Non-equilibrium Thermodynamics

Entropy production

Entropy is not a conserved quantity and entropy change can takes place. For any natural and spontaneous process always there is increase in entropy, that is entropy produced in natural and spontaneous process. Entropy is an extensive property.

If d_eS is entropy flow due to the interaction with the surroundings.

d_iS is entropy contribution due to the change in the inside of the system

then total change in entropy

$$dS = d_eS + d_iS$$

$d_iS = 0$ for a reversible process

$d_iS > 0$ for a irreversible process

this quantity can never be negative this is entropy production .

suppose we consider that our system is made up of two phases that is phase I and phase II. Phase I is maintained at temperature T^I and phase II is maintained at temperature T^{II}

we have already studied that the second law of thermodynamics which says that

$$dS = dq/dT \qquad ....(1)$$

dS is entropy change and it is positive

dq is the heat received from the surroundings

T is the temperature

From equation (1)

$$dS = dS^{I} + dS^{II} \qquad \text{....... (2)}$$

eq. 2 is for the whole system

$$d^{I}S = d^{I}q/T^{I}$$

$$= d_e^{I}q/T^{1} + d^{I}_{i}q/T^{I}$$

$$d^{II}S = d^{II}q/T^{II}$$

$$= d_e^{II}q/T^{II} + d^{II}_{i}q/T^{II}$$

Total change in entropy

$$dS = d_e^{I}q/T^{1} + d_e^{II}q/T^{II} + d^{I}_{i}q(1/T^{I} - 1/T^{II}) \qquad \text{...(3)}$$

($d^{I}_{i}q + d^{II}_{i}q = 0$ conservation of energy in the system)

$d_e^{I}q/T^{1} + d_e^{II}q/T^{II}$ represents d_eS

$d^{I}_{i}q(1/T^{I} - 1/T^{II})$ represents d_iS

the entropy production can only be zero when thermal equilibrium is established.

The rate of production of entropy denoted as σ

$$\sigma = d_iS/dt = d^{I}_{i}q/dt\ (1/T^{I} - 1/T^{II}) > 0 \qquad \text{..(4)}$$

The rate of entropy production is expressed as a sum of the products of generalized forces (X_j) and the corresponding fluxes denoted by J_j.

$$\sigma = d_iS/dt = \sum_j J_j X_j > 0 \qquad \text{........(5)}$$

Entropy production in a steady state

If the parameters of the system do not change with time called steady state. In this state the incoming fluxes are balanced by the outgoing fluxes while in equilibrium the fluxes vanish.

If a system consist of two flows J_1 &J_2 and two forces X_1 & X_2

Then the entropy production and phenomenological equations will be

$$\sigma = J_1 X_1 + J_2 X_2 \quad \ldots\ldots.(6)$$

$$J_1 = L_{11} X_1 + L_{12} X_2 \quad \ldots\ldots\ldots(7)$$

$$J_2 = L_{21} X_1 + L_{22} X_2 \quad \ldots.(8)$$

$$\sigma = L_{11} X_1{}^2 + (L_{12} + L_{21}) X_1X_2 + L_{22}X_2{}^2 \quad \ldots\ldots(9)$$

on differentiating σ with respect to the variable X_2 at constant X_1

$$(\partial\sigma/\partial X_2)_{x1} = (L_{12} + L_{21}) X_1 + 2L_{22}X_2 \quad \ldots\ldots(10)$$

We know Onsagar's law $L_{12} = L_{21}$

So $L_{12} + L_{21} = 2L_{12} = 2L_{21}$

$$(\partial\sigma/\partial X_2)_{x1} = 2(L_{12}X_1 + 2L_{22}X_2) = 2J_2 \quad \ldots\ldots.(11)$$

$$J_2 = L_{21}X_1 + L_{22}X_2$$

If X_2 is unrestricted the conjugate flow must vanish so $J_2 = 0$

So equation (11) will be

$$\left(\partial \boldsymbol{\sigma} / \partial \mathbf{X}_2\right)_{x_1} = \mathbf{0}$$

In the steady state the entropy production assumes the minimum value under conditions when the system obeys linear phenomenological laws, the phenomenological coefficients are independent of the forces and the Onsager's reciprocal relations are valid.