

Phenomenological Laws and Onsager's Reciprocal Relations

Irreversible processes involve the transport of quantities such as heat, mass, momentum and electric charge. The transport takes place because a driving force is present in the system. In a one-dimensional system, the driving force is generally related to the gradient of an appropriate physical property. A temperature gradient produces heat flow, a concentration gradient produces mass transport and a potential gradient produces an electric current.

The flux is the quantity transported per unit area per unit time. For a simple one-dimensional transport process, the flux is proportional to the corresponding driving force and can be written as

$$J = LX$$

Here J is the flux, X is the driving force and L is the transport coefficient. The value of L depends on the nature of the material and on the particular transport process.

| Phenomenological Laws

The general relation $J = LX$ gives the form of the phenomenological equations for different transport processes. The important examples are heat transfer, mass transfer, momentum transfer and electrical conduction.

For heat transfer, the flux is related to the temperature gradient by

$$J_Q = -K \frac{dT}{dx}$$

This is Fourier's law. The heat flux is directed from the region of higher temperature towards the region of lower temperature.

For mass transfer,

$$J_m = -D \frac{dc}{dx}$$

This is Fick's law of diffusion. Here D is the diffusion coefficient and dc/dx is the concentration gradient.

For momentum transfer,

$$J_M = -\mu \frac{du}{dx}$$

which represents Newton's law in transport form. Here du/dx is the velocity gradient and μ is the corresponding transport coefficient.

For electrical transport,

$$J_e = -\lambda \frac{dE}{dx}$$

which represents Ohm's law in phenomenological form.

These relations are called phenomenological laws because they establish the observed relation between a transport flux and its driving force. They are not fundamental laws in the same sense as the basic laws of thermodynamics; rather, they provide a convenient description of transport behaviour. The coefficients K , D , μ and λ characterize the corresponding transport processes.

Generalization of a Phenomenological Law

A phenomenological equation such as Fick's law is sufficient when the transport process can be considered independently. To see why a more general treatment is required, consider a system in which two solutes are diffusing simultaneously.

For the first solute, the simple equation would involve only its own concentration gradient. However, the second solute is also moving through the same system and has its own concentration gradient. There is therefore no general reason to assume that the movement of the second solute has no effect on the movement of the first.

The same situation can arise when a temperature gradient is present while diffusion is taking place. The system then contains both a mass-transfer process and a heat-transfer process. The flux associated with one process may contain a contribution arising from the driving force of the other process.

For two diffusing components, the rate of movement of the first component may therefore be written in the generalized form

$$\frac{dm_1}{dt} = D \frac{dc_1}{dx} + E \frac{dc_2}{dx}.$$

The first term represents the contribution of the gradient of component 1, while the second term represents the contribution associated with the gradient of component 2.

Similarly, for the second component,

$$\frac{dm_2}{dt} = F \frac{dc_2}{dx} + G \frac{dc_1}{dx}.$$

The coefficients D , E , F and G describe the corresponding transport contributions. If additional components or other driving forces are present, additional terms have to be included.

Coupled Flows

For one driving force, the associated irreversible flow can be described by an appropriate phenomenological equation. If two irreversible flows occur simultaneously and remain independent,

they can also be treated separately.

In a real system, however, simultaneous flows may depend on one another. A gradient responsible for one transport process may contribute to another flux. Such transport processes are called **coupled flows**.

This coupling is the reason why the single-process equation $J = LX$ has to be replaced by a set of phenomenological equations when several irreversible processes occur simultaneously.

| Notation for Coupled Processes

To treat all these processes using a common notation, the flux of the different transported quantities is represented by $J_1, J_2, J_3, \dots$.

The corresponding driving forces are represented by $X_1, X_2, X_3, \dots$.

The different transport coefficients are represented by L_{ij} . The first subscript identifies the flux, while the second subscript identifies the driving force associated with that contribution.

For example, L_{12} represents the contribution of X_2 to J_1 , whereas L_{21} represents the contribution of X_1 to J_2 .

Thus, for the diffusion example, D can be represented by L_{11} , while the coefficient E becomes L_{12} .

The driving forces are denoted by X_i . For example, for the two concentration gradients considered above,

$$X_1 = \frac{dc_1}{dx}$$

and

$$X_2 = \frac{dc_2}{dx}.$$

Linear Phenomenological Relations

The generalized equations become particularly simple when the driving forces are not too large. In this region the fluxes can be treated as linear functions of the driving forces.

For n simultaneous irreversible processes,

$$J_i = \sum_j L_{ij} X_j$$

where $i = 1, 2, 3, \dots, n$.

For two processes this relation gives

$$J_1 = L_{11}X_1 + L_{12}X_2$$

and

$$J_2 = L_{21}X_1 + L_{22}X_2.$$

The first term in each equation represents the direct response of a flux to its corresponding driving force. The second term represents the coupling with the other process.

Thus, L_{11} and L_{22} are the primary phenomenological coefficients, whereas L_{12} and L_{21} are the coupling coefficients associated with the cross-effects.

The assumption of linearity is important. The equation above is applicable when the driving-force gradients are sufficiently small that the flux can be represented as a linear function of the driving forces.

Onsager's Reciprocal Relations

The phenomenological equations contain the two coupling coefficients L_{12} and L_{21} .

The first describes the influence of X_2 on J_1 , while the second describes the influence of X_1 on J_2 .

Onsager showed theoretically that, for a properly selected pair of conjugate fluxes and driving forces, these two coefficients are equal:

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

In general, the relation is

$$L_{ij} = L_{ji}.$$

This is called **Onsager's reciprocal relation** or the **reciprocity relation**.

The relation has a specific meaning. L_{12} describes the effect of the second driving force on the first flux, whereas L_{21} describes the effect of the first driving force on the second flux.

Onsager's result states that these reciprocal coupling coefficients are equal when the appropriate conjugate variables are used.

It is important not to interpret the relation as saying that all transport coefficients are equal. For example,

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

does not imply

$$L_{11} = L_{22}.$$

The reciprocal relation concerns the corresponding off-diagonal or coupling coefficients.

Example of Conjugate Flows

Consider a one-dimensional conducting rod in which there is both a potential difference ΔE and a temperature difference ΔT between the two ends. With the appropriate choice of thermodynamic forces, the electric current I and the entropy flux J_S form a conjugate pair.

Their phenomenological equations can be written as

$$I = L_{11}\Delta E + L_{12}\Delta T$$

and

$$J_S = L_{21}\Delta E + L_{22}\Delta T.$$

The reciprocal relation provides the additional equation

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

Thus, the four phenomenological coefficients are not all independent. Once the appropriate measurable relations are used together with the reciprocal relation, the coefficients can be

determined.

The important condition is that the flows must be selected as appropriate conjugate flows. The reciprocal relation is therefore not a statement about arbitrary pairs of transport processes.

The microscopic basis for Onsager's reciprocal relation is provided separately by the **Principle of Microscopic Reversibility**.