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Notes for:
B. Sc. Part III
Paper – VIth "Entropy and Probability"

In 1896. Boltzmann discovered a relation between entropy and Probability. According to him, the Probability of the system in equilibrium state is maximum. But from the thermodynamical Point of view the equilibrium state of a system is the state of maximum entropy. Thus in the equilibrium state both the entropy and thermodynamical ~~Probability~~ ~~have Probab~~ Probability have the maximum values.

According to thermodynamics, entropy S of a system is related with the temperature by the relation

$$\frac{1}{T} = \frac{\delta S}{\delta E} \longrightarrow (1)$$

According to Statistical Mechanics, we have

$$\frac{1}{T} = k\beta = k \frac{\delta}{\delta E} \log \Omega \longrightarrow (2)$$

from equation (1) and (2) we have –

$$\frac{\delta S}{\delta E} = k \frac{\delta}{\delta E} \log_e \Omega \longrightarrow (3)$$

This is the required relation between entropy and Probability and is called Boltzmann's statistical definition for entropy.

So, clearly, the entropy is a function of Probability.

i.e. $S = f(\Omega) \longrightarrow (4)$

where S is entropy and Ω is the thermodynamical Probability of the state.

Let us consider two completely independent systems A and B having entropies S_1 and S_2 respectively. The entropy S of the two systems together must be equal to the sum of their separate entropies. i.e. $S = S_1 + S_2 \longrightarrow (5)$

If the Probability of A is Ω_1 and that of B is Ω_2 then Probability of finding both the systems at their respective given conditions is – $\Omega = \Omega_1 * \Omega_2 \longrightarrow (6)$

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(from Page 11)

→ Thus we have, $S = f(\Omega) = f(\Omega_1 \Omega_2) \longrightarrow (7)$

$$S_1 = f(\Omega_1) \longrightarrow (8)$$

$$S_2 = f(\Omega_2) \longrightarrow (9)$$

Substituting values of eqn (7), eqn (8) and eqn (9) in eqn (5) we get -

$$f(\Omega_1, \Omega_2) = f(\Omega_1) + f(\Omega_2) \longrightarrow (10)$$

Differentiating Partially the above eqn with respect to Ω_1 and Ω_2 we get -

$$\Omega_2 f'(\Omega_1 \Omega_2) = f'(\Omega_1) \longrightarrow (11)$$

$$\Omega_1 f'(\Omega_1 \Omega_2) = f'(\Omega_2) \longrightarrow (12)$$

Equation (11) and (12) gives - $\dfrac{f'(\Omega_1)}{f'(\Omega_2)} = \dfrac{\Omega_2}{\Omega_1}$

This gives, $f'(\Omega_1) = \dfrac{k}{\Omega}$ and $f'(\Omega_2) = \dfrac{k}{\Omega_2}$

Integrating we get,

$$S = k \log \Omega + C \longrightarrow (13)$$

This is required relation between entropy and Probability. Here k is universal constant known as Boltzmann's Constant while the constant C is the constant of integration. At absolute zero temperature $S = 0$ and $\Omega = 1$

$$\therefore C = 0$$

Putting $C = 0$ in equation no (13) we get the relation between entropy and Probability to be

$$S = k \log \Omega \longrightarrow (14)$$

The above equation states that the entropy of a System is Proportional to the logarithm of the Probability of that System.

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