Lecture Notes of B.Sc.(HONS.) PHYSICS ,Part-III, Paper -VI

By: Sonu Rani,
Assistant Professor ,
Department of Physics ,MMC,P.U.

TOPIC:-- Boltzmann's Statistical Relation

In 1896, Boltzmann discovered a relation between entropy (a thermodynamic quantity) and probability (a statistical quantity) Boltzmann started from a simple idea that the equilibrium state of the system is the state of maximum probability i.e. the probability of the system in equilibrium state is maximum. But from thermodynamic point of view the equilibrium state of the system is the state of maximum entropy. If the system is not in equilibrium, then changes takes place within the system so that equilibrium state (or the state of maximum entropy) is reached. Thus in equilibrium state both the entropy and thermodynamical probabilities have their maximum values.

This led Boltzmann's to expect some correlation between them .

Therefore $\mathbf{S=f\ (\Omega)}$ ……………………………………………………………**(1)**

Where S is entropy and Ω is thermodynamical probability of the state.

To find out the nature of the function let us consider two completely Independent systems A and B having entropies S_1 and S_2 respectively. An entropy is an extensive (additive) quantity therefore the entropy S of two systems together must be equal to the sum of their separate entropies,

i.e. $\mathbf{S = S_1 + S_2}$ ……………………………………………………………………**(2)**

If the probability of A is Ω_1 and that of B is Ω_2, then probability Ω of finding both the system at the respective given condition will be product of these two probabilities (As the probability of composite event is equal to the product of probabilities of individual and independent events).

Hence $\Omega = \Omega_1 . \Omega_2$ ……………………………………………………………(3)

Thus we have $S = f(\Omega) = f(\Omega_1 . \Omega_2)$ ……………………………………………(4)

$S_1 = f(\Omega_1)$ ………………………………………………………………………(5)

$S_2 = f(\Omega_2)$ …………………………………………………………………………(6)

Using eqn. (4), (5) and (6), eqn. (2) becomes

$f(\Omega_1.\Omega_2) = f(\Omega_1) + f(\Omega_2)$ ……………………………………………………………(7)

Differentiating partially above eqn. with respect to Ω_1 and Ω_2 we get,

$\Omega_2\, f'(\Omega_1\, \Omega_2) = f'(\Omega_1)$ and ……………………………………………………(8)

$\Omega_1\, f'(\Omega_1\, \Omega_2) = f'(\Omega_2)$ ………………………………………………………………(9)

Dividing eqn. (8) and (9) we get,

$$\frac{f'\Omega_1}{f'\Omega_2} = \frac{\Omega_2}{\Omega_1}$$

i.e., $\Omega_1\, f'(\Omega_1) = \Omega_2\, f'(\Omega_2) = \ldots\ldots\ldots k$

where k is any constant.

This gives,

$f'(\Omega_1) = \frac{k}{\Omega_1}$ and $f'(\Omega_2) = \frac{k}{\Omega_2}$

Integrating we get,

$f(\Omega_1) = k \log \Omega_1 + C_1$

and $f(\Omega_2) = k \log \Omega_2 + C_2$

In general we can write

$f(\Omega) = k \log \Omega + C$

i.e. $S = k \log \Omega + C$ …………………………………………………………………(10)

Now according to Third Law of Thermodynamics also known as Nernst Heat Theorem, the entropy of thermodynamic system tends to zero as its temperature tends to absolute zero. Also at absolute zero there is no thermal energy to disturb the system therefore at absolute zero, the thermodynamic probability =1.

∴ at T =0, S=0 and Ω =1 using this condition in eqn. (10) we get C=0.

$$\therefore \quad \boxed{\mathbf{S = k \log \Omega}} \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(11)$$

This is a well known relation between **Entropy and Probability** or **Boltzmann's relation of Statistical Mechanics** or **Fundamental relation of Statistical Mechanics**.

Identification of constant k

The constant k appearing in relation (11) can be identified by considering an equivalent situation in thermodynamics, For this consider the expansion of one mole of an ideal gas originally at pressure p_1 and volume V_1 into an evacuated chamber of volume V_2. The final pressure is p_2 and the final volume is V_1+V_2. The problem is to find the isothermal change in the entropy of the gas.

When the containers of volume V_1 and V_2 are connected, the probability of finding one molecule in the first container of volume V_1 is $\frac{V_1}{V_1+V_2}$.

As one mole of an ideal gas contains N (=Avogadro no.) molecules and the probability of a composite event is equal to the product of the probabilities of individual and independent events, therefore the probability of finding one mole of the gas in the container of volume $V_1 = \left(\frac{V_1}{V_1+V_2}\right)^N = \Omega_1$

The probability of finding one mole of an ideal gas in the final volume (V_1+V_2) is $\left(\frac{V_1+V_2}{V_1+V_2}\right)^N = (1)^N = \Omega_2$

Hence from Boltzmann's relation ,

$$\Delta S = S_2 - S_1 = k \log \Omega_2 - k \log \Omega_1 = k \log \frac{\Omega_2}{\Omega_1}$$

$$= k \log\left(\frac{V_1+V_2}{V_1}\right)^N$$

$$= N\, k \log_e \left(\frac{V_1+V_2}{V_1}\right) \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(12)$$

But the entropy when the gas changes from one state (V_1, T_1) to another state (V_1+V_2, T_2) is given by,

$$\Delta S = C_V \log_e \frac{T_2}{T_1} + R \log_e \left(\frac{V_1+V_2}{V_1}\right)$$

As the change in isothermal entropy is given by

$$\Delta S = R \log_e \left(\frac{V_1+V_2}{V_1}\right) \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(13)$$

Comparing eqn. (12) and (13) we get,

$N\,k = R$

i.e. $k = \frac{R}{N}$

using R= 8.31 J/mol k and N_A =6.023 x 10^{23} mol^{-1} we get,

$$\boxed{\mathbf{k = 1.38 \times 10^{-23}\ J/k}}$$

Hence the constant k occurring in Boltzmann's entropy relation (11) is identified as Boltzmann's Constant.