Exception to the Le Châtelier Principle

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Letters

The authors reply:

Recently, we considered the effects of nonideality on the direction in which the ammonia synthesis reaction shifts upon addition of both an infinitesimal and a finite quantity of nitrogen at constant pressure and temperature *(1).* Depending upon the initial mole fraction of nitrogen, the reaction shifts either to the right (producing more ammonia) or to the left (producing more nitrogen and hydrogen). While Herrinton agrees with these results, he disagrees with our (as well as many others before us) description of those shifts to the left as exceptions to the Le Châtelier principle. Herrinton claims that the addition of a component at constant temperature and pressure represents a type of perturbation to which the principle was not meant to be applied. In contrast to several discussions appearing in the literature for at least 50 years (e.g., *2–8*), the ammonia synthesis reaction apparently does not provide a counterexample, or exception, to the Le Châtelier principle. Interestingly, we and Herrinton both agree that the addition of a given component at constant pressure illustrates a limitation of the Le Châtelier principle, though for different reasons: we (and many others) interpret the differing shifts of the direction of the reaction as a *failure* of the principle while Herrinton argues that this perturbation is not covered by the principle. The Le Châtelier principle has never been rigorously proven *(2),* so this distinction appears to be semantic rather than scientific in origin. Nevertheless, this difference is still important, at least from a pedagogical viewpoint, since it affects how the principle should be presented in the classroom as well as students' understanding of what are the fundamental descriptors of a thermodynamic system.

From our understanding of the original intent of the Le Châtelier principle, as inferred from several articles in the literature that discuss exceptions to the principle *(2–8),* the Le Châtelier principle was an attempt to formulate a general statement from a large number of observations about the directions that reactions, both ideal and nonideal, take upon return to equilibrium after various perturbations are introduced. As stated in ref *4,* the Le Châtelier principle is as follows: "In a system at equilibrium, a change in one of the variables that determines the equilibrium will shift the equilibrium in the direction counteracting the change in that variable." Apparently, to remain as general as possible, the complete nature of the change is not specified. For example, one may consider a change in the temperature at fixed volume or fixed pressure. Or, as we and many others have interpreted the above statement, one may invoke the principle to predict the shift in the direction of the reaction upon the further addition of one of the components at constant volume or constant pressure (as well as constant temperature).

Herrinton's argument that the Le Châtelier principle does not apply to the constant pressure addition of more nitrogen rests upon the correct observation (for an ideal gas mixture only) that adding nitrogen at constant pressure serves to change the partial pressures of all three components. Hence, one has inadvertently imposed multiple perturbations upon the system. While this is true, partial pressures are not, however, the fundamental descriptors of the system (particularly so for a nonideal gas or liquid solution). The partial pressures should not be confused with those (albeit vaguely defined) variables referred to in the principle that determine the equilibrium state, and so how they vary is irrelevant to the way in which the principle was presumably meant to be applied. (We also note that several perturbations likewise modify all the partial pressures at once; one example is a change in the total pressure.) Being intensive properties, partial pressures cannot be used, along with the temperature, T, and pressure, P, to characterize completely the system (specifically its size or extent) at equilibrium. Instead, the equilibrium state is uniquely characterized for a three component system by specifying the mole numbers of each species, n_1, n_2, and n_3, and two other independently variable properties, such as T and P *(9).* The condition of chemical reaction equilibrium, which is a relation that must be satisfied by the chemical potentials of the components participating in the reaction, imposes a constraint on the intensive properties of the system. For the case of an ideal gas mixture, one obtains a relation between the partial pressures, or equivalently the mole fractions and the total pressure, at equilibrium. Yet, without knowledge of the initial mole numbers of each component, the final mole numbers at equilibrium cannot be obtained solely from the condition of chemical reaction equilibrium. In addition, the extent of reaction, the sign of which determines the direction that the reaction shifts, is determined directly from the change in the number of moles of any reacting component (given a stoichiometrically balanced reaction).

In other words, the equilibrium state is uniquely determined by the following set of five variables: T, P, n_1, n_2, and n_3. These are the variables to which the Le Châtelier principle is referring when it purports to predict how the reaction will shift upon changes in any one of the variables that determines the equilibrium state. As we understand it, the principle was formulated so as to apply to either changes in T while keeping P fixed and n_1, n_2, and n_3 initially unchanged (prior to the reaction that results to re-establish equilibrium) or to changes in n_1, keeping T and P fixed with n_2 and n_3 initially unchanged (again prior to the reaction that ensues to return to equilibrium). Whether the addition of n_1 at constant T and P alters all the partial pressures is irrelevant, since the perturbation keeps the other two more fundamental variables, n_2 and n_3, initially fixed. And so, by exhibiting a shift of the reaction to the left upon the addition of more nitrogen, while keeping the temperature, pressure, and the initial mole numbers of hydrogen and ammonia unchanged, the ammonia synthesis reaction provides a valid example of an *exception* to the Le Châtelier principle.

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Literature Cited

1. Uline, M. J.; Corti, D. S. *J. Chem. Educ*. **2006**, *83,* 138–144.
2. de Heer, J. *J. Chem. Educ*. **1957**, *34,* 375–380.
3. Katz, L. *J. Chem. Educ*. **1961**, *38,* 375–377.
4. Levine, I. N. *Physical Chemistry,* 3rd ed.; McGraw-Hill Book Co.: New York, 1988.
5. Sandler, S. I. *Chemical and Engineering Thermodynamics,* 3rd ed.; John Wiley & Sons, Inc.: New York, 1999.
6. Liu, Z.-K.; Agren, J.; Hillert, M. *Fl. Phase Equil*. **1996**, *121,* 167–177.
7. Corti, D. S.; Franses, E. I. *Chem. Eng. Educ*. **2003**, *37,* 290–295.
8. Lacy, J. E. *J. Chem. Educ*. **2005**, *82,* 1192–1193.
9. Tester, J. W.; Modell, M. *Thermodynamics and Its Applications,* 3rd ed.; Prentice Hall PTR: Upper Saddle River, NJ, 1997.

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