"Sur un énoncé générale des lois des équlibres chimiques," C. R. Acad. Sci. Paris **99** (1884), 786-789.

On a general statement of the laws of chemical equilibrium

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In a recent paper on chemical equilibrium, Van't'Hoff showed that most of the experimental laws for that phenomenon can be summarized in the following statement:

Any equilibrium between two different states of matter (i.e., systems) displaces under a lowering of temperature towards that one of the two systems whose formation develops heat ([1]).

It seems to me that this law can be further generalized by extending it to the condensation that comes about with the temperature, and that one can, moreover, give an identical form to those of the laws of all equilibria that produce mechanical work by their displacement and which depend upon Carnot's theorem, as a result. The statement that I just proposed includes *reversible* chemical phenomena within the class of *reciprocal* phenomena, to which LIPPMANN ([2]) recently attached reversible electrical phenomena.

Any system in stable chemical equilibrium that is subject to an external cause that tends to vary either its temperature or its condensation (pressure, concentration, number of molecules per unit volume), in total or only in some of its parts, can experience only those internal modifications that would bring about a change in temperature or condensation of opposite sign to the one that would result from the external cause if only those modifications were produced.

Those modifications are generally progressive and partial.

They will be rapid and complete when they can be produced with no change in the individual condensation of the various homogeneous parts that constitute the system in equilibrium, while nonetheless changing the condensation of the total system.

They will be zero when their production cannot induce changes that are analogous to the ones that are due to the external cause.

Finally, although those modifications are possible, they are not necessary for that to happen. In the cases where they are not produced and the system remains unaltered, an equilibrium that

([1]) VAN'T'HOFF, *Études de Dynamique chimique*, pp. 161.
([2]) LIPPMANN, Annales de Chimie et de Physique (5) **24** (1882), pp. 172.

was stable will become unstable, and it can exhibit only those modifications that tend towards the conditions of stability.

Some examples of equilibrium, which are mostly well-known, will show the generality of the applications of that law, which simultaneously embraces the phenomena of fusion, evaporation, and dissolution, which can in no way be distinguished from chemical phenomena, properly speaking.

1. *The heating of the total system leads to endothermic modifications* of the entire body, such as *fusion* and *volatilization*, as well as *polymerization* of C_2 Az, etc., reversible *dimorphic transformations* of Ag I, Az H_4 O and Az O_3, *dissociation* of CO_2, Ca O and CO_2, Bi_2O_3 and 3 Az O_5, 4 HO, reversible *endothermic combination* of CS_2, and very probably Az O_5, as well, etc., endothermic *dissolution* of most salts, and the endothermic *crystallization* of some salts, such as Na O and SO_3, Ca O and HO, which are well-known to have a solubility that decreases with temperature.

2. *The partial heating of a system leads to modifications that all tend to cool the heated part*, such as the *propagation of heat* by conduction, the production of *thermo-electric* currents, *changes in concentration* by diffusion, the *transport of metal* from one point to another of a strip that is immersed in a solution of one of its salts.

3. *Increasing the condensation of the total system when it is kept at constant temperature will lead to modifications that tend to reduce the condensation of the system*, such as the *fusion* of ice, the *solidification* of paraffin, the *dimorphic transformation* of Ag I, and the *combination* of the dissociated products of CO_2 .

4. *Increasing the condensation of one part of a system will lead to modifications that tend to reduce the condensation of the altered part*, such as the *condensation* of water vapor, the *combination* of Ca O + CO_2 into rouge, the *diffusion* of unequally-concentrated solutions, the *transport of metal* from a strip that is immersed in a solution of one of its salts with a variable concentration, the *lowering of the fusion point* for an alloy or a mixture of salts during its progressive solidification.

5. *Modifications of equilibrium are generally progressive:* For example, in the dissociation of CO_2, and generally in all systems whose elements are not simply juxtaposed, but some of them form homogeneous mixtures.

6. *The modifications of equilibrium are total when they can be produced without changing the condensation in each part of the system, while changing the condensation of the total system*, such as the *condensation* of water vapor, the *fusion* of ice, the *dimorphic transformation* of Ag I, the *dissociation* of Ca O, CO_2, and solid Cu O, and the *solution* of some salts. Under an infinitely-small change in condensation of one of their parts, those systems will pass from one extreme limit of their equilibrium state to the opposite extreme limit.

7. *The modifications of equilibrium will be zero when they cannot produce an effect that is analogous to the one that is due to the external cause.* Dissociation is independent of *pressure* for mixtures that combine with no change in volume, such as hydroiodic acid, for example. The limit of equilibrium is independent of *temperature* when its transformation does not release heat, which is the case for etherification.

8. *Finally, all of those modifications of equilibrium are only possible, but are not necessarily produced*, as is shown by *super-fusion*, *superheating*, and the rapid cooling of dissociated carbonic acid. The unstable systems thus-obtained can be modified only in such a way as to approach the conditions of stable equilibrium. The transformation of those unstable equilibria generally happens with a release of heat, which conforms to the *principle of maximum work*, because, as Van't'Hoff remarked, the usual temperatures differ only slightly from absolute zero, for which stable equilibrium would correspond to the release of all of the heat that is contained in the body.

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