shift the equilibrium position, they do not affect the value of the equilibrium constant.

Ammonia produced in the Haber process is continuously removed by condensing it to liquid ammonia. This condensation removes most of the product from the gas phase in which the reaction occurs. The resulting decrease in the partial pressure of NH_3 gas in the reaction vessel is a stress and is the same as a decrease in product concentration, which shifts the equilibrium to the right.

The introduction of an inert gas, such as helium, into the reaction vessel for the synthesis of ammonia increases the total pressure in the vessel. But it does not change the partial pressures of the reaction gases present. Therefore, increasing pressure by adding a gas that is not a reactant or a product *cannot* affect the equilibrium position of the reaction system.

Changes in Concentration

An increase in the concentration of a reactant is a stress on the equilibrium system. Consider the following hypothetical reaction.

$$A + B \rightleftharpoons C + D$$

An increase in the concentration of A creates a stress. To relieve the stress, some of the added A reacts with B to form products C and D. The equilibrium is reestablished with a higher concentration of A than before the addition and a lower concentration of B. **Figure 4** illustrates the effect on a system in equilibrium produced by increasing the concentration of a reactant. Similarly, an increase in the concentration of B drives the reaction to the right. An increase in the concentration of either C or D shifts the equilibrium to the left. A decrease in the concentration of C or D has the same effect on the position of the equilibrium as does an increase in the concentration of A or B; the equilibrium shifts to the right.

Changes in concentration have no effect on the value of the equilibrium constant. Because of this, such changes have an equal effect on the numerator and the denominator of the chemical equilibrium expression. Thus, the new concentrations give the same value or numerical ratio for the equilibrium constant when equilibrium is reestablished.

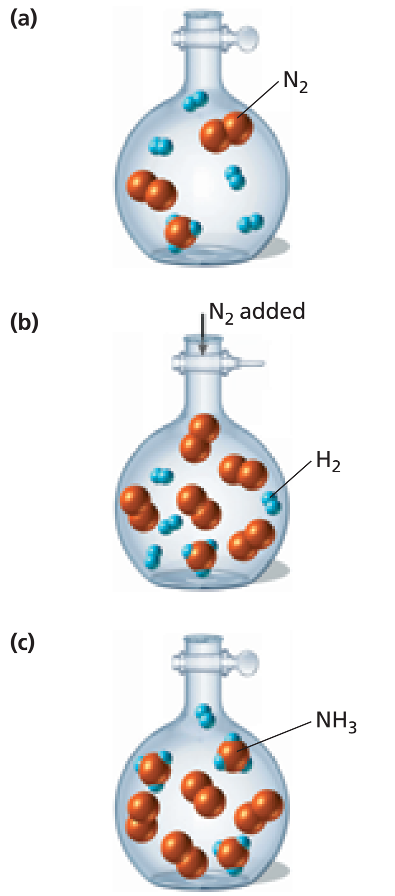
Many chemical processes involve heterogeneous reactions in which reactants or products are in different phases. The concentrations of pure solids and liquids do not change, and by convention are not written in the equilibrium expression. Also, when a solvent such as water, in a system involving acids and bases, is in an equilibrium equation, it is not included in the equilibrium expression. In Chapter 15, the expression for K_w used this convention. The reaction representing the self-ionization of water is

$$2H_2O(l) \rightleftharpoons H_3O^+(aq) + OH^-(aq)$$

and the equation for K_w is $K_w = [H_3O^+][OH^-]$.

The following equation describes the equilibrium system established by the decomposition of solid calcium carbonate.

$$CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$$



$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$

FIGURE 4 (a) N_2, H_2, and NH_3 are in equilibrium within a closed system. (b) Addition of more N_2 causes a stress on the initial equilibrium. (c) The new equilibrium position for this system has a higher concentration of N_2, a lower concentration of H_2, and a higher concentration of NH_3 than initially.

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