Study Notes on Onsager Reciprocal Relations

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Onsager's Reciprocal Relations

The irreversible processes involve the transport of one or more quantities such as mass momentum and electric charge. In all these cases, a quantity called the flux is transported because of a driving force which-is derived from the gradient of some physical property of the system. Thus, the driving force for a heat flux is the temperature gradient; that for a mass, flux is the concentration gradient and that for an electric current is the potential gradient. In all these cases, the magnitude of the flux (or flow) is directly related to the driving force. In general, the transport phenomenon for a one-dimensional system can be expressed as:

$$J = LX \qquad ...(1)$$

Here, J is the flux (flow per unit area) of the quantity transported along a given direction; X is the driving force (or the gradient) which causes the flow in that direction and L is the proportionality constant called the transport coefficient.

For the various transport (transfer) processes, we can now write the following relations:

1. Heat Transfer: JQ = $J_Q = -\kappa \frac{dT}{dx}$ (Fourier's law) ...(2)

2. Mass Transfer J_m = $D = -D\frac{dc}{dx}$ (Fick's law) ...(3)

3. Momentum Transfer: $J_M = -\mu \frac{du}{dx}$ (Newton's law) ...(4)

4. Flow of electricity: $J_e = -\lambda \frac{dE}{dx}$ (Ohm's law) ...(5)

Here, the J_is are the corresponding fluxes: J_Q is the heat flux; J_m, the mass flux; J_M, the momentum flux and J_e, the electric flux (i.e., the electric current). The transport coefficients κ, D, μ and λ depend upon the material properties of the system.

Phenomenological equations describe in a simple way how the system changes. Ohm's law and Fick's law of diffusion are some familiar examples of phenomenological equations. The phenomenological equations of irreversible thermodynamics are like these equations but are more general. Fick's law of diffusion, dm/dt = D(dc/dx), where dm/dt is the rate of change of solute across unit surface area under the influence of the concentration gradient dc/dx and D is the diffusion coefficient, may be adequate in a simple system.

We can generalize the equation dm/dt = D(dc/dx) for a one-dimensional flow as follows:

$$\frac{dm_1}{dt} = D\frac{dc_1}{dx} + E\frac{dc_2}{dx} \qquad ...(6)$$

Here, the second term incorporates the influence of the gradient of the second solute on the movement of the first solute. Similarly, we can write down another equation for the movement of the second solute:

$$\frac{dm_2}{dt} = F\frac{dc_2}{dx} + G\frac{dc_1}{dx} \qquad ...(7)$$

Here, D, E, F, G are the corresponding diffusion coefficients. If there are more solutes and thermal gradients, other terms will have to be written.

To simplify notation, we use a single symbol J for dm/dt. Symbols J_1, J_2 ……… are used for the rates of movement of different entities (solute, heat, etc.). Again, the multiplicity of coefficients D, E, F, G, ……… can be replaced by a single symbol L with appropriate subscripts. Accordingly, D becomes L_{11}, E becomes L_{12}. Here the first subscript refers to the component that moves (and is thus the same as the subscript on the corresponding J) while the second subscript refers to the component whose gradient is being considered. The gradient or driving force is designated by the symbol X. Thus, $X_1 = dc_1/dx$, $X_2 = dc_2/dx$, and so on. This notation is both convenient and easy to remember.

For a given driving force in a system, they associated with it a single irreversible flow which can be described by an appropriate phenomenological relation. Likewise, two simultaneous irreversible flows, provided they are independent of each other, can be described by appropriate phenomenological relations. In practice, however, the simultaneous flows are not independent of each other's gradient. Such flows are known as coupled flows. Onsager developed the irreversible thermodynamics (or non-equilibrium thermodynamics) in 1931 for analyzing coupled irreversible flows.

If the gradients X_is are not too great, the fluxes J_is are linear functions of the driving forces. Thus, we can write

$$J_i = L_{i1}X_1 + L_{i2}X_2 + \ldots\ldots.. + L_{in}X_n \qquad \ldots(8)$$

where i = 1, 2, 3, n.

The relations depicted by Eq. 8 are called linear phenomenological relations. The coefficients L_{ii} are called the primary phenomenological coefficients while the coefficients L_{ij} are called Onsager's phenomenological coefficients. In the Onsager coefficients, the subscript i denotes the flux and the subscript j denotes the driving force.

The solution of Eq. 8 is extremely difficult. Onsager finally solved it in 1931. The difficulty in solving this equation lies in the fact that the phenomenological coefficients must be determined experimentally. The primary coefficients can, of course, be determined easily. The coupling coefficients (Onsager's phenomenological coefficients, L_{ij}), however, present severe difficulties for their experimental measurement since they involve the control of many experimental parameters. Onsager theoretically showed that

$$L_{ij} = L_{ji} \qquad \ldots(9)$$

Eq. 9 gives Onsager's reciprocal relations (also called reciprocity relations).

Onsager showed that these relations exist for a properly selected pair of flows, called the conjugate flows. It is, however, not clear what constitutes a properly selected pair. Suffice it to say that in the case of a one-dimensional conducting rod or wire, if ΔE is the potential difference and ΔT is the temperature difference between the ends, then using ΔE and ΔT as the driving forces, the electric current I (= J_e) and the entropy current (or entropy flux) J_s, form a pair of conjugate flows, though the electric current and the heat flux J_Q do not do so. The expressions for I and J_s are

$$I = L_{11}\Delta E + L_{12}\Delta T \qquad \ldots(10)$$

$$J_s = L_{21}\Delta E + L_{22}\Delta T \quad ...(11)$$

Using the definitions of electrical and thermal conductivities, we can obtain two equations relating the four phenomenological coefficients L_{11}, L_{12}, and L_{22} to measurable properties of the system. The fourth expression is furnished by the Onsager reciprocity relation, viz.,

$$L_{12} = L_{21} \quad ...(12)$$

Thus, all the coefficients can be determined. In general,

$$L_{ij} = L_{ji} \quad ...(13)$$

In simple words this means that the coefficient which expresses the influence of force j on the flux i is the same as the coefficient which expresses the effect of force i on the flux j.

Consider, for instance, Ohm's law, E =IR or I = E(1/R), where E is the potential difference, I the current, R the resistance and 1/R the conductance, Comparing this equation with the equation

$$J1 = L_{11}X_1 + L_{12}X_2 + L_{13}X_3 \ ..... + ... \quad ...(14)$$