Onsager's Reciprocal Relations

Biman Bagchi

The article is a brief write-up on the Nobel Prize winning paper of Lars Onsager which appeared in *Physical Review*, Vol.37, 1931.

In one of the best known relations that connects thermodynamics with chemical kinetics, the ratio of the forward (k_f) to the backward (k_b) rate constant of a chemical reaction A $\rightleftharpoons$ B is equal to the equilibrium constant (K_{eq}) of the reaction; that is $\frac{k_f}{k_b} = K_{eq}$. This relationship between the forward and the backward rates of a binary reaction plays an important role in complex processes, where a system of, say consecutive binary reactions, are involved. A popular textbook example is a ternary reaction when A, B and C form a triangle. In this case, we invoke the principle of detailed balance, which states that at equilibrium each binary reaction step must be balanced independently. That is, at equilibrium, $k_{AB}P_A = k_{BA}P_B$, $k_{BC}P_B = k_{CB}P_C$, and so on. This is sometimes referred to as the 'principle of microscopic reversibility'. This serves as a strong condition because we can have a time-independent solution which is not the equilibrium condition. That is, there could be a net flow from A to B, B to C and C to A in such a way that the concentrations of A, B and C are time independent. The latter is called a steady state solution. The principle of microscopic reversibility is not applicable to the latter case as it is not an equilibrium state.

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Even though formulated at equilibrium, these relations, derived using the principle of microscopic reversibility, offer powerful conditions, and also restrictions, on the non-equilibrium dynamics of complex chemical systems. They assure that in the long time, the system approaches the proper equilibrium state because they select the equilibrium state from other time-independent solutions which describe the steady state. Now, the question

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naturally arises: can we extend such relations to irreversible macroscopic processes where there are no chemical reactions but there are flows of energy and matter under forces which are the gradients? Examples of such flows are provided by Fick's law of diffusion and Fourier law of heat conduction. Let us briefly dwell on this as this was where Lars Onsager made his important contribution.

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Onsager observed that when two or more irreversible transport processes, like heat conduction, electrical conduction and diffusion take place simultaneously in a macroscopic system, the processes may interfere with each other. In fact, such interferences or cross-connections were already known. We see this in the example of the Peltier effect. When an electric current flows in a circuit that consists of different metallic conductors, we observe the production or absorption of heat at the junctions. The reverse is the Seebeck effect when junctions of different metals maintained at different temperatures give rise to an electromotive force in the circuit called the thermoelectric force, which can be used to light a lamp. Many of us have seen the demonstration of this in science museums.

Next, we note that individual transport processes in the absence of the interference effects mentioned above, like mass transport (described by Fick's law) and heat transport (the Fourier law) are well described by a relation between the flux (J) and the force (X). However, the presence of the examples of coupled irreversible processes mentioned above (the thermoelectric phenomena, the transference phenomena in electrolytes and heat conduction in an anisotropic medium) clearly shows that the phenomenological laws to be generalized by including cross-terms. Hence, for two such related processes, we need to write the transport laws as:

$$\mathbf{J}_{\mathrm{i}} = \Sigma \mathbf{L}_{\mathrm{ij}} \mathbf{X}_{\mathrm{j}} \,, \tag{1}$$

where $\mathbf{J}_{\mathrm{i}}$ and $\mathbf{X}_{\mathrm{i}}$ are the flux and the force of the individual transport process 'i'. $\mathbf{L}_{\mathrm{ij}}$ is the proportionality coefficients. For the diagonal case, these are the transport properties like diffusion coefficient and conductivity. However, nothing much was known for the off-diagonal coefficients.

In a seminal paper in 1931, Onsager established, using the principle of microscopic reversibility and the assumption of regression to show that

$$\mathbf{L}_{\mathrm{ij}} = \mathbf{L}_{\mathrm{ji}} \ for \ \mathrm{j} \neq \mathrm{i}. \tag{2}$$

i.e., the off-diagonal terms are equal. This is Onsager's reciprocal relations [1].

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Suggested Reading

[1] **Lars Onsager, Reciprocal Relations in Irreversible Processes. I, *Phys. Rev.*, Vol.37, No.4, p.405, 1931.**

[2] **Lars Onsager, *Nobel Lecture-Chemistry*, Nobel Foundation, Stockholm, 1968. https://www.nobelprize.org/prizes/chemistry/1968/ceremony-speech/.**

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