THE PRINCIPLE OF MICROSCOPIC REVERSIBILITY

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In recent years increasing use has been made of a new postulate which perhaps cannot yet be stated in its final form, but which requires in a general way in the case of a system in thermodynamic equilibrium not only that the total number of molecules leaving a given state in unit time shall on the average equal the number arriving in that state in unit time, but also that the number leaving by any particular path shall on the average be equal to the number arriving by the reverse of that particular path, thus excluding any cyclical maintenance of the equilibrium state. The writer has ventured to name this postulate *the principle of microscopic reversibility*. The recognition that some such principle is often applicable has had a considerable history, and a brief statement as to some of the previous considerations which have come to the writer's attention will not be out of place.

As early as 1911, Kohnstamm and Scheffer[1] in considering the rates of two opposing reactions concluded that the same intermediate states occurred as steps in the reverse reactions. And in 1915, Marcelin[2] correctly concluded that the energy of the molecules in the activated states which lead to reaction has to be the same for two opposing reactions, since otherwise the temperature coefficients for the two reaction rates would not lead to the correct temperature coefficient for the equilibrium constant as given by the van't Hoff equation. Marcelin very illuminatingly likens the two opposing reactions to the migrations of people between two countries separated by a mountain range. For migration in either direction the top of the range must be crossed, in analogy with the equal energies of the activated molecules for the two opposing reactions.

A number of applications of the principle of microscopic reversibility have been made by Langmuir,[3] and as early as 1916 in connection with the problem of evaporation and condensation, he gave the following statements of the principle.

"Since evaporation and condensation are in general thermodynamically reversible phenomena, *the mechanism of evaporation must be the exact reverse of that of condensation*, even down to the smallest detail." And in a footnote "According to the principle already enunciated, by which every element in the mechanism of a reversible process must itself be reversible, it follows that any rearrangement of molecules on the surface, which takes place during the condensation of a vapor, must take place to the same extent, but in a reverse direction, in the evaporation of the substance."

Noting the words which Langmuir has italicized in the first statement, we see that by regarding this phrase as applying also to the simultaneous evaporation and condensation which are presumably taking place when the system is in equilibrium, we have a statement of the principle which agrees with the one given in the first paragraph, and as far as the writer knows this is the first explicit formulation of the principle. Furthermore, it is evident from his second statement that Langmuir appreciated the generality of the principle.

In 1917, Einstein,[4] as a necessary step in his famous deduction of the Planck radiation law, considered a molecule capable of existing in different quantum states in equilibrium with radiation, and taking a given pair of the quantum states S_m and S_n ($\epsilon_n > \epsilon_m$), equated the number of molecules passing from state S_m to state S_n by the absorption of a quantum $h\nu = \epsilon_n - \epsilon_m$ with the number passing in the reverse direction through the emission of a quantum of the same frequency. He thus used the principle of microscopic reversibility without, however, making any explicit statement of it.

In 1921, Klein and Rosseland[5] considered two reverse processes which they named collisions of the first and second kinds. In a collision of the first kind an atom is raised from a lower to a higher quantum state by using the kinetic energy of a swiftly moving electron, and in a collision of the second kind the atom drops back to the lower state giving up its energy to an electron and thus raising its velocity. By applying the principle of microscopic reversibility, Klein and Rosseland calculated the relative probability of these two kinds of collision, but again gave no explicit statement of the principle.

Several applications of the principle of microscopic reversibility especially in connection with the transfer of energy between colliding atoms have also been made by Franck,[6] and in at least two places he has made explicit statements which are closely connected with the principle. In 1923[7] he makes the statement:

"Im thermodynamischen Gleichgewicht muss jeder Elementarprozess, der in einer bestimmten Richtung *n* mal pro Sekunde vorkommt, einem ebensooft vorkommonenden Elementarprozess umgekehrter Richtung entsprechen." And in 1924[8] "Dieses Prinzip lautet in vereinfachter Fassung: Ein Prozess, der in einer bestimmten Richtung *n* mal pro Sekunde in einem gegebenen Volumen abläuft, läuft bei thermodynamischem Gleigewicht ebenfalls *n* mal pro Sekunde in umgekehrter Richtung ab."

It will be seen that the first of these two statements of Franck—strictly taken—seems to be merely a necessary consequence of the statistical equilibrium, since it does not definitely assert that the two opposing elementary processes which correspond to each other are the exact reverse of each other. The second statement, on the other hand, definitely equates the number of times per second that a given elementary process proceeds in the forward and reverse direction. The impression is gained, however, that Franck has not considered the possibility of cyclical elementary processes and hence has regarded the principle as a logical necessity rather than as an independent postulate.

In 1924, it was pointed out by R. H. Fowler in connection with collisions of the first and second kind that the exclusion of cyclical elementary processes is a definite and not obviously necessary postulate, and the same thing was pointed out by the present writer for quantum transitions in general. It also seemed to the writer that the postulate was of enough interest so that it should be given a definite name, and the proposal was made that it be called "the principle of microscopic reversibility."

The statement of Fowler was made in connection with the expression of Klein and Rosseland for the relative probabilities of collisions of the first and second kinds. This expression was obtained by Klein and Rosseland with the help of the principle of microscopic reversibility, which they tacitly introduced since they stated that there would be no loss in generality in limiting their considerations to an atom which could only exist in two quantum states thus eliminating from the very start the consideration of the possibility of cyclical processes. In the case of a molecule with three quantum states, Fowler[9] makes the following remark with the reference to the possibility of making a generalization of the Klein and Rosseland result:

"But it can only be made when by an artificial limitation we have ruled out the possibility of the cyclic process $1 \longrightarrow 2$, $2 \longrightarrow 3$, $3 \longrightarrow 1$. I cannot find any convincing *a priori* reason to believe that such cycles are not permissible."

The statement of the writer[10] was as follows:

"This assumption should be recognized as a distinct postulate and might be called the principle of *microscopic* reversibility. In the case of a system in thermodynamic equilibrium, the principle would require not only that the total number of molecules leaving a given quantum state in unit time shall equal the number arriving in that state in unit time, but also the the number leaving by any one particular path shall be equal to the number arriving by the reverse of that particular path."

In 1925, Lewis[11] considered the principle of microscopic reversibility and proposed for it the name of "the law of entire equilibrium." There seems to be no reason, however, for abandoning the earlier name. Lewis stated the law in the form:

"Corresponding to every individual process there is a reverse process, and in a state of equilibrium the average rate of every process is equal to the average rate of its reverse process."

In addition to indicating some of the historical relations, the main purpose of this note is to point out that the principle of microscopic reversibility can be regarded at the present time only as an unproved assumption. Although closely connected with the second law of thermodynamics, it cannot be derived therefrom. Lewis's attempted derivation with the help of the notion of catalytic acceleration is not convincing, since there is no reason why catalysts should not have the property of producing compensatory increases in the rates of the steps of a cyclical process. It would seem as if the postulate were a useful one, leading often at least to correct results. Nevertheless the best formulation of the principle and the precise range of its validity are matters for the future to determine.

[1] Kohnstamm and Scheffer, *Proc. Amst. Acad.*, **13,** 789 (1911). See footnote on page 795.

[2] Marcelin, *Ann. d. physique*, **3,** 173 (1915).

[3] Langmuir, *J. Amer. Chem. Soc.*, **38,** pp. 2253, 2262 (1916).

[4] Einstein, *Phys. Zts.*, **18,** 121 (1917).

[5] Klein and Rosseland, *Zts. f. Phys.*, **4,** 46 (1921).

[6] Franck, *Zts. f. Phys.*, **9,** 289 (1922); Cario and Franck, **11,** 161 (1922).

[7] Franck, "Ergebuisse der Exakten Naturwissenschaften," Zweiter Band, p. 112, Berlin, Julius Springer, 1923.

[8] Franck, "Die Naturwissenschaften, Heft 47 Zwölfter Jahrgang," p. 1066, Berlin, Julius Springer, 1924.

[9] Fowler, *Phil. Mag.*, **47,** see p. 264 (1924).

[10] Tolman, *Phys. Rev.*, **23,** see p. 699 (1924).

[11] Lewis, *Proc. Nat. Acad. Sci.*, **11,** 179 (1925).

THE DYNAMICAL FUNCTION OF THE TYMPANIC MEMBRANE AND ITS ASSOCIATED OSSICLES

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It is common knowledge to otologists and to physicists also who have been engaged in the study of deafness that lesions in the conducting mechanism of the middle ear cause a depression in the acuity of hearing for low frequency sounds only. Lesions in the internal ear with its associated nerves and nerve endings in practically all cases cause depression in hearing for the high frequency region. If the depression occurs only at high frequencies it is certain that the middle ear dynamical system functions in a normal manner. On the other hand, depressions at low frequency only, mean that the internal ear is normal.

The internal ear mechanism together with its associated nerves and their endings have been intensively studied during the past five or six years by