When push comes to shove: Disturbing the equilibrium

by *Derek A. Davenport*

The French have a strange saying: "Cet animal est très méchant; quand on l'attaque, il se défend," which may be roughly translated, "This animal is very wicked; when attacked it defends itself." A system in chemical equilibrium is just such an animal and appropriately a Frenchman, Henry Louis Le Châtelier, in 1884 first pointed this out. The original statement of his famous principle is somewhat obscure even in the original French:

> Any system in stable chemical equilibrium subjected to the influence of an external cause which tends to change either its temperature or its condensation (pressure, concentration, number of molecules in unit volume), either as a whole or in some of its parts, can only undergo such internal modifications as would, if produced alone, bring about a change of temperature or of condensation of opposite sign to that resulting from the external cause.

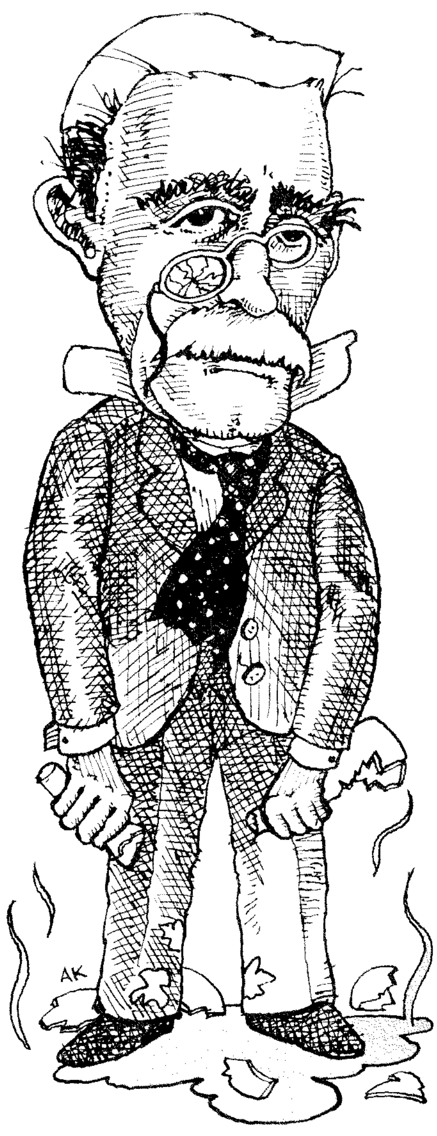
Succeeding examples, however, make clear what Le Châtelier had in mind. Thus his statement that "heating the total system favors the endothermic modification" was illustrated by the melting of ice, the vaporization of water, and the increased solubility of (most) salts in water on adding heat. His further statement that "the increase in condensation of a whole system maintained at constant temperature produces modifications which tend to reduce the condensation of the system" was exemplified by the effect of increasing pressure (caused for example by a skate blade) on the melting point of ice and by the reduction in the dissociation of $N_2O_{4(g)}$ to $NO_{2(g)}$ as the total pressure increases.

Four years later Le Châtelier developed his ideas in a long article that became one of the classic statements of the science of thermodynamics. One section is subtitled "Loi d'Opposition de la Réaction à l'Action." The resemblance to Newton's familiar law—action and reaction are equal and opposite—is obvious and no doubt deliberate. However applications of Le Châtelier's principle tend to be more subtle than those of Newton's law, if not quite so far-reaching.

The most common textbook example of such application is no doubt the equilibrium between nitrogen, hydrogen, and ammonia, an equilibrium that is central to the commercial manufacture of ammonia by the Haber process:

$$N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)} + \text{heat}$$

Since the reaction is *exo*thermic as written, the equilibrium concentration of $NH_{3(g)}$ will be lowered by increasing the temperature in accordance with Le Châtelier's "heating the total system favors the *endo*thermic modification." Since one mole of $N_{2(g)}$ and three moles of $H_{2(g)}$ react to produce two moles of $NH_{3(g)}$, the equilibrium concentration of $NH_{3(g)}$ will be increased by raising the total pressure, or, in Le Châtelier's terms, "the increase in condensation of a whole system . . . produces modifications which tend to reduce the condensation of the system." However, neither Le Châtelier's principle nor even classical thermodynamics in all its majesty could (or can) predict the *rate* at which *equilibrium* is reached under any given set of conditions.



Le Châtelier made a careful experimental study of both the rate and equilibrium aspects of the ammonia synthesis reaction under a variety of temperature and pressure conditions. In 1901 he attempted the direct union of nitrogen and hydrogen at 60 °C under a pressure of 200 atmospheres with metallic iron serving as catalyst, conditions not too far removed from current industrial practice. Because of an accidental admixture of air, a violent explosion took place; it was left to Fritz Haber (1868–1934) to develop the process several years later. In old age, Le Châtelier rather ruefully wrote, "I let the discovery of the ammonia synthesis slip through my hands. It was the greatest blunder of my scientific career."

But there were many nonblunders, and Le Châtelier's was a long (1850–1936) and fruitful life. Like many other leading 19th century scientists, he was much interested in important (and often lucrative) industrial processes. He did pioneer work on the hardening of cements, the prevention of mine explosions, and the chemistry of the blast furnace. He was one of the founders of modern metallurgy and an early advocate of scientific management practices. As an inventor he developed the oxyacetylene torch for welding and the use of the platinum–platinum–iridium thermocouple for

Chickens lose equilibrium . . . Prefer Perrier water to panting

by *David B. Brown* and *John A. MacKay III*

Chickens can not perspire, so when they get hot they pant. This seemingly trivial fact leads to a serious economic loss for egg producers. In hot weather, chickens lay eggs with thin shells that are easily (and frequently) broken. A little reflection shows that this is an inevitable consequence of Le Châtelier's principle and the well-known carbon equilibrium system,

$$\underset{\text{(chicken breath)}}{CO_{2(g)}} \rightleftharpoons CO_{2(aq)} \rightleftharpoons H_2CO_{3(aq)} \rightleftharpoons H^+ + HCO^-_{3(aq)} \rightleftharpoons H^+ + CO^{2-}_{3(aq)} \xrightleftharpoons{Ca^{2+}} \underset{\text{(egg shell)}}{CaCO_{3(s)}}$$

When the chicken pants, the equilibrium is perturbed by the rapid loss of carbon dioxide. Because this effect cascades through all of these equilibria, the effect is a loss of solid calcium carbonate, which ultimately produces weaker egg shells.

Ted Odom, while a graduate student at the University of Illinois, found the deceptively simple "solution" to this problem—give the chickens carbonated water. Now the equilibrium has been perturbed in the opposite direction. The addition of aqueous carbon dioxide shifts all of the equilibria to the right and results in stronger egg shells. Moreover, the chickens seem to like the carbonated water, and there are rumors that they spend their spare time singing familiar jingles about "spirit" and "the real thing." Philosophical questions about which came first are left to the reader, but in this case, at least, Le Châtelier's principle comes before the egg (shell).

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accurate measurement of temperature. At heart he was a theorist but typically he wrote:

These investigations of a rather theoretical sort are capable of much more immediate practical application than one would be inclined to believe. Indeed the phenomena of chemical equilibrium play a capital role in all operations of industrial chemistry.

It is known that in the blast furnace the reduction of iron oxide is produced by carbon monoxide, according to the reaction

$$Fe_2O_3 + 3CO = 2Fe + 3CO_2$$

but the gas leaving the chimney contains a considerable proportion of carbon monoxide, which thus carries away an important quantity of unutilized heat. Because this incomplete reaction was thought to be due to an insufficiently prolonged contact between carbon monoxide and the iron ore, the dimensions of the furnaces have been increased. In England they have been made as high as 30 meters. But the proportion of carbon monoxide escaping has not diminished, thus demonstrating, by an experiment costing several hundred thousand francs, that the reduction of iron oxide by carbon monoxide is a limited reaction. Acquaintance with the laws of chemical equilibrium would have permitted the same conclusion to be reached more rapidly and far more economically.

It was these two statements by Le Châtelier that G. N. Lewis chose to include in Chapter 1 of his classic text, "Thermodynamics," published in 1923. In some ways science is a very conservative discipline. It progresses mainly by absorbing and modifying the past, only very rarely by revolutionizing it. Einstein hung portraits of Faraday and Maxwell on the walls of his study and even the not-always humble Newton could say," If I have seen further than Descartes it is by standing on the shoulders of giants."

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