

* Equilibrium Phenomena:

1) Thermal :-

We consider a system isolated from universe comprising two system A and B. The total internal energy $U_T = U_A + U_B$ is constant. The entropy of total system $S = S_A(U_A) + S_B(U_B)$

∴ Rate of change of entropy with time $\frac{dS}{dt}$

$$\begin{aligned} \frac{dS}{dt} &= \frac{\partial S_A}{\partial U_A} \frac{\partial U_A}{\partial t} + \frac{\partial S_B}{\partial U_B} \frac{\partial U_B}{\partial t} \\ &= \frac{\partial U_A}{\partial t} \left(\frac{\partial S_A}{\partial U_A} - \frac{\partial S_B}{\partial U_B} \right) \\ &= \frac{\partial U_A}{\partial t} \left(\frac{1}{T_A} - \frac{1}{T_B} \right) \end{aligned}$$

$$\begin{aligned} \partial U_B &= -\partial U_A \\ dU &= T dS \end{aligned}$$

By Clausius Principle $\frac{dS}{dt} \geq 0$

If $\frac{dS}{dt} = 0$ S is constant. So the system is in thermal equilibrium or $T_A = T_B$

If $T_A > T_B$ $\frac{dU_A}{dt} < 0 \Rightarrow$ A loses energy

∴ Heat is transferred from hot to cold system.

2) Mechanical :-

If we consider a movable piston separates two system A and B in thermal equilibrium, and the volume of A and B changes.

Total volume $V_T = V_A + V_B = \text{const}$

∴ Total Entropy $S = S_A(V_A) + S_B(V_B)$

$$\begin{aligned} \frac{dS}{dt} &= \frac{\partial S_A}{\partial V_A} \frac{\partial V_A}{\partial t} + \frac{\partial S_B}{\partial V_B} \frac{\partial V_B}{\partial t} \\ &= \frac{dV_A}{dt} \left(\frac{\partial S_A}{\partial V_A} - \frac{\partial S_B}{\partial V_B} \right) \end{aligned}$$

$$\begin{aligned} V_T &= V_A + V_B \\ \therefore \partial V_T &= \partial V_A + \partial V_B \\ \therefore \partial V_A &= -\partial V_B \end{aligned}$$

$$\therefore \frac{ds}{dt} = \frac{dV_A}{dt} \left(\frac{P_A}{T_A} - \frac{P_B}{T_B} \right)$$

Here $T_A = T_B$ since they are thermal equilibrium

if $P_A = P_B$ then $\frac{ds}{dt} = 0$ and $S = \text{const}$

Here the system is in mechanical equilibrium

if $P_A > P_B$ then $\frac{dV_A}{dt} > 0 \Rightarrow$ Higher pressure side expands

3) Chemical equilibrium

We consider the no. of particles changes from A to B system. The total no. of particles is

$$N_T = N_A + N_B = \text{const}$$

\therefore Total entropy $S = S_A(N_A) + S_B(N_B)$

$$\begin{aligned} \therefore \frac{ds}{dt} &= \frac{dN_A}{dt} \cdot \frac{\partial S_A}{\partial N_A} - \frac{dN_A}{dt} \cdot \frac{\partial S_B}{\partial N_B} \\ &= \frac{dN_A}{dt} \left(\frac{\partial S_A}{\partial N_A} - \frac{\partial S_B}{\partial N_B} \right) \end{aligned}$$

$$\mu = -T \left(\frac{\partial S}{\partial N} \right)_{U, V} = \frac{dN_A}{dt} \left(\frac{\mu_A}{T_A} - \frac{\mu_B}{T_B} \right)$$

chemical potential

In thermal equilibrium $T_A = T_B$

If $\mu_A = \mu_B$ then $\frac{ds}{dt} = 0 \therefore S = \text{const}$
system in chemical equilibrium

If $\mu_A > \mu_B$ then $\frac{dN_A}{dt} < 0 \Rightarrow$ particles escape from system with higher chemical potential

Phase Space

The states of a system of particles can be specified by position and momentum of each of its constituent particles. x, y, z, p_x, p_y, p_z . The combined position and momentum space is called phase space.

Uncertainty principle restricts the point in phase space whose sides are $dx, dy, dz, dp_x, dp_y, dp_z$.

$$\therefore d\Omega = dx dy dz dp_x dp_y dp_z = \text{volume of cell}$$

According to uncertainty principle $dx dp_x \geq \frac{h}{4\pi} \therefore d\Omega \geq \left(\frac{h}{4\pi} \right)^3$

A point in phase space is actually a cell whose minimum volume is of the order of h^3 . A particle in phase space is being located some where in such a cell instead being properly at a point.

Micro and Macro state:

Microscopic system - system of atomic dimension or small size; generally means system of individual.
 Macroscopic system - large scale system; generally means system comprising large no of particle and its collective behaviour.

Micro state means the individual behaviour of system. Macro state means the ^{collective} ~~individual~~ behaviour of a large no particle based system.

Planck Boltzmann Principle:

On the steady state, thermodynamic probability is maximum and in equilibrium entropy also maximum. Let us relate the two by the relation

$S = k \ln(w)$ $w =$ probability of the state which is proportional to thermodynamic probability

Let us have two independent system whose probabilities are w_1 and w_2 and entropies are S_1 and S_2 respectively.

\therefore probabilities of combined system

$S = S_1 + S_2 = k \ln(w_1 w_2) = k \ln(w_1) + k \ln(w_2)$

$\therefore k \ln(w_1 w_2) = k \ln(w_1) + k \ln(w_2)$

diffⁿ w.r.to w_1 , keeping w_2 const.

$w_2 k \ln'(w_1 w_2) = k \ln'(w_1)$

Again diffⁿ with w_2 , keeping w_1 const

$k \ln'(w_1 w_2) + w_1 w_2 k \ln''(w_1 w_2) = 0$

$k \ln'(w) + w k \ln''(w) = 0$

$\therefore x \frac{dy}{dx} + y = 0$

$\therefore \frac{d}{dx} \left(x \frac{dy}{dx} \right) = 0$

Since probabilities are multiplicative and entropy are additive

$w = w_1 w_2$

$x \frac{dy}{dx} = k$ (const)

$\therefore \frac{dy}{dx} = \frac{k}{x}$

$\therefore dy = \frac{k}{x} dx \therefore y = k \log x + const$

$\therefore S = k \log w + const$ Boltzmann Relation

Comparison of different statistics

① Maxwell - Boltzmann:-

Molecules of a Gas. Identical Particle of any Spin, Distinguishable

② Bose - Einstein:-

Identical particle of zero or integral spin. Not distinguishable. Not obey exclusion principle. Boson - photon, phonon.

③ Fermi - Dirac:-

Identical particle of Half integral spin. Not distinguishable. obey exclusion principle. Fermion - electron.

* Principle of A priori Probability:-

It states that an isolated system in equilibrium have equal probability in each of its accessible states.

* Probability of Distribution:-

Let us take a large box divided into k cells whose area is $a_1, a_2, a_3, \dots, a_k$ and throw N balls into the box in random way. The probability w that the balls distributed in a certain way among the cells depends on two factor

1. The A priori probability Q based upon properties of each cell.
2. Thermodynamic probability M of the distribution which is the number of different sequences in which the balls distributed among the cells without affecting the po of balls in cell.

1. A priori Probability g_i , that a ball falls in i th cell is the ratio betⁿ area of this particular cell (a_i) and the total area (A) of box

$\therefore g_i = \frac{a_i}{A}$ where $a_1 + a_2 + \dots + a_k = A$

Since the ball falls some where in the box

$g_1 + g_2 + g_3 + \dots + g_k = \sum g_i = 1$

The probability that two ball falls in i th cell = g_i^2 = Product of ~~probability~~ probability g_i and g_i that each ball separately fall in

The A priori Probability for n_i balls to fall in i th cell = $(g_i)^{n_i}$

\therefore A priori Probability Q of any particular distribution of N balls among k cell is $Q = (g_1)^{n_1} (g_2)^{n_2} \dots (g_k)^{n_k}$ where $\sum n_i = N$

If the cells are equal in size they all have same a priori probability g .

$\therefore Q = (g)^{n_1} (g)^{n_2} \dots (g)^{n_k} = (g)^{n_1 + n_2 + \dots + n_k} = (g)^N$

(2) The total no. of Permutation possible for N balls in L or N balls can be arranged in L^N way, if n_1 balls in 1 cell, n_2 in 2 cell, n_i in i th cell then permuting them among themselves has no significance in a particular cell.

So there are $L^{n_1} L^{n_2} L^{n_3} \dots L^{n_k}$ independent permutation

$$\therefore \text{Thermodynamic Probability } M = \frac{L^N}{L^{n_1} L^{n_2} \dots L^{n_k}}$$

$$\therefore \text{Total Probability } W = GM = \frac{L^N}{L^{n_1} L^{n_2} \dots L^{n_k}} (g_1)^{n_1} (g_2)^{n_2} \dots (g_k)^{n_k}$$

\therefore Probability for all possible distribution is

$$\begin{aligned} \sum W &= \sum \frac{L^N}{L^{n_1} L^{n_2} \dots L^{n_k}} (g_1)^{n_1} (g_2)^{n_2} \dots (g_k)^{n_k} \\ &= (g_1 + g_2 + \dots + g_k)^N \\ &= 1^N = 1 \end{aligned}$$

With the help of Multinomial theorem of algebra.

Most probable Distribution

Most probable distribution means the distribution

which yields largest value of W .

$$\text{Now } W = \frac{L^N}{L^{n_1} L^{n_2} \dots L^{n_k}} (g_1)^{n_1} (g_2)^{n_2} \dots (g_k)^{n_k}$$

$$\therefore \log_e W = \log_e L^N - \sum \log_e L^{n_i} + \sum n_i \log_e g_i$$

where $i = 1 \dots k$

from following formulae $\log_e m^n = n \log_e m$ or $n \log_e m = \log_e m^n$ for $n \gg 1$

$$\begin{aligned} \therefore \log_e W &= N \log_e L - N - \sum n_i \log_e n_i + \sum n_i + \sum n_i \log_e g_i \quad \left| \sum n_i = N \right. \\ &= N \log_e L - \sum n_i \log_e n_i + \sum n_i \log_e g_i \end{aligned}$$

$$\text{Now } (\log_e W)_{\max} = \log_e W_{\max}$$

\therefore for most probable distribution or for W_{\max}

$$\delta \log_e W_{\max} = - \sum n_i \delta \log_e n_i - \sum \log_e n_i \delta n_i + \sum \log_e g_i \delta n_i = 0$$

$$\text{Now } \delta \log_e n_i = \frac{1}{n_i} \delta n_i$$

$$\therefore n_i \delta \log_e n_i = \delta n_i$$

$$\therefore \sum n_i \delta \log_e n_i = \sum \delta n_i = 0, \text{ since total no. of balls constant}$$

$$\therefore - \sum \log_e n_i \delta n_i + \sum \log_e g_i \delta n_i = 0$$

Now let α be a quantity that does not depend upon any of the n_i using the method of Lagrange undetermined multipliers, we get $\sum \alpha \delta n_i = 0$

$$\therefore - \sum \log_e n_i \delta n_i + \sum \log_e g_i \delta n_i + \sum \alpha \delta n_i = 0$$

$$\therefore \sum (-\log_e n_i + \log_e g_i + \alpha) \delta n_i = 0$$

$$\therefore -\log_e n_i + \log_e g_i + \alpha = 0 \quad \therefore \log_e \frac{g_i}{n_i} = -\alpha \quad \therefore n_i = g_i e^\alpha$$