

4_Entropy Production in Open System & Transformation of Fluxes and Forces_Irreversible Thermodynamics

Link: https://www.youtube.com/watch?v=R-30Zc3iEEU&list=PLdBDmcnzLC_ZMUWMdy7SmcTgnnzyiRpqI&index=4

System : 2 Phases : Phase I & II

Each phase can exchange its mass matter & energy with one another.

But these 2 phases are enclosed into a closed system, where Only the energy can be transferred with the environment, but NOT matter (mass).

Internal Energy : $dU = Tds - PdV + \sum_r \mu_r dn_r$



the # of components which are present in each phase.

$$Tds = dU + PdV - \sum_r \mu_r dn_r$$

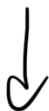


$$(dU = dq - PdV)$$

$$(dn_r = v_r d\xi)$$

$$Tds = dq - \sum_r \mu_r v_r d\xi$$

$$ds = \frac{dq}{T} - \frac{1}{T} \sum_r \mu_r v_r d\xi$$



$$(A = - \sum_r \mu_r v_r)$$

$$ds = \frac{dq}{T} + \frac{A}{T} d\xi$$

T... open system (there's always heat transfer)

In open system, there may be

(We can replace dQ by $d\phi$)

(which represents the energy flow or heat transfer, and the exchange of matter)

As the phases are mixing, there are also chances of a certain chemical reaction taking place in each phase.



When the entropy is exchanging with the surrounding, it is written as deS .

$$\text{Thus, } deS = \frac{dQ}{T} - \sum_r \frac{\mu_r}{T} deN_r$$

So our general expression for dS is :

$$dS = \frac{d\phi}{T} - \sum_r \frac{\mu_r}{T} deN_r + \frac{A}{T} d\zeta \rightarrow \text{Phase I \& II}$$

For Phase I & II.

$$dS = \frac{d^I\phi}{T^I} + \frac{d^{II}\phi}{T^{II}} - \sum_r \left(\frac{\mu_r^I}{T^I} - \frac{\mu_r^{II}}{T^{II}} \right) deN_r^I + \frac{A^I}{T^I} d\zeta^I + \frac{A^{II}}{T^{II}} d\zeta^{II}$$

of components entering

the phase I from phase II

$I, I, 0$

$I, I, 0$

$I, I, 0$

$$\frac{d\varphi}{T^I} = \frac{de\varphi}{T^I} + \frac{di\varphi}{T^I}$$

$$\frac{d^II\varphi}{T^{II}} = \frac{de^II\varphi}{T^{II}} + \frac{di^II\varphi}{T^{II}}$$

Thus, our final expression will become:

$$ds = \frac{de^I\varphi}{T^I} + \frac{de^II\varphi}{T^{II}} + \frac{di^I\varphi}{T^I} \left(\frac{1}{T^I} - \frac{1}{T^{II}} \right) - \sum_r \left(\frac{\mu_r^I}{T^I} - \frac{\mu_r^{II}}{T^{II}} \right) de n_r^I$$

$$+ \frac{A^I d\xi^I}{T^I} + \frac{A^{II} d\xi^{II}}{T^{II}}$$

→ represent the entropy change due to the energy exchange between phase I and II.

represents the entropy flow which is arising when the heat is exchanging between the closed system & the surrounding.

(External Entropy change)

diS : ↓
(represent the entropy change or entropy production when there is an internal change)

This term represents the entropy change which is due to the change in the matter between Phase I & II.

This term represents the entropy change due to the chemical reactions which is taking place in each phase.

$$\text{Thus, } \sigma = \frac{diS}{dt} = \frac{di^I\varphi}{dt} \left(\frac{1}{T^I} - \frac{1}{T^{II}} \right) - \sum_r \left(\frac{\mu_r^I}{T^I} - \frac{\mu_r^{II}}{T^{II}} \right) \frac{de n_r^I}{dt}$$

$$+ \left(\frac{A^I}{T^I} \right) v^I + \left(\frac{A^{II}}{T^{II}} \right) v^{II} \geq 0$$

(since $\frac{d\xi}{dt} = v$)

From the expression, we can see that each coefficient of v is enclosed in the bracket

definition of rate is given as:

In this case, the whole expression can be generalized as:

$$\sigma = \frac{diS}{dt} = \sum_j J_j X_j > 0$$

Entropy Flow
in an open
system.

↑
Entropy Flow

↓
Flux: rate
of the reaction

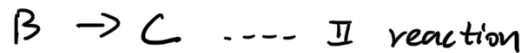
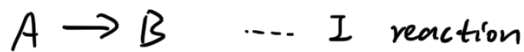
↑
 X_j : forces

Transformation Properties of Fluxes & Forces

$$\sigma = \frac{diS}{dt} = JX = \sum_j J_j X_j$$

$X = \frac{A}{T}$
 $\sigma = \left(\frac{A}{T}\right) v$

For consecutive reaction:



(when chemical
reaction is taking
place).

Affinity for reaction I: $A_1 = -(\mu_B - \mu_A) = \mu_A - \mu_B$

Affinity for reaction II: $A_2 = \mu_B - \mu_C$

$$-\frac{dn_A}{dt} = v_1 \Rightarrow \frac{dn_A}{dt} = -v_1$$

(change in the # of
moles of A per unit
time)

Similarly,

$$\frac{dn_C}{dt} = v_2$$

Thus, $\frac{dn_B}{dt} = -\frac{dn_A}{dt} - \frac{dn_C}{dt} = v_1 - v_2$
(rate of formation for B)

We know from Notes (3).

$$\sigma = \frac{1}{T} \sum_i A_i v_i \quad \text{(Entropy Production in Chemical Reaction)}$$

$$\text{Thus, } T \frac{dS}{dt} = A_1 v_1 + A_2 v_2 \quad \text{----- ①}$$

Suppose that a reaction is taking place, so they are our set of forces & fluxes for the first type of reactions.

Suppose if the reaction is taking a different path, for example: (Path ②)



The corresponding Affinities:

$$\begin{aligned} A_1' &= \mu_A - \mu_C = A_1 + A_2 \\ A_2' &= \mu_B - \mu_C = A_2 \end{aligned}$$

Similarly, $\frac{dn_A}{dt} = -v_1'$, $\frac{dn_B}{dt} = -v_2'$, $\frac{dn_C}{dt} = v_1' + v_2'$

Thus, comparing path ① & ②

$$v_1 = v_1', \quad v_2 = v_1' + v_2', \quad \rightarrow v_2' = v_2 - v_1'$$

Similarly, the entropy production for this particular reaction (Path ②) is:

$$\begin{aligned} T \frac{dS}{dt} &= A_1' v_1' + A_2' v_2' \\ &= (A_1 + A_2) v_1 + A_2 (v_2 - v_1') \\ &= A_1 v_1 + A_2 v_2 \end{aligned}$$

We can see that the new set of equations (Note: If the product form is the same!) are equal to the old set of equations.

If the final product form is the same, under such

circumstances, irrespective of the path that we are following, the transformation properties of fluxes & forces will always be same.

$$\sum_j J_j X_j = \sum_j J_j' X_j'$$