energy level i.e.,

$$n_0 = 2, n_1 = 1, n_2 = 1, n_3 = 0$$

Solution

The probability equation gives

$$W = \frac{4!}{2!\ 1!\ 1!\ 0!} \qquad\qquad (\therefore\ N = 4)$$

$$= \frac{4 \times 3 \times 2 \times 1}{(2 \times 1) \times 1 \times 1 \times 1} = 12$$

4.5 THE BOLTZMANN DISTRIBUTION LAW

The Boltzmann distribution law or Maxwell-Boltzmann distribution law (also known as the most probable distribution) is very important in statistical thermodynamics. It deals with the probability distribution of the total energy among the particles or molecules of the system, and leads to the introduction of the concept of partition function, a very important quantity used in statistical thermodynamics. This law fails, however, to harmonize with quantum theory and to account for the behaviour of the particles at high densities.

Consider a system of constant energy E composed of N identical particles at temperature T and possess the following characteristics.

(i)   Each particle is distinguishable from the other.

(ii)   Particles do not attract or repel each other.

(iii) No restriction on assigning various energy levels to the particles is being imposed.

(iv)   The particles are localized.

These assumption lead to the classical Boltzmann distribution law. Now we shall consider the distribution of the total energy E among the various energy levels say $\epsilon_1, \epsilon_2, \epsilon_3 ... \epsilon_n$ of the N particles. As we know that each particle may exist in a number of allowable energy levels, the total number of particles N may be assigned to the energy levels in such a way that n_1 particles be present in energy level ϵ_1, n_2 in the level with ϵ_2, n_3 in the level with ϵ_3 and so on. Irrespective of this distribution, the total number of particles and the energy of the system remain constant i.e.,

$$N = \Sigma n_i \quad \text{and} \quad \Sigma n_i \epsilon_i$$

Such summations are to be carried over all energy levels. The number of ways in which N particles can be put in these energy level is the number of permutations of N things in groups of $n_1, n_2, n_3, ...,$ i.e.,

$$W = \frac{N!}{n_0!\, n_1!\, n_2! \, ...} \qquad ...... (4.4)$$

On taking logarithm of both sides of above equation

$$\ln W = \ln N! - [\ln n_0! + \ln n_1! + \ln n_2! + ...]$$

$$\ln W = \ln N! - \Sigma \ln_i! \qquad ...... (4.5)$$

Stirling's approximation can be used for factorials of large number as N is also very large

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

Under these conditions n_i is also large, and have

$$\Sigma \ln n_i! = \Sigma n_i \ln n_i - \Sigma n_1$$

$$= \Sigma n_i \ln n_i - N \qquad ...... (4.6)$$

On substituting these values in equation (4.5)

$$\ln W = N \ln N - N - \Sigma n_i \ln n_i + N$$

$$\ln W = N \ln N - \Sigma n_i \ln n_i \qquad ...... (4.7)$$

The most probable distribution of particles or molecules in a system is the one for which W is maximum. Hence for these condition δW and $\delta \ln W$ will have to be zero

$$\delta W = \delta \ln W = 0 \qquad ...... (4.8)$$

On differentiating equation (4.7), the result is

$$\delta \ln W = -\delta \Sigma \, n_i \ln n_i \qquad\qquad [\delta(N) = \delta(\text{constant}) = 0]$$

and now placing the condition of equation (4.8), we get

$$\delta [\Sigma n_i \ln n_i] = 0 \qquad\qquad \text{...... (4.9)}$$

or $\qquad \Sigma \left[n_i \cdot \dfrac{\delta n_i}{n_i} + \ln n_i \, \delta n_i \right] = 0 \qquad\qquad \left(\therefore \delta \ln n_i = \dfrac{1}{n_i} \delta n_i \right)$

or $\qquad \Sigma [\delta n_i + \ln n_i \, \delta n_i] = 0$

or $\qquad \Sigma [1 + \ln n_i] \delta n_i = 0 \qquad\qquad \text{...... (4.10)}$

We must remember that for the given molecular system, the total energy E and number of particles N remains constant.

$$N = \Sigma n_i = \text{constant} \qquad \therefore \; \delta N = \Sigma \delta n_i = 0 \qquad\qquad \text{...... (4.11)}$$

$$E = \Sigma n_i \epsilon_i = \text{constant} \qquad \therefore \; \delta E = \Sigma \epsilon_i \, \delta n_i = 0 \qquad\qquad \text{...... (4.12)}$$

Multiplying equations (4.11) and (4.12) by two arbitrary constant α' and β respectively and adding to equation (4.10), we get

$$\Sigma [(1 + \ln n_i) \, \delta n_i + \delta n_i \alpha' + \epsilon \, \delta n_i \beta)] = 0$$

or $\qquad \Sigma [(1 + \ln n_i) + \alpha' + \epsilon_i \beta)] \, \delta n_i = 0$

let $\qquad 1 + \alpha' = \alpha$

$$\Sigma [\ln n_i + \alpha + \beta \epsilon_i] \, \delta n_i = 0 \qquad\qquad \text{...... (4.13)}$$

As the variables $\delta n_1, \delta n_2, \delta n_3 \dots$, are independent of each other so that the equation (4.13) is to hold good, then each term in the summation must be zero

$$\ln n_i + \alpha + \beta \epsilon_i = 0 \qquad\qquad (\; \therefore \; \delta \neq 0)$$

or $\qquad \ln n_i = -(\alpha + \beta \epsilon_i)$

or $\qquad n_i = e^{-(\alpha + \beta \epsilon_i)} \qquad\qquad \text{...... (4.14)}$

or $\qquad n_i = e^{-\alpha} \cdot e^{-\beta \epsilon_i} \qquad\qquad \text{...... (4.15)}$

This is one form of celebrated Boltzmann distribution law. The value of $c^{-\alpha}$ can be found by using the following equation

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

$$e^{-\alpha} = \dfrac{N}{\Sigma e^{-\beta \epsilon_i}} \qquad\qquad \text{...... (4.16)}$$

Substitute this value is equation (4.15)

$$n_i = \frac{N}{\Sigma e^{-\beta \epsilon_i}} e^{-\beta \epsilon_i}$$

...... (4.17)

The constant β can be identified by equating the internal energy of a monatomic gas with that obtained from the kinetic theory of gases.

We may express the distribution law in terms of quantum energy levels instead of energy states. For an ideal gas it can be shown that

$$\beta = \frac{1}{kT}$$

...... (4.18)

where k is the Boltzmann constant. Inserting equation (4.18) into equation (4.17), one cm have

$$n_i = \frac{N e^{-\epsilon_i/kT}}{\Sigma e^{-\epsilon_i/kT}}$$

or
$$\frac{n_i}{N} = \frac{e^{-\epsilon_i/kT}}{\Sigma e^{-\epsilon_i/kT}}$$

...... (4.19)

In equation (4.19) it is assumed that each energy levels is non-degenerate, i.e., it is composed of only a single level. However, when such is not the case, thus each level must be assigned a statistical weight g_i and Eq. (4.19) becomes

$$\frac{n_i}{N} = \frac{g_i e^{-\epsilon_i/kT}}{\Sigma g_i e^{-\epsilon_i/kT}}$$

...... (4.20)

or
$$\frac{n_i}{N} = \frac{g_i e^{-\epsilon_i/kT}}{Q}$$

...... (4.21)

where $Q = \Sigma g_i e^{-\epsilon_i/kT}$ is called the partition function of the system. Equation (4.21) is known as Boltzmann distribution law and it gives at any temperature T, the fraction of total number of particles in a system which in the most probable or equilibrium state will possess the energy ϵ_i. Hence this equation gives the most probable distribution of the particles in a system among all the allowable energy levels. Equation (4.21) is also known as Boltzmann statistics.

Limitations

Boltzmann distribution law gives the most probable distribution of molecules or particles in a system among all allowable energy levels. However, this law has the following limitations.

(i)   This law is only an approximation and is valid for gases at comparatively low density.

(ii)   In the metallic conductors electrons are confined within the volume of the metal just as gaseous molecules are confined within the containing vessel.

When Boltzmann law is applied to an electron gas, discrepancies appear between these and observations.

(iii)   In a similar manner as in (ii), the photon gas presents another difficulty. This law predicts a continuous number of photons per unit range of frequency as the latter increases, whereas the actual distribution is given by the well known law of Planck, exhibits a minimum.

4.6 PARTITION FUNCTION

Statistical thermodynamic analysis is facilitated through the use of partition function. This great analytical tool is defined as

$$Q = \Sigma\ g_i\ e^{-\epsilon_i/kT} \qquad\qquad \text{...... (4.22)}$$

where g_i is the statistical weight factor and is equal to the degree of degeneracy, i.e., the number of super-imposed energy levels, k is the Boltzmann constant, ϵ_i is the energy of quantum state in excess of the lowest possible value and T is the absolute temperature. In equation (4.22) summation is taken over all integral of i from zero to infinity corresponding to all possible energy states of the molecules. For general purpose, it is required to measure energy level, relative to the ground state. Therefore, equation (4.22) becomes

$$\frac{n_i}{n_o} = \frac{g_i\, e^{-\epsilon_i/kT}}{g_o\, e^{-\epsilon_o/kT}}$$

or $\qquad \dfrac{n_i}{n_o} = \dfrac{g_i}{g_o}\, e^{-(\epsilon_i-\epsilon_o)/kT}$

...... (4.24)

For computational purposes, it is convenient to consider $\epsilon_0 = 0$ and to take all ϵ_i values relative to this ground state. On this basis equation (4.24) becomes

$$\frac{n_i}{n_o} = \frac{g_i}{g_o}\, e^{-\epsilon_i/kT}$$

or $\qquad n_i = \dfrac{n_o}{g_o}\, g_i\, e^{-\epsilon_i/kT}$

...... (4.25)

where n_i is the number of molecules in the ith state, n_o, the number of molecules in the zero energy level, g_i and g_o represent the degeneracies in the ith and zero levels respectively.

When $\epsilon_o = 0$, then $g_o = 1$, therefore one can write

$$\frac{n_i}{n_o} = g_i\, e^{-\epsilon_i/kT}$$

or $\qquad n_i = n_o\, g_i\, e^{-\epsilon_i/kT}$

...... (4.26)

Now $\qquad N = \Sigma\, n_i$

Substituting the value of n_i from equation (4.26) in above equation, we get

$$N = \Sigma\, n_o\, g_i\, e^{-\epsilon_i/kT}$$

or $\qquad N = n_o\, g_o\, e^0 + n_o\, g_1\, e^{-\epsilon_1/kT} + n_o\, g_2\, e^{-\epsilon_2/kT} + ...$

or $\qquad N = n_o\, [g_o + g_1\, e^{-\epsilon_1/kT} + g_2\, e^{-\epsilon_2/kT} + ...]$

or $\qquad N = n_o\, \Sigma\, g_i\, e^{-\epsilon_i/kT} \qquad (g_o = 1)$

or $\qquad N = n_o\, Q$

or $\qquad Q = N/n_o$

...... (4.27)

From equation (4.27) it follows that the partition function (Q) may be defined as the ratio of the number of particles or molecules in the ith levels to that of zero level. At absolute zero,

$$N \to n_o \quad \text{and} \quad Q \to 1 \quad \text{as} \quad T \to 0$$

Hence the value of partition function increases with temperature. As the temperature is raised, there are more molecules in the highest energy levels and few

$\varepsilon = $ epsilon =

$g_i = $ degree of degeneracy

number of molecules in zero energy level. Therefore, the partition function is larger at higher temperature.

statistical weight.

factor.

Factorization of Partition Function

Partition function is defined as

...... (4.28)

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

The energy ϵ of a molecule is the sum of contribution from the different modes of motion like translational, rotational, vibrational, electronic, etc. If we assume that energy associated with any one mode of behaviour is independent of all other modes, then we can define energy by

$$E = E_T + E_r + E_v + E_c$$

and $$g_i = g_T + g_r + g_v + g_c$$

where E_T, E_r, E_v and E_c are translation, rotational, vibrational and electronic contribution, respectively and g_T, g_r, g_v and g_c are degeneracy of translational, vibrational, rotational and electronic energy level, respectively. So equation (4.28) can be written as

$$Q = \Sigma (g_T\, g_r\, g_v\, g_c)\, e^{-(\epsilon_t+\epsilon_r+\epsilon_v+\epsilon_c)/kT}$$

or $$Q = \Sigma\, g_T\, e^{-\epsilon_t/kT} \times \Sigma\, g_r\, e^{-\epsilon_r/kT} \times \Sigma\, g_v\, e^{-\epsilon_v/kT} \times \Sigma g_c\, e^{-\epsilon_c/kT}$$

or $$Q = Q_T \cdot Q_r \cdot Q_v \cdot Q_c$$ ...... (4.29)

Equation (4.29) is known as *multiplication theorem* or *factorization of partition function*. This factorization means that we can investigate each contribution separately. From equation (4.29), it follows that the net partition function is equal to be the product of the separate partition functions in respect of different types of energy independently associated with molecules.

4.7 TRANSLATIONAL PARTITION FUNCTION

By definition partition function is given by,

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

For translational energy, as the translational energy levels are non-degenerate, e.g., $g_i = 1$, tranalational partition function can be written as

$$Q_t = \Sigma\, e^{-\epsilon_t/kT}$$ ...... (4.30)

The Schrodinger wave equation when solved for the particle moving in a rectangular box of dimension a, b, and c gives the expression for translational energy as

$$E_t = \frac{h^2}{8m}\left(\frac{n_x^2}{a^2} + \frac{n_y^2}{b^2} + \frac{n_z^2}{c^2}\right)$$ ...... (4.31)