327a Demonstrating an Exception to Le Chatelier'S Principle with the Ammonia Synthesis Reaction: the Effects of Nonideality and a Molecular Simulation Study

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Le Chatelier's principle, which is usually introduced while discussing chemical reaction equilibria, provides a rule of thumb to determine the direction in which a reaction will shift due to a perturbation. However intuitively appealing, this principle is not exact in general and several exceptions have been noted in the literature, the ammonia synthesis reaction being a widely discussed example. In particular, if the initial mole fraction of nitrogen exceeds 0.5, the infinitesimal addition of more nitrogen at constant temperature and pressure causes the reaction to shift to the left, producing more nitrogen, in violation of Le Chatelier's principle[1].

The value of 0.5, however, is obtained from an analysis that assumes ideal gas behavior. We revisit this exception, but now consider the effects of nonideality on the shifts in the reaction[2]. The mole fraction of nitrogen at which the reaction shifts direction from right to left (upon the addition of more nitrogen) is found to be strongly dependent upon the temperature and pressure, approaching 0.1 under some conditions. We also consider the shifts in the direction of the reaction upon addition of finite amounts of nitrogen (to which Le Chatelier's principle no longer applies). In some cases, both infinitesimal and finite additions of nitrogen always cause the reaction to shift to the left. At other conditions, large enough additions of nitrogen also cause the reaction to shift to the left, even though the reaction satisfied Le Chatelier's principle (i.e., shifted to the right) upon smaller additions of nitrogen. This analysis provides an interesting example of the effects of nonidealities that instructors can apply towards the development of lectures or problems appropriate for students at various skill levels.

We also discuss Reactive Canonical Monte Carlo simulations[3] using an ideal gas mixture to further explore and verify the results of the above analysis. The exceptions to Le Chatelier's principle are clearly seen for finite additions of nitrogen. These simulation studies provide a set of straightforward and easy to implement "computer experiments" that can be used in Thermodynamics/Statistical Mechanics classes during the analysis of chemical reaction equilibria.

[1]Corti, D.S. and Franses, E.I., Chem. Eng. Educ. Fall, 290-295 (2003).

[2]Uline, M.J. and Corti, D.S., J. Chem. Educ., in press (2005).

[3]Johnson, J.K., Panagiotopoulos, A.A. and Gubbins, K.E., Mol. Phys. 81, 717-733 (1994).