

Non-Equilibrium Stationary States

A non-equilibrium stationary state is a state in which the macroscopic state variables of a system do not change with time, although the system is still away from thermodynamic equilibrium and irreversible processes continue to occur.

The important distinction is that **stationary** does not mean **equilibrium**.

At equilibrium, the thermodynamic driving forces and the corresponding net fluxes vanish, and therefore

$$\sigma = 0$$

In a stationary non-equilibrium state, the state variables remain constant with time, but one or more fluxes can remain non-zero. Consequently, entropy continues to be produced:

$$\sigma > 0$$

A simple example is a system maintained between two reservoirs at different temperatures. If the temperature difference is maintained continuously, heat flows through the system at a constant rate. The temperature distribution can become time-independent, but heat transfer and entropy production continue.

Thus,

$$\frac{\partial(\text{state variables})}{\partial t} = 0$$

does not necessarily imply

$$\sigma = 0$$

It only means that the system has reached a stationary condition.

Stationary State and Equilibrium State

Equilibrium state	Stationary non-equilibrium state
State variables are independent of time	State variables are independent of time
Driving forces vanish	Driving forces may remain finite
Net irreversible fluxes are zero	Irreversible fluxes may be non-zero
Entropy production is zero	Entropy production is generally non-zero
No continuous transport is required	Continuous exchange of energy or matter may maintain the state

Example of a Stationary Non-Equilibrium State

Consider a system in which a temperature gradient and a concentration gradient are maintained. Let the corresponding thermodynamic forces be X_{th} and X_{m} .

In the region close to equilibrium, the heat flux and matter flux can be written as

$$J_{\text{th}} = L_{11}X_{\text{th}} + L_{12}X_{\text{m}}$$

and

$$J_{\text{m}} = L_{21}X_{\text{th}} + L_{22}X_{\text{m}}$$

Here L_{ij} are phenomenological coefficients. The cross-coefficients L_{12} and L_{21} describe the coupling between heat and matter transport.

The entropy production is

$$\sigma = J_{\text{th}}X_{\text{th}} + J_{\text{m}}X_{\text{m}}$$

Substituting the two flux equations gives

$$\sigma = (L_{11}X_{\text{th}} + L_{12}X_{\text{m}})X_{\text{th}} + (L_{21}X_{\text{th}} + L_{22}X_{\text{m}})X_{\text{m}}$$

On applying the reciprocal relation

$$L_{12} = L_{21}$$

the expression becomes

$$\sigma = L_{11}X_{\text{th}}^2 + L_{12}X_{\text{m}}X_{\text{th}} + L_{12}X_{\text{th}}X_{\text{m}} + L_{22}X_{\text{m}}^2$$

Therefore,

$$\sigma = L_{11}X_{\text{th}}^2 + 2L_{12}X_{\text{th}}X_{\text{m}} + L_{22}X_{\text{m}}^2$$

Condition for a Stationary State

Consider a stationary state in which the matter flux is zero, while the thermal driving force is maintained externally:

$$J_{\text{m}} = 0$$

From the phenomenological equation for matter flow,

$$J_{\text{m}} = L_{21}X_{\text{th}} + L_{22}X_{\text{m}}$$

Therefore, at the stationary state,

$$L_{21}X_{\text{th}} + L_{22}X_{\text{m}} = 0$$

Hence,

$$X_{\text{m}} = -\frac{L_{21}}{L_{22}} X_{\text{th}}$$

Using the reciprocal relation $L_{21} = L_{12}$,

$$X_{\text{m}} = -\frac{L_{12}}{L_{22}} X_{\text{th}}$$

Thus, although the matter flux is zero, the matter-related thermodynamic force need not be zero. It adjusts itself so that the two coupled contributions to the matter flux cancel each other.

Minimum Entropy Production in the Stationary State

The entropy production is

$$\sigma = L_{11} X_{\text{th}}^2 + 2L_{12} X_{\text{th}} X_{\text{m}} + L_{22} X_{\text{m}}^2$$

Let X_{th} remain fixed and vary X_{m} . The condition for an extremum of entropy production is

$$\left(\frac{\partial \sigma}{\partial X_{\text{m}}} \right)_{X_{\text{th}}} = 0$$

Differentiating,

$$\frac{\partial \sigma}{\partial X_{\text{m}}} = 2L_{12}X_{\text{th}} + 2L_{22}X_{\text{m}}$$

Taking 2 common,

$$\frac{\partial \sigma}{\partial X_{\text{m}}} = 2(L_{12}X_{\text{th}} + L_{22}X_{\text{m}})$$

But

$$J_{\text{m}} = L_{21}X_{\text{th}} + L_{22}X_{\text{m}}$$

and since

$$L_{21} = L_{12}$$

we have

$$\boxed{\frac{\partial \sigma}{\partial X_{\text{m}}} = 2J_{\text{m}}}$$

Therefore, in the stationary state, where

$$J_{\text{m}} = 0$$

we obtain

$$\frac{\partial \sigma}{\partial X_m} = 0$$

Hence, the entropy production has an extremum at the stationary state.

Nature of the Extremum

To determine whether the extremum is a maximum or a minimum, differentiate once more with respect to X_m :

$$\frac{\partial^2 \sigma}{\partial X_m^2} = 2L_{22}$$

For a physically permissible irreversible process, the diagonal phenomenological coefficient L_{22} is positive:

$$L_{22} > 0$$

Therefore,

$$\frac{\partial^2 \sigma}{\partial X_m^2} > 0$$

Hence, the extremum is a **minimum**.

Therefore, for the stationary state,

$$\left(\frac{\partial \sigma}{\partial X_m} \right)_{X_{th}} = 0$$

and

$$\left(\frac{\partial^2 \sigma}{\partial X_m^2} \right)_{X_{th}} > 0$$

so that the entropy production has its minimum value.

Prigogine's Principle of Minimum Entropy Production

The result can be generalized to a system having several independent thermodynamic forces.

Suppose there are n independent forces

$$X_1, X_2, \dots, X_n$$

and the entropy production is

$$\sigma = \sum_i J_i X_i$$

If some of the forces are fixed externally and the remaining forces are free to adjust, the stationary state is characterized by the vanishing of the fluxes corresponding to the unrestricted forces:

$$J_j = 0 \quad (j = k + 1, \dots, n)$$

These conditions are equivalent to the minimum conditions

$$\left(\frac{\partial \sigma}{\partial X_j} \right)_{\text{fixed forces}} = 0$$

with the second derivative condition giving a minimum under the appropriate linear-regime conditions.

This result is known as **Prigogine’s principle of minimum entropy production**. It applies to stationary non-equilibrium states in the linear region close to equilibrium, with specified external constraints. □□

The physical meaning is that the system cannot reach ordinary equilibrium because some external conditions continuously maintain the driving forces. It instead settles into a stationary state in which the irreversible processes are balanced by the imposed exchange with the surroundings.

If the external constraints are removed, the driving forces disappear and the system can proceed towards equilibrium:

$$\text{Non-equilibrium} \rightarrow \text{stationary non-equilibrium state} \rightarrow \text{equilibrium}$$

when the external constraints maintaining the non-equilibrium condition are no longer present.