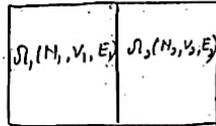


* Boltzmann's Definition of Entropy \rightarrow

$$S = k_B \ln \Omega$$

Consider two independent system having macrostates are described by (N_1, V_1, E_1) & (N_2, V_2, E_2) with thermodynamic probabilities $\Omega_1(N_1, V_1, E_1)$ & $\Omega_2(N_2, V_2, E_2)$ respectively.



Thermodynamical probability of composition

$$\Omega = \Omega_1 \times \Omega_2 \quad \text{--- (1), En. of composition } E = E_1 + E_2$$

If energy is allowed to exchange

$$\Omega = \Omega_1(E_1) \times \Omega_2(E_2)$$

Let equilibrium energy is \bar{E}

$$\Omega = \max$$

$$\left. \frac{\partial \Omega}{\partial E_1} \right|_{E=\bar{E}} = 0$$

$$0 = \Omega_2 \frac{\partial \Omega_1}{\partial E_1} \frac{\partial E_1}{\partial E_1} + \Omega_1 \frac{\partial \Omega_2}{\partial E_2} \frac{\partial E_2}{\partial E_1} \Omega_1$$

$$\frac{1}{\Omega_1} \frac{\partial \Omega}{\partial E_1} = \frac{1}{\Omega_2} \frac{\partial \Omega_2}{\partial E_2}$$

$$\frac{1}{\Omega} \frac{\partial \Omega}{\partial E} = \text{const} \quad \text{--- (2)}$$

$$\frac{\partial}{\partial E} (\ln \Omega) = \text{const} \quad \beta = \frac{1}{k_B T} \quad \text{--- (3) } S = \text{entropy} = \frac{1}{T}$$

By thermodynamic

$$\left. \frac{\partial S}{\partial E} \right|_{N, V} = \frac{1}{T} \quad \text{--- (4) } \left[\text{from } TdS = dE + PdV - \mu dN \right]$$

Dividing (3) by (4)

$$\frac{\partial S}{\partial (\ln \Omega)} = \frac{1}{\beta T} = k_B$$

$$S = k_B \ln \Omega + C$$

$$C = 0 \quad \text{at } T \rightarrow 0K \quad S \rightarrow 0$$

$$S = k_B \ln \Omega$$



$$\frac{\partial S}{\partial V} = \frac{P}{T}$$

\rightarrow If we allow volume to exchange

$$\frac{\partial}{\partial V} (\ln \Omega) = \eta = \frac{P}{k_B T} = \frac{P}{T}$$

If allow N to exchange

$$\frac{\partial}{\partial N} (\ln \Omega) = \gamma = -\frac{\mu}{k_B T}$$

$$\left. \frac{\partial S}{\partial E} \right|_{N, V} = \frac{1}{T}$$

$$\left. \frac{\partial S}{\partial V} \right|_{N, E} = \frac{P}{T}$$

$\sigma \rightarrow$ statistical entropy

$\tau \rightarrow$ statistical temp.

$\beta =$ inverse temp.

$$\text{Th. En. } S = k_B \sigma \rightarrow S(E)$$

$$\left. \frac{\partial \sigma}{\partial E} \right|_{N, V} = \frac{1}{T}$$

$$\left. \frac{\partial \sigma}{\partial V} \right|_{E, N} = \frac{P}{T}$$

$$\left. \frac{\partial \sigma}{\partial N} \right|_{E, V} = -\frac{\mu}{T}$$

Prob: Consider a system of N magnetic ions with spin $1/2$. At low temp. the system is ferromagnetic while at high temp. T it is paramagnetic. Neglecting all DOF except spins, find entropy of the system at.

- (i) $T \rightarrow 0$ b) $T \rightarrow \infty$

(i) $T \rightarrow 0K$

Distribution of spins

→ Almost all spins are aligned in same dirⁿ.

No. of ways of distribution

$$\Omega \rightarrow 1$$

$$S = k_B \ln \Omega$$

$$S \rightarrow 0$$

gmb
(ii)

$T \rightarrow \infty$

System attain equilibrium.

$$\Omega = \max$$

No. of distr. = $(2S+1)^N = \left(2 \times \frac{1}{2} + 1\right)^N = 2^N$
 Max. No. of microstate

$$\text{Entropy } S = k_B \ln(2^N) \\ = (N \ln 2) k_B$$

Q. Consider a system of N paramagnetic atoms each having mag. moment M , are placed in mag. field B . n atoms are alligned \parallel to B & $(N-n)$ alligned antipar^l to B . find

- (i) Internal En. of the system
 (ii) Entropy of the system
 (iii) The thermodynamic temp. of the system.

(i) $E = nE_{\parallel} + (N-n)E_{\text{antipar}}$
 $= n(-\mu B) + (N-n)\mu B$
 $E = (N-2n)\mu B$

(ii) $\Omega = \frac{N!}{n!(N-n)!} = \frac{N!}{n!(N-n)!}$

$$S = k_B \ln \Omega$$

$$= k_B \ln \left(\frac{N!}{n!(N-n)!} \right)$$



$$= N k_B \ln N - N k_B - N k_B \ln n + n k_B \\ - (N-n) k_B \ln(N-n) + (N-n) k_B$$

$$S = k_B \left[N \ln \left(\frac{N}{N-n} \right) - n \ln \left(\frac{n}{N-n} \right) \right]$$

(iii) $\frac{1}{T} = \frac{\partial S}{\partial E} = \frac{\partial S}{\partial n} \cdot \frac{\partial n}{\partial E}$

$$= \frac{\partial S}{\partial n} \left(\frac{-1}{2\mu B} \right)$$

$$= \frac{k_B}{2\mu B} \ln \left(\frac{n}{N-n} \right)$$

$$T = \frac{2\mu B}{k_B \ln \left(\frac{n}{N-n} \right)}$$