

A NEW PRINCIPLE OF EQUILIBRIUM

BY GILBERT N. LEWIS

DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CALIFORNIA

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The Non-Existence of Cyclic Equilibrium.—At a given temperature a system is said to be in a state of physical and chemical equilibrium if none of the describable properties of the system change, on the average, with the time. Any given substance may be regarded as made up of *groups*, each group being defined by certain macroscopic or microscopic properties. Thus a heterogeneous substance such as a mixture of ice and water naturally divides itself into the two groups ice and water, but each of these may be divided into sub-groups. Thus the liquid water may contain several molecular species, such as H_2O , $(H_2O)_3$, H^+ , H_3O^+ , OH^- and each of these species may be taken as a group. The molecules of each such species may be further divided. One group may consist of all the molecules of the species H_2O located within a certain cubic centimeter, and having such motion of translation that the component in an X direction lies between certain specified limits, that in the Y direction between other specified limits, and so on. (By taking these limits as close together as we please, we may diminish the *average* content of any one group without limit.) Every group so defined would be still further sub-divided if we should specify the positions and the motions of the several particles of which the molecule itself is composed.

When once we have specified the characteristics of a group, no matter how closely it may be delimited, the average number of molecules which it contains must remain constant when equilibrium is attained. In other words, the average number of molecules which in unit time cease to belong to a given group must be equal to the average number of new molecules entering that group.

In some cases thermodynamics gives more information than this concerning equilibrium. Let us consider a system of ice, water and water vapor, and indicate by s_{wi} , s_{iw} , s_{vw} , s_{wv} , s_{vi} , s_{iv} the average number of molecules changing per second from water to ice, from ice to water, from vapor to water, and so on. The definition of equilibrium which we have stated requires only that the average amount of each group remain constant. The condition that the amount of ice be constant is

$$s_{iv} + s_{iw} = s_{vi} + s_{wi}$$

It does not prohibit a condition of cyclic equilibrium such that

$$s_{iw} > s_{wi}; s_{wv} > s_{vw}; s_{vi} > s_{iv}$$

Nevertheless we know that such a condition is impossible, for the ice may be removed from the system in such a manner as neither to change the relative rates of vaporization of the liquid and of liquefaction of the vapor, nor to disturb the equilibrium between these two groups. But after the ice is removed we must have s_{vw} equal to s_{vw} , and therefore this must have been the condition before the removal of the ice.

Let us suppose that an equilibrium exists between two chemical substances $A \rightleftharpoons B$, and that there are two paths by which A can be converted into B and two corresponding reverse paths. The four rates of reaction may be expressed by s_{AB} , s_{BA} , s'_{AB} and s'_{BA} . Often we know that we cannot have a cyclic equilibrium such that

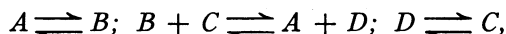
$$s_{AB} > s_{BA}; s'_{AB} < s'_{BA},$$

but rather must write

$$s_{AB} = s_{BA}; s'_{AB} = s'_{BA}.$$

For if this were not the case we could add a minute amount of some catalyst which would increase the rate of the reaction and its inverse along one of the paths, without affecting the two rates in the other path. This would disturb the existing equilibrium, contrary to the results of observation and of thermodynamics.

In the absence of catalytic phenomena we are still led to similar conclusions. Let us consider Wegscheider's paradox.¹ He writes, for example, the simultaneous reactions,



and points out that if we impose the sole condition that the amount of each substance is constant, the ordinary laws of chemical kinetics lead to a different equation for the equilibrium concentrations than the one obtained from thermo-dynamics; it reduces to the latter only when certain further conditions are imposed. The assumption that the rate in each individual reaction is equal to the inverse rate removes the paradox. This is not the only way of avoiding the paradox in this particular example, but if we were to consider a great many different types of simultaneous reactions we should probably find that the only general way of avoiding the paradox, that is applicable to all cases, would be to assume that in every case of equilibrium, involving a number of simultaneous reactions, a state of equilibrium also exists for each separate reaction and its inverse.

In the more purely physical types of equilibrium, such as are dealt with in statistical mechanics, we know in certain simple cases not only that the number of molecules in a certain limited group remains constant, but that, for example, the number of molecules in a certain group L colliding with those in a group M to give molecules in groups L' and M' is equal to the

number of molecules in groups L' and M' colliding to give molecules in groups L and M .² Here again we are tempted to generalize and assume that the same principle holds for all cases.

Finally let us turn to the phenomenon of absorption and emission of light. If it be assumed that the emission of a certain spectral line indicates that some molecules have undergone a process by which they have passed from one group to another, and if we assume that when the same line is absorbed the molecules undergo the reverse process and are transferred from the second group to the first, it seems inevitable that in a state of thermal equilibrium the two processes must occur at the same average rate. Otherwise it would be hard to see how such a substance could be introduced into an isothermal Hohlraum without permanently changing the character of the radiation therein.

These diverse examples suggest very strongly that cyclic equilibrium does not exist, and we have seen that this supposition could be proved correct if an independent catalyst could be found for each individual reaction or process. There are, however, numerous cases in which it would be difficult, if not impossible, to find such catalysts. In applying thermodynamics to solutions, some of the more important results have been obtained by the use of a semi-permeable membrane. Now there are solutions in which it would be difficult, if not impossible, to find such a membrane, but we do not hesitate to apply to them the same laws which can be demonstrated to be true for cases where semi-permeable membranes can be employed. So in our present case we should hesitate to believe that there are different laws for reactions which are subject to catalysis and for those which are not.

The Law of Entire Equilibrium.—Thus I am led to propose a law which in its general form is not deducible from thermodynamics, but proves to be compatible with the laws of thermodynamics in all cases where a comparison is possible. It may be called the law of *entire equilibrium*, and may be stated as follows. *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.* The rate at which one group or set of groups L goes over into another group or set of groups L' is the same as the rate at which the groups L' go over into the groups L . Moreover if there are various paths by which the first process occurs, there is an equal number of paths by which the second process occurs, and the rate is the same in both directions along every path. This will be true no matter how detailed are the specifications which define the several groups and the several paths.

In cases to which pure quantum theory may be applied there is a number of discrete paths by which molecules of one group may change to another. Thus in Bohr's theory of the hydrogen atom, the atom may pass from a

higher to a lower quantum state, either immediately or through a finite number of intervening states. The meaning of the principle is here obvious; in a condition of thermal equilibrium the rate of change for each step is equal to the rate for the reverse step.

In other cases we must assume, not a discrete number, but an infinite continuum of paths. Then we must employ the term "path" to mean some specified zone of paths more or less arbitrarily demarked from the continuum. Yet however narrow or however arbitrary this path, or zone of paths, is, our principle asserts that the rate along this path is the same in both directions. For example, in discussing statistical mechanics it is often convenient to plot the position of each particle in a "phase space" of as many dimensions as there are numbers required to specify the position and the momentum of one particle. As a particle changes its position and momentum, it describes a curve in this space, and we may segregate for discussion all of these curves which lie within a certain "tube." Let us suppose that two molecules collide in such manner that the molecule *A* goes from the group *L* to the group *L'*, and the molecule *B* from the group *M* to the group *M'*, and further that each molecule traces a curve lying within a specified tube, one from *L* to *L'* and one from *M* to *M'*. Then our law states that in equilibrium the average rate (or chance) of a molecule *A* going, within the prescribed tube, from *L* to *L'* while a molecule *B* goes through its prescribed tube from *M* to *M'* is the same as the average rate (or chance) of molecules *A* and *B* going through the same tubes from *L'* to *L* and from *M'* to *M*.

Perhaps the significance of this law may be made a little more evident by means of a crude analogy. Suppose that during a period in which there are no births or deaths the population of the several cities of the United States remains constant, the number leaving each city being balanced by the number entering it. This stationary condition would not correspond to our case of thermal equilibrium. We should require further, to complete the analogy, that as many people go from New York to Philadelphia as from Philadelphia to New York. If there were three railway lines between these two cities we should require that the number of passengers going by each line be equal in both directions. If some of the travel were not by railway or roads but across country, then, if we should draw on the map two non-intersecting lines from New York to Philadelphia, we should require that the number of persons passing through any such zone in one direction be equal to the number passing through the same zone in the opposite direction. By such illustrations we may appreciate how extremely far-reaching are the consequences of the proposed law.

The law of entire equilibrium might have been called the law of reversibility to the last detail. If we should consider any one of the elementary processes which are occurring in a system at equilibrium, and could, let us say, obtain a moving-picture film for such a process, then this

film reeled backward would present an equally accurate picture of a reverse process which is also occurring in the system and with equal frequency. Therefore in any system at equilibrium, time must lose the unidirectional character which plays so important a part in the development of the time concept. In a state of equilibrium there is no essential difference between backward and forward direction in time, or, in other words, there is complete symmetry with respect to past and future.

I believe that some of the ideas contained in this paper have been suggested by the work of Einstein, but he has not proposed this law of equilibrium. Indeed one of the first applications which I shall make, in a subsequent paper, will be to the interaction between matter and light, where I shall attempt to demonstrate the invalidity of Einstein's derivation of Planck's radiation formula. Another application will shortly appear in a paper by Dr. D. F. Smith and myself on the mechanism of chemical reactions.

¹ Wegscheider, *Z. physik. Chem.*, **39**, 273 (1901).

² See Lewis and Adams, *Physic. Rev.* **5**, 10 (1915).

STUDIES ON DISEASE RESISTANCE IN THE ONION

BY J. C. WALKER

UNIVERSITY OF WISCONSIN AND OFFICE OF COTTON, TRUCK AND FORAGE CROP DISEASE INVESTIGATIONS, BUREAU OF PLANT INDUSTRY, UNITED STATES DEPARTMENT OF AGRICULTURE

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The nature of resistance to disease in plants is a subject which has been of increasing interest to botanists in general and to plant pathologists in particular for several years past.¹ Earlier there was a tendency to assume that in various instances of disease resistance the causes were sufficiently similar to justify some single type or comparatively few types of explanation, as appears to be the case in certain cases of immunity in animals. Investigations indicate, however, that the causes of resistance in plants are widely varied and relatively complex, and that sound progress is dependent, for the present at least, upon critical study of specific examples wherever practicable. Some years ago it came to the writer's attention that the bulbs of the common onion show a wide range in susceptibility or resistance to certain fungous parasites and that this apparently is correlated with the occurrence of scale pigments. The studies summarized here are therefore presented as a contribution to the general subject of disease resistance in plants.

Horticultural varieties of the common onion (*Allium cepa*) are grouped