Irreversible Thermodynamics

Phenomenological Laws & Onsanger's Reciprocal relations

Heat flows due to Temperature difference – Temperature gradient

Mass transfer due to concentration difference - concentration gradient

Electricity transfer due to potential difference - potential gradient

Temperature gradient, concentration gradient, potential gradient etc derived a driving force for transport of these thermodynamic quantities.

This transport is the continuous process called flux (flow).

$$\text{Flux} \propto \text{driving force}$$

$$J \propto X$$

$$\mathbf{J = LX}$$

J= flux, flow per unit area

X= driving force which causes the flux

L= transport coefficient

$$\mathbf{J_Q = -k \; dT/dx} \quad \textbf{(Fourier Law)}$$

J_Q = heat flux for heat transfer

K= transport coefficient

dT/dx = rate of change of temperature

$$\mathbf{J_m = -D \; dc/dx} \quad \textbf{(Fick's law)}$$

J_m= mass flux for mass transfer

D= transport coefficient (for diffusion)

dc/dx= rate of change of concentration

$$J_M = -\mu \, du/dx \text{ (Newton's law)}$$

J_M= momentum flux for momentum transfer

μ=transport coefficient for momentum

du/dx= rate of change of momentum

$$J_e = -\lambda \, dE/dx \text{ (Ohms Law)}$$

J_e= electricity flux for flow of electricity

λ = transport coefficient for electricity

dE/dx = rate of change of electricity

Above four expressions are known as **Phenomenological laws**.

There are no particular derivations for these laws.

These laws defined several transport process.

J = Lx is the general formula for Phenomenological laws.

These laws describe the several irreversible processes as functions.

If we take the example of Fick's law of diffusion for a one dimensional system

$$dm/dt = D(dc/dx)$$

dm/dt =rate of change of solute across the surface

dc/dx = diffusion coefficient

For example in Osmosis process, the solute flows from higher concentration to lower concentration. Solute flows in both the directions with change in temperature . so eq 1 is not sufficient to describe concentration and temperature coefficient both. Solute move from both the direction. So there is change in Concentration gradient in both side.

For one dimensional flow

$$dm_1/dt = D \, dc_1/dx + E \, dc_2/dx = J_1 \quad \text{--} 2$$

For other side

$$\mathbf{dm_2/dt = F\ dc_2/dx + G\ dc_1/dx = J_2} \quad \text{--} \mathbf{3}$$

we can replace coefficients with symbol L

for $D = L_{11}$

$E = L_{12}$

$F = L_{22}$

$G = L_{21}$

In General $\mathbf{L_{xy}}$

Where x=component that moves

y=component whose gradient is being considered

equation 2 and 3 two simultaneous irreversible flows if independent of each other, then described by a phenomenological laws or relations like E $dc_{2/}dx$ or G dc_1/dx.

But however, the simultaneous flows are not independent of each others gradient called **Coupled flows**. (eq 2 +eq 3)

Onsager developed a general equation for these type of coupled flows.

$$\mathbf{J_i = L_{i1}X_1 + L_{i2}X_2 + \ldots\ldots\ldots\ldots\ldots + L_{in}X_n} \quad \text{--} \mathbf{4}$$

Equation 4 is called **Linear phenomenological relations.**

$L_{ii} = L_{11}$ or L_{22} or L_{33} and so on are called **Primary phenomenological coefficients**

$L_{ij} = L_{12}, L_{13}, L_{14}$ and so on are called **Onsanger phenomenological coefficients**.

Equation 4 is very difficult to solve and phenomenological coefficients have to be determined experimentally. ($L_{ii} + L_{ij}$)

L_{ii} = primary coefficient can be determined easily

L_{ij} = coupling coefficients show many difficulties for their experimental measurement

L_{ij} requires several controls and several parameters to get solved.

So Onsanger gave theoretically with some control and parameter.

$$\mathbf{L_{ij} = L_{ji}}$$

It is known as **Onsanger's Reciprocal relation** or **Reciprocity Relations**. This reciprocal relationship exists only for a selected pair of flows and those flows are known as **Conjugate Flows**.

To understand Conjugate Flows, we take an example.

Suppose in a one dimensional conducting wire,

ΔE = Potential Difference

ΔT = Temperature Difference

They are driving forces. Because of these driving forces, ΔE form I (electric current) and ΔT is responsible for entropy flow = J_s

There will be also Heat Flux due to ΔT but for conjugate flow entropy and current will be considered. (I and J_s)

$$\mathbf{I = L_{11}\Delta E + L_{12}\Delta T}$$

$$\mathbf{J_s = L_{21}\Delta E + L_{22}\Delta T}$$

$$\mathbf{L_{12} = L_{21}}$$

The influence of L_{12} is equal to L_{21}