Henri Le Châtelier, "Experimental and Theoretical Studies on Chemical Equilibrium"

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Henri Sainte-Claire Deville (*Leçons sur la dissociation*, 1864) was the first to recognize the universal importance of ... the phenomena of equilibrium. All substances—even the most stable, like water or carbon dioxide—are subject to a limited decomposition at certain temperatures and pressures, or a "dissociation," to use the new word he introduced for a completely new idea in science. Not only did he indicate the existence of these phenomena; he also set forth the principles that should guide us to arrive at the governing laws. He pointed out the analogy [between association and] the physical phenomena of vaporization, fusion ... and thus was able to foresee the existence of definite tensions of dissociation, analogous to the definite tensions of vaporization.

In this work, I have taken as my guide the idea that had led Sainte-Claire Deville to the discovery of the phenomena of dissociation, and I have sought to generalize it still more.

The Nature of Equilibrium; Reversibility

The chemical reactions, including changes of state, are also connected with phenomena of equilibrium. They can stop, before being complete, in a stable state that is independent of the prior states of the system; and the deformations of the system in equilibrium are reversible, i.e., the state of the system becomes the same again with the exterior conditions of the medium in which it is placed...

The Factors of Equilibrium

The factors of chemical equilibrium are the same for all reactions and much less numerous than is often thought. They can be divided into two distinct categories:

1. The external factors of equilibrium, which can be changed in magnitude independently of the system that is in equilibrium. I shall show that there are three such factors—temperature, electromotive force, pressure—corresponding to the three forms of free energy: heat, electricity, and work.

2. The internal factors of equilibrium, which are intimately connected in their magnitude with the state of the system in equilibrium. They can be divided into three groups, according to whether they depend on the chemical nature, the physical state, or the condensation of the substances present; these are circumstances related to the internal energy of the substances. ...

The Law of Opposition of Reaction to Action

After having established that any alteration of one of the three factors of equilibrium necessarily leads to a change of a system that was in equilibrium, the first question that arises is whether there is a correlation between the direction of the change of the system and the direction in which the factor varies. This correlation is very simple:

When one of the factors of equilibrium changes, any system that was in equilibrium undergoes a transformation in such a direction that, if it occurred by itself, it would change this factor in the contrary direction.

This is a purely experimental law; however, it is based on so many facts that it can be considered as very strong.

This law brings the reversible chemical phenomena into the class of reciprocal phenomena of Lippmann: a change of one of the factors leads to a deformation of the system and, reciprocally, a deformation of the system leads to a change of the factors.

I am going to describe this law by reviewing the several factors of equilibrium.

Temperature: Every increase in temperature imposes on a chemical system in equilibrium a transformation corresponding to an absorption of heat; i.e., a transformation that would produce a lowering of the temperature if it occurred by itself. This law has been given by van't Hoff for the chemical phenomena alone; I have shown that it is more general than its author thought.

Electricity: Every change of electromotive force exerted at one point of a system in equilibrium produces a change of the system, which, if it occurred by itself, would lead to a variation of the electromotive force in the contrary direction.

Example: The Peltier effect in a heterogeneous conductor; this is reciprocal to the phenomenon of thermoelectricity. Electrolysis: the imposed chemical decomposition tends to regenerate a current of opposite sign; this is the principle of secondary chemical batteries or accumulators. ...

Pressure: The increase of pressure on any chemical system in equilibrium leads to a transformation that tends to reduce the pressure.

It is known that compression lowers or raises the melting point, depending on whether the melting is accompanied by an increase or a diminution of the volume.

The same is true for gaseous systems, whether homogeneous or not; compression leads to the condensation of vapors, to the combination of carbon dioxide with chalk, etc.

Condensation: The change in condensation of one of the elements causes a transformation in such direction that a certain quantity of that element disappears, so that its condensation can be diminished.

This is the mass action that is applicable so widely in chemistry.

The experiments by Berthelot on esterification and by Lemoine on the dissociation of hydrogen iodide have clearly shown that the addition of a new quantity of one of the substances already present in an equilibrized mixture increases the extent of that reaction which tends to consume the added substance.

This general law about the opposition of action and reaction ... is only a generalization of the condition for the stability of equilibrium in mechanical systems.

[1] [Copied from Eduard Farber, Ed., *Milestones of Modern Chemistry*, Basic Books, New York, 1966, pp 165-168. Translation by Farber. —CJG]