Statistical Equilibrium

When a system achieved the most probable distribution it is called statistical equilibrium.

Consider a system of N molecules. If the system is isolated, i.e., its pressure, temperature and volume are kept constant, the total energy of the system must remain constant.

$$E = \sum_i n_i E_i = \text{Constant} \qquad N = \sum_i n_i = \text{Constant}$$

At a particular time the particles are distributed among the different energy states, so that n_1 particles have energy E_1, n_2 particles have energy E_2 and so on.

But, the molecules of the gas collide with each other and also with the walls of the containing vessel.

Statistical Equilibrium (cont.)

After the collision the fast molecules may have slowed down while the slow ones may have speed up. Hence the particles after the collision are in different states. In other words, the numbers n_1, n_2, n_3 ...., which give the distribution of the N particles among the available energy states, may be changing.

It can be reasonably assumed that for each microscopic state of a system of particles, there is a distribution which is more favored than any other. We may say that, the particles in the system achieved the most probable distribution. In this state, the entropy is achieving maximum.

Entropy and Probability

Boltzmann establish a relation between probability (a statistical quantity) and entropy (a thermodynamical quantity). Boltzmann argued that, the probability of the system in equilibrium is maximum. But from the thermodynamic point of view, the equilibrium state of the system is the state of maximum entropy. Thus in the equilibrium state, both the thermodynamic probability and entropy have their maximum values. Therefore, $S = f(W)$

S = entropy, W = thermodynamic probability of the state.

For two separate systems, $S_1 = f(W_1)$ and $S_2 = f(W_2)$
Total entropy of the system $S_1 + S_2 = f(W_1) + f(W_2)$

But the thermodynamic probability of the two systems taken together is $W_1 W_2$. Therefore, $f(W_1 W_2) = f(W_1) + f(W_2) = S_1 + S_2$

It would be valid if it must be a logarithmic function of W.

$$f(W) = k\log W \text{ or, } S = k\log W \qquad \text{[Boltzmann cons.]}$$

Maxwell-Boltzmann Distribution Law

Consider a system that contains N number of identical but distinguishable particles. Identical because the particles have the same structure and distinguishable because the particles may be in different energy states at a given instant.

It is assumed that all the energy states are accessible to each particle.

In state E_1: particle "a" is distributed in N different ways. Particles "a, b, c, d" is distributed by

$$N(N-1)(N-2)(N-3) = \frac{N!}{(N-4)!}$$

Again in state E_1: 4 particle "a, b, c, d" is arranged in 4! ways.
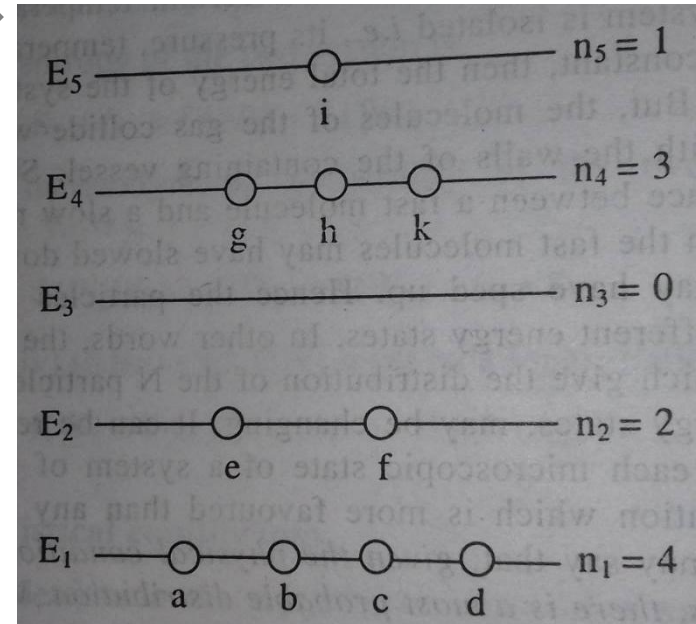
Thus, the total number of distinguishable different ways are,

$$\frac{N!}{4!(N-4)!}$$

In general, if the state E_1 consists of n_1 particles, the distinguishable different ways in which n_1 particles can be arranged in state E_1 are,

$$p_1 = \frac{N!}{n_1!(N-n_1)!} \tag{1}$$

In state E_2: The number of available particles is $(N-n_1)$. Then the number of distinguishable ways in which these n_2 particles may be arranged are,

$$p_2 = \frac{(N-n_1)!}{n_2!(N-n_1-n_2)!} \tag{2}$$

If the process is continued for all the available states, the total number of distinguishable ways are obtained by

$$P = p_1 p_2 p_3 .... = \frac{N!}{n_1! n_2! n_3! ......}$$ (3)

Let g_i be the number of cells (intrinsic probability of locating a particle) in a certain energy states E_i. Therefore, n_1 particles is distributed in g_1 number of cells.

$$P = \frac{N! g_1^{n_1} g_2^{n_2} g_3^{n_3} ......}{n_1! n_2! n_3! ......} = N! \prod_i^N \frac{g_i^{n_i}}{n_i!}$$ (4)

$\prod_i$ **is called the product.**

When the gas is in equilibrium, the probability is maximum. When P is maximum logP is maximum in eq(4). Hence, the most probable distribution can be obtained by evaluating the maximum value of logP. This should also satisfy the two conditions that

$$N = \sum_i n_i = \text{Constant} \qquad E = \sum_i n_i E_i = \text{Constant}$$ (5)

Taking logarithm of P,
$$\log P = \log N! + \sum_i^N (n_i \log g_i - \log n_i!)$$

By Stirling's theorem, logx! = xlogx - x

$$\log P = N\log N - N + \sum_i^N (n_i \log g_i - n_i \log n_i + n_i)$$

$$\log P = N\log N - N + \sum_i^N n_i - \sum_i^N n_i (\log n_i - \log g_i)$$

$$\log P = N\log N - N + N - \sum_i^N n_i \{\log(n_i/g_i)\} \qquad \text{(6)}$$

Differential form of eq. (6) as follows:

$$d(\log P) = \left[d(N\log N) - \sum_i^N \{(dn_i)\log(n_i/g_i) + n_i d(\log(n_i/g_i))\} \right]$$

$$d(\log P) = 0 - \sum_i^N \{dn_i \log\frac{n_i}{g_i} + n_i \frac{g_i}{n_i} \frac{1}{g_i} dn_i\}$$

For most probable distribution (for maximum value): dlogP = 0

$$0 = -\sum_i^N \log\left(\frac{n_i}{g_i}\right) dn_i - \sum_i^N dn_i \Rightarrow 0 = -\sum_i^N \log\left(\frac{n_i}{g_i}\right) dn_i - 0$$

$$or, \sum_i^N \log\left(\frac{n_i}{g_i}\right) dn_i = 0 \tag{7}$$

$$N = \sum_i n_i = \text{Constant} \Rightarrow \sum_i dn_i = 0 \tag{8}$$

$$E = \sum_i n_i E_i = \text{Constant} \Rightarrow \sum_i E_i dn_i = 0 \tag{9}$$

Eq. (8) and (9) can be incorporated into eq (7) by making use of Lagrange's method of undetermined multipliers. Multiplying eq (8) by α and eq (9) by β and adding to eq (7), we get

In mathematical optimization, the **method of Lagrange multipliers** is a strategy for finding the local maxima and minima of a function subject to equality constraints. 8

$$\sum_i^N \log\left[\left(\frac{n_i}{g_i}\right) + \alpha + \beta E_i\right] dn_i = 0 \quad Or, \log\left[\left(\frac{n_i}{g_i}\right) + \alpha + \beta E_i\right] dn_i = 0$$

After integration with integrating cons. 0 (let).
$$or, \frac{n_i}{g_i} = e^{-\alpha - \beta E_i} \tag{10}$$

Eq. (10) gives the distribution of molecules over the various energy states for the most probable configuration and α and β are two parameters that depend upon the physical property of the system. The total number of molecules

$$N = n_1 + n_2 + n_3 + .. = e^{-\alpha} \sum_i^N g_i e^{-\beta E_i} \tag{11}$$

$$\sum_i^N g_i e^{-\beta E_i} = Z \quad \textbf{where Z is called partition function.} \quad e^{-\alpha} = N/Z$$

$$n_i = \frac{N}{Z}\left[g_i e^{-\beta E_i}\right] \tag{12}$$

Eg. (12) is known as Maxwell-Boltzmann Distribution law.

Partition function

In physics, a partition function describes the statistical properties of a system in thermodynamic equilibrium[citation needed. Partition functions are functions of the thermodynamic state variables, such as the temperature and volume. Most of the aggregate thermodynamic variables of the system, such as the total energy, free energy, entropy, and pressure, can be expressed in terms of the partition function or its derivatives.