3_Entropy Production in Chemical Reaction_Irreversible Thermodynamics

Link: https://www.youtube.com/watch?v=7kT6LZ1ea0c&list=PLdBDmcnzLC_ZMUWMdy7SmcTgnnzyiRpql&index=2

Cosidering a chemical reaction @ constant Temperature and pressure.

Considering the surrounding absorbs a very small quantity of heat dH. (at T)

$$d_eS = \frac{dq}{T} = \frac{dH}{T}$$

(From Note 2, $\sigma = \frac{d_iS}{dt}$)

$$dS = d_eS + d_iS$$

$$= \frac{dH}{T} + d_iS$$

$$\Downarrow$$

$$-Td_iS = dH - TdS = dG$$

$(dG = dH - TdS)$

$$\Downarrow$$

$$d_iS = -\frac{dG}{T}$$

Rate of Entropy Production:

$$\sigma = \frac{d_iS}{dt} = -\frac{1}{T}\left(\frac{dG}{dt}\right)$$

Assuming the reaction is in open system.

Component: C (γ: 1, 2, ..., c)

Since $dG = -SdT + VdP + \sum_\gamma \mu_\gamma dn_\gamma$

(If the system is a closed syLtem, th.

, then

$$\sum_{\gamma} \mu_\gamma dn_\gamma = 0 \;, \Rightarrow dG = -SdT + VdP\,)$$

Since in the beginning, we have the assumption of constant T & P, $\Rightarrow dT = 0$, $dP = 0$

$$\Downarrow$$

$$(dG)_{T,P} = \sum_{\gamma} \mu_\gamma dn_\gamma$$

Thus, $\sigma = \dfrac{d_i S}{dt} = -\dfrac{1}{T} \sum_{\gamma} \mu_\gamma \dfrac{dn_\gamma}{dt}$

$$\Downarrow$$

For reaction:

$\nu_A A + \nu_B B \rightarrow \nu_C C + \nu_D D$

($\nu_i < 0$ for reactants; $\nu_i > 0$ for products)

$$\underbrace{(\,dn_\gamma = d\xi\, \nu_\gamma}$$

$\dfrac{d\xi}{dt}$ is chemical Reaction Rate per unit time

This ν_γ is the stoichiometric coefficient

$$\Downarrow$$

$$\sigma = -\frac{1}{T}\frac{d\xi}{dt}\underline{\sum_{\gamma} \mu_\gamma \nu_\gamma}$$

This term is equal to Affinity of a chemical reaction.

$$A = -\sum_{\gamma} \mu_\gamma \nu_\gamma$$

(Tendency of 2 atoms/compounds reacting with each other) (Tendency to what extent the reaction will take place)

Source: https://www.researchgate.net/publication/230883323_Entropy_generation_in_a_chemical_reaction
Paper: Entropy generation in a chemical reaction

The affinity of a chemical reaction is:

$$\mathcal{A} = -\sum_i \nu_i \mu_i. \tag{5}$$

It is zero in equilibrium because the chemical potentials of reactants and products are equal. A positive value of the affinity means that the chemical potentials of the reactants are greater that those of the products, and the reaction still goes forward.

Thus $\sigma = \frac{d_i S}{dt} = \frac{1}{T} A \frac{d\xi}{dt} > 0$

This term $\frac{d\xi}{dt} = \nu$ (Chemical reaction rate per unit time can be written as ν)

Thus, $\boxed{\sigma = \frac{1}{T} A \nu} > 0 \Rightarrow \sigma T = A\nu > 0$

If A & $\nu > 0$, then

the Forward Reaction $A + B \rightarrow C + D$ will take place.

If A & $\nu < 0$, then

the backward Reaction $A + B \leftarrow C + D$ will take place.

This expression can be extended to multiple components reactions or several reactions which are taking place at the same time.

K $\quad \ell = 1, 2, 3, \cdots r$

r $(= 1, 2, 3, \ldots r)$

Assuming there are
r amount of reactions.
which are taking place simultaneously

$$\frac{d_i S}{dt} = \sigma = \frac{1}{T} \sum A_\rho v_\rho > 0$$

At Equilibrium, $A_1 = A_2 = \cdots A_\rho = 0$

The following case is possible: $A_1 v_1 < 0$, $A_2 v_2 > 0$

but $|A_1 v_1| < |A_2 v_2|$, $\Rightarrow$ $\underbrace{A_1 v_1 + A_2 v_2}_{\Downarrow} > 0$

referred as coupled reactions.