

IRREVERSIBLE THERMODYNAMICS

KENNETH S. PITZER

University of California, Berkeley, California, U.S.A.

There are alternative sets of postulates which yield entirely equivalent results for several important theories. In such cases the choice of a particular set of postulates may be based upon mathematical simplicity, close relationship to experiments or to the nature of the theory, or merely personal taste. While the postulate of conservation of energy is usually presented in similar form for thermodynamics or statistical mechanics, the form of the postulate comprising the second law is commonly very different. In thermodynamics the postulate may be in terms of the impossibility of an isothermal engine producing work at the expense of heat while in quantum statistical mechanics one postulates equal *a priori* probability for all individual quantum states. It is the purpose of the present paper to point out that there are such alternatives for the additional postulate necessary to derive the Onsager equations for the irreversible thermodynamics of processes in the linear rate law region near equilibrium.

The heat engine, which was the primary subject of interest during the original development of classical thermodynamics, comprises both reversible and irreversible processes. In such machines the separation of the reversible changes of the working fluid from the frictional effects and the irreversible heat leaks is practically self-evident. Thus in his classic paper "On the dynamical theory of heat", Kelvin¹ assumes this separation of processes to be obvious in ordinary heat engines where he simply specifies "perfect engine", but he discusses the separation at length for thermo-electric phenomena as a separate postulate.

The magnificent work of Gibbs, van't Hoff, and others, showing the applicability of thermodynamics to physicochemical equilibria distracted attention for a time from steady-state problems. But in 1926 Eastman² applied Kelvin's method to thermo-osmosis, the Soret effect, and the properties of thermocells. Wagner³ and London⁴ used similar methods soon thereafter. In these treatments it is assumed that the irreversible heat flow constitutes a process which is independent of the processes transferring the material components. Then the second law of thermodynamics requires the entropy to be a maximum with respect to any transfer of matter and thus determines the steady-state distribution.

The new formulation of the near-equilibrium problems in 1931 by Onsager⁵ in terms of linear rate laws and his derivation of the reciprocal relationships gave new impetus to theoretical work and de Groot⁶, Prigogine⁷ and others soon applied this new formulation to a wide variety of phenomena. It was implied in some of these treatments that the new methods were more rigorous in spite of the fact that in so far as the problems had been treated previously by Kelvin's methods, the results were identical. However, the

new formulation is more convenient in many instances. Onsager's derivation of his reciprocal relationships is based upon the postulate of microscopic reversibility and upon statistical arguments concerning the decay of fluctuations. Among the several other statistical derivations which have been given is that by Parlin, Marcus and Eyring⁸ in terms of absolute reaction rate theory.

While the convenience and power of the Onsager formulation is a great advantage, this may be attained from the Kelvin postulate of independent processes, as has been demonstrated by Li⁹. Indeed, the present author believes that this form of the basic postulate is most appropriate to thermodynamics as well as having a historical precedent. A simple derivation of the Onsager relationships from the Kelvin postulate is given below. This presentation is essentially similar to that of Li but is more concise and avoids one possibly misleading implication*.

Following the usual definitions, one selects co-ordinates a_i which measure the amounts of various components of matter, of heat, *etc.*, transferred from one portion of the system to another. The zeros of these co-ordinates are selected at the state of equilibrium. Hence the entropy change from equilibrium, to the second order, is

$$\Delta S = -\frac{1}{2} \sum_{i,j} g_{ij} a_i a_j \quad (1)$$

The rate of change of a co-ordinate, \dot{a}_i is a flux which is commonly given the symbol \mathcal{J}_i . Also the restoring force or potential difference associated with the i -th co-ordinate is defined by the equation

$$X_i = \frac{\partial(\Delta S)}{\partial a_i} = - \sum_j g_{ij} a_j \quad (2)$$

The rate of increase of entropy, within the region of validity of equation (1), is

$$\dot{S} = - \sum_{i,j} g_{ij} \dot{a}_i a_j = \sum_i \mathcal{J}_i X_i \quad (3)$$

where we note the particularly simple form of the expression as a sum of terms $\mathcal{J}_i X_i$.

In practice it is usually easier to write an expression for the rate of entropy increase directly in terms of defined fluxes and differences of temperature, pressure, concentration, *etc.*, within the system. Then the potential conjugate to a given flux may be found by identifying the complete factor which, multiplied by \mathcal{J}_i , constitutes a term in the equation for \dot{S} .

* It should be noted that there is no limit upon the number of independent microscopic processes. For example in a thermo-osmosis system there might be several different membranes and each would have its characteristic heat of transfer for passage of matter. However, the number of fluxes required to describe the macroscopic system is fixed by the number of components, *etc.* While Li's result is identical with that given here, his use of a square transformation matrix implies an unnecessary limitation of equal numbers of fluxes in the two sets.

IRREVERSIBLE THERMODYNAMICS

At equilibrium all gradients X_i are zero and by thermodynamics all fluxes must be zero. Also for systems not at equilibrium \dot{S} must be positive regardless of the signs of the X_i . Consequently the \mathcal{J}_i must change sign with the X_i and one expects a linear dependence of \mathcal{J}_i on X_i to be a good approximation for small X_i .

An arbitrary selection of fluxes cannot be expected to yield those microscopic processes which are actually independent of one another but we postulate that such non-interacting processes exist in the region of first-order rate laws. For this special set of fluxes, \mathcal{J}'_j , each flux depends only upon its corresponding potential gradient X'_j , hence

$$\mathcal{J}'_j = L'_j X'_j \quad (4)$$

where L'_j is the linear rate constant.

The arbitrary fluxes \mathcal{J}_i can be expressed in terms of the non-interacting fluxes \mathcal{J}'_j by a linear transformation

$$\mathcal{J}_i = \sum_j \alpha_{ij} \mathcal{J}'_j \quad (5)$$

and this transformation may be substituted into equation (3) for entropy production

$$\dot{S} = \sum_j \sum_k \alpha_{ij} \mathcal{J}'_j X_i \quad (6)$$

The coefficient of \mathcal{J}'_j in equation (6) is

$$X'_j = \sum_i \alpha_{ij} X_i \quad (7)$$

Substitution of these results and the rate equations (4) for the independent processes into equations (5) yields

$$\mathcal{J}_i = \sum_j \sum_k \alpha_{ij} L'_j \alpha_{kj} X_k \quad (8)$$

and if we define a new rate constant L_{ik} :

$$\mathcal{J}_i = \sum_k L_{ik} X_k \quad (9)$$

$$L_{ik} = \sum_j \alpha_{ij} \alpha_{kj} L'_j \quad (10)$$

But it is evident from equation (10) that

$$L_{ik} = L_{ki} \quad (11)$$

which, for various i, k , constitute the Onsager reciprocal relationships.

References

- ¹ W. Thomson (Lord Kelvin). *Math. Phys. Papers*, Vol. I, Art. XLVIII, The University Press, Cambridge (1882); reprinted from articles in *Trans. Roy. Soc. Edinburgh*, 1851-1854
- ² E. D. Eastman. *J. Am. Chem. Soc.*, **48**, 1482 (1926); **49**, 794 (1927); **50**, 283, 292 (1928)
- ³ C. Wagner. *Ann. Physik.*, **3**, 629 (1929); **6**, 370 (1930)
- ⁴ H. London. *Proc. Roy. Soc. London, A* **171**, 484 (1939)
- ⁵ L. Onsager. *Phys. Rev.*, **37**, 405 (1931); **38**, 2265 (1931)
- ⁶ S. R. de Groot. *Thermodynamics of Irreversible Processes*, North Holland Publishing Co., Amsterdam (1951)
- ⁷ I. Prigogine. *Introduction to Thermodynamics of Irreversible Processes*, C. C. Thomas, Publisher, Springfield, Ill. (1955)
- ⁸ R. B. Parlin, R. J. Marcus and H. Eyring. *Proc. Nat. Acad. Sci., U.S.*, **41**, 900 (1955)
- ⁹ J. C. M. Li. *J. Chem. Phys.*, **29**, 747 (1958)