

Entropy Production and Entropy Flow in an Open System

An open system can exchange both **energy and matter** with its surroundings. Therefore, the entropy balance of an open system is more involved than that of a closed system. In addition to entropy transferred with heat, entropy can also be transferred with matter entering or leaving the system. Irreversible transfer of heat and matter between different regions, as well as chemical reactions occurring inside the system, produces entropy.

Consider a system consisting of two phases, I and II. The two phases can exchange energy and matter with each other, while the whole system may also exchange heat with the external surroundings.

Fundamental Thermodynamic Relation

For an open system containing several components, the fundamental thermodynamic equation is

$$dU = TdS - PdV + \sum_i \mu_i dn_i$$

Rearranging for dS ,

$$TdS = dU + PdV - \sum_i \mu_i dn_i$$

Therefore,

$$dS = \frac{dU}{T} + \frac{PdV}{T} - \sum_i \frac{\mu_i}{T} dn_i$$

This equation shows that the entropy change of an open system is affected not only by its energy change but also by the transfer of matter.

Entropy Balance for an Open System

The entropy balance is written as

$$dS = d_e S + d_i S$$

where $d_e S$ represents entropy flow across the boundary and $d_i S$ represents entropy production inside the system.

For heat transferred from the surroundings to the system at temperature T_e , the entropy entering with heat is

$$d_e S_{\text{heat}} = \frac{\delta Q_e}{T_e}$$

When matter enters or leaves an open system, it also carries entropy. If dn_i moles of component i are transferred, the associated entropy flow is represented by the appropriate partial molar entropy of that component.

Thus, for an open system, entropy flow contains contributions from both **energy transfer** and **matter transfer**.

Two-Phase System

Consider two phases, I and II, at temperatures T_I and T_{II} . Let energy and matter be transferred between the two phases.

Let $d_i q$ denote the heat transferred internally from phase II to phase I. Conservation of energy requires that the corresponding heat lost by phase II is equal to the heat gained by phase I:

$$d_I q = -d_{II} q$$

The entropy changes associated with this internal heat transfer are

$$dS_I = \frac{d_I q}{T_I}$$

and

$$dS_{II} = \frac{d_{II} q}{T_{II}}$$

Since

$$d_{II} q = -d_I q$$

we obtain

$$dS_{\text{heat}} = \frac{d_I q}{T_I} - \frac{d_I q}{T_{II}}$$

Therefore,

$$d_i S^{(\text{heat})} = d_I q \left(\frac{1}{T_I} - \frac{1}{T_{II}} \right)$$

This is the entropy produced because of heat transfer between the two phases.

Entropy Production Due to Transfer of Matter

Suppose component i is transferred from phase II to phase I. Let dn_i be the amount transferred to phase I. The corresponding changes in the amounts of the component are

$$dn_i^I = dn_i$$

and

$$dn_i^{II} = -dn_i$$

The chemical-potential contribution to the entropy change of phase I is

$$-\frac{\mu_i^I}{T_I} dn_i$$

For phase II, because it loses the amount dn_i ,

$$-\frac{\mu_i^{II}}{T_{II}} (-dn_i) = \frac{\mu_i^{II}}{T_{II}} dn_i$$

Therefore, the entropy production associated with the transfer of component i is

$$d_i S^{(i)} = dn_i \left(\frac{\mu_i^{II}}{T_{II}} - \frac{\mu_i^I}{T_I} \right)$$

For several components, summing over all components gives

$$d_i S^{(\text{matter})} = \sum_i dn_i \left(\frac{\mu_i^{II}}{T_{II}} - \frac{\mu_i^I}{T_I} \right)$$

The quantity in parentheses acts as the thermodynamic driving force for the transfer of matter between the two phases.

Entropy Production Due to Chemical Reaction

If a chemical reaction occurs in phase I, let $d\xi_I$ be the extent of reaction. Using the convention

$$A_I = \sum_i \nu_i \mu_i^I$$

the Gibbs free-energy change associated with the reaction is

$$dG_I = A_I d\xi_I$$

For the present affinity convention, the entropy production associated with the reaction is

$$d_i S^{(r, I)} = -\frac{A_I}{T_I} d\xi_I$$

Similarly, for a reaction occurring in phase II,

$$d_i S^{(r, II)} = -\frac{A_{II}}{T_{II}} d\xi_{II}$$

Therefore, the total entropy production due to chemical reactions in the two phases is

$$d_i S^{(\text{reaction})} = -\frac{A_I}{T_I} d\xi_I - \frac{A_{II}}{T_{II}} d\xi_{II}$$

Total Entropy Balance

The total entropy change can now be separated into entropy flow and entropy production.

The entropy flow from the external surroundings is

$$d_e S = \frac{\delta Q_e^I}{T_e^I} + \frac{\delta Q_e^{II}}{T_e^{II}} + \text{entropy carried by matter crossing the external boundary}$$

The internally produced entropy contains contributions from heat transfer, matter transfer and chemical reactions:

$$d_i S = d_i S^{(\text{heat})} + d_i S^{(\text{matter})} + d_i S^{(\text{reaction})}$$

Hence,

$$\begin{aligned}
d_i S = & d_I q \left(\frac{1}{T_I} - \frac{1}{T_{II}} \right) \\
& + \sum_i dn_i \left(\frac{\mu_i^{II}}{T_{II}} - \frac{\mu_i^I}{T_I} \right) \\
& - \frac{A_I}{T_I} d\xi_I - \frac{A_{II}}{T_{II}} d\xi_{II}
\end{aligned}$$

where

$$J_q = \frac{d_I q}{dt}$$

is the heat flux,

$$J_i = \frac{dn_i}{dt}$$

is the matter flux of component i , and

$$v_I = \frac{d\xi_I}{dt}, \quad v_{II} = \frac{d\xi_{II}}{dt}$$

are the reaction rates in the two phases.

General Form

The important result is that the rate of entropy production can be expressed as a sum of products of corresponding fluxes and thermodynamic forces:

$$\sigma = \sum_j J_j X_j$$

For the processes considered above, the individual products have the forms

$$J_q X_q$$

for heat transfer,

$$J_i X_i$$

for matter transfer, and

$$v X_r$$

for chemical reaction.

Thus, an open system provides the general situation in which several irreversible processes can occur simultaneously. Each process has its own flux and thermodynamic driving force, and the total entropy production is obtained by adding their contributions.

Since entropy production is governed by the second law,

$$\sigma \geq 0$$

with equality only when all irreversible processes have reached their corresponding equilibrium conditions.