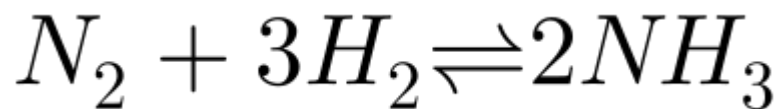


Entropy Production in Chemical Reactions

Consider a chemical reaction occurring at constant temperature and constant pressure. The reaction may be represented in the general form

$$\sum_i \nu_i A_i = 0$$

Here, A_i denotes the i -th chemical species and ν_i is its stoichiometric coefficient. The stoichiometric coefficient is negative for a reactant and positive for a product. For example, the reaction



can be written as

$$-N_2 - 3H_2 + 2NH_3 = 0$$

Thus,

$$\nu_{N_2} = -1, \quad \nu_{H_2} = -3, \quad \nu_{NH_3} = 2$$

Let $d\xi$ be the infinitesimal extent of reaction. The change in the amount of the i -th component is related to the extent of reaction by

$$\boxed{dn_i = \nu_i d\xi}$$

For a multicomponent system, the Gibbs free energy is given by

$$dG = -S dT + V dP + \sum_i \mu_i dn_i$$

Since the reaction is considered at constant temperature and pressure,

$$dT = 0$$

$$dP = 0$$

Therefore,

$$dG = \sum_i \mu_i dn_i$$

Substituting

$$dn_i = \nu_i d\xi$$

gives

$$dG = \sum_i \mu_i \nu_i d\xi$$

or

$$dG = \left(\sum_i \nu_i \mu_i \right) d\xi$$

Chemical Affinity

The chemical affinity of the reaction is defined as

$$A = \sum_i \nu_i \mu_i$$

Therefore, the change in Gibbs free energy can be written as

$$dG = A d\xi$$

Thus, the affinity is directly related to the change in Gibbs free energy with the extent of reaction:

$$A = \left(\frac{\partial G}{\partial \xi} \right)_{T, P}$$

The affinity therefore provides a thermodynamic measure of the tendency of the chemical reaction to proceed in the chosen direction.

Entropy Balance for the Reaction

For an irreversible process, the entropy balance is

$$dS = d_e S + d_i S$$

where $d_e S$ is the entropy exchanged with the surroundings and $d_i S$ is the entropy produced inside the system.

At constant temperature, if the surroundings receive an infinitesimal quantity of enthalpy dH , the entropy transferred to the surroundings is

$$d_e S = \frac{dH}{T}$$

Hence,

$$dS = \frac{dH}{T} + d_i S$$

Multiplying by T ,

$$TdS = dH + Td_i S$$

Rearranging,

$$Td_i S = TdS - dH$$

or

$$-Td_i S = dH - TdS$$

At constant temperature and pressure, the Gibbs free-energy relation is

$$dG = dH - TdS$$

Therefore,

$$-T d_i S = dG$$

and hence

$$d_i S = -\frac{dG}{T}$$

Entropy Production in Terms of Affinity

From the definition of chemical affinity,

$$dG = A d\xi$$

Substitution into the entropy-production equation gives

$$d_i S = -\frac{A d\xi}{T}$$

Therefore,

$$d_i S = -\frac{A}{T} d\xi$$

Dividing by dt ,

$$\frac{d_i S}{dt} = -\frac{A}{T} \frac{d\xi}{dt}$$

If the reaction rate is defined as

$$v = \frac{d\xi}{dt}$$

then the rate of entropy production is

$$\sigma = -\frac{Av}{T}$$

where σ is the rate of entropy production.

For a spontaneous reaction proceeding in the forward direction, $d\xi > 0$ and the Gibbs free energy decreases. Thus,

$$dG < 0$$

and from

$$dG = A d\xi$$

we have

$$A < 0$$

Consequently,

$$-\frac{Av}{T} > 0$$

which satisfies the second law of thermodynamics:

$$\sigma \geq 0$$

Condition for Chemical Equilibrium

At chemical equilibrium, there is no net thermodynamic tendency for the reaction to proceed. Therefore, the affinity becomes zero:

$$A = 0$$

Since

$$A = \sum_i \nu_i \mu_i$$

the condition for chemical equilibrium is

$$\sum_i \nu_i \mu_i = 0$$

At this condition,

$$dG = A d\xi = 0$$

and consequently

$$d_i S = 0$$

Thus, at constant temperature and pressure, the entropy production associated with a chemical reaction is related to the Gibbs free-energy change and can be expressed in terms of the chemical affinity and the reaction rate.

The important relation obtained for the reaction is

$$\boxed{\frac{d_i S}{dt} = -\frac{Av}{T}}$$

where A is the chemical affinity and v is the rate of reaction.