Suggested Problems: Chapter 13

13.9: For (a), the equilibrium constant expression is

$$K = [\mathrm{Ag}^+][\mathrm{Cl}^-]$$

and its value is less than 1 as $\mathrm{AgCl}(s)$ is considered insoluble and, therefore, dissolves to a very limited extent such that the concentration of Ag^+ and of Cl^- are small. For (b), the equilibrium constant expression is

$$K = \frac{1}{[\mathrm{Pb}^{2+}][\mathrm{Cl}^-]^2}$$

and its value is greater than 1 as $\mathrm{PbCl_2}(s)$ is considered insoluble and, therefore dissolves to a very limited extent. The small concentrations of Pb^{2+} and of Cl^- appear in the denominator and, therefore, result in a large value for K.

13.15: For (a) we have

$$Q = \frac{[\mathrm{CH_3Cl}][\mathrm{HCl}]}{[\mathrm{CH_4}][\mathrm{Cl_2}]}$$

For (b) we have

$$Q = \frac{[\mathrm{NO}]^2}{[\mathrm{N_2}][\mathrm{O_2}]}$$

For (c) we have

$$Q = \frac{[\mathrm{SO_3}]^2}{[\mathrm{SO_2}]^2[\mathrm{O_2}]}$$

For (d) we have

$$Q = [\mathrm{SO_2}]$$

For (e) we have

$$Q = \frac{1}{[\mathrm{P_4}][\mathrm{O_2}]^5}$$

For (f) we have

$$Q = \frac{[\mathrm{Br}]^2}{[\mathrm{Br_2}]}$$

For (g) we have

$$Q = \frac{[\mathrm{CO_2}]}{[\mathrm{CH_4}][\mathrm{O_2}]^2}$$

For (h) we have

$$Q = [\mathrm{H_2O}]^5$$

13.17: For (a) we have

$$Q = \frac{[\mathrm{N_2}][\mathrm{H_2}]^3}{[\mathrm{NH_3}]^2} = \frac{(1.00)(1.00)^3}{(0.20)^2} = 25$$

As $Q > K = 17$, the reaction proceeds to the left to make more reactants For (b) we have

$$Q = \frac{[\mathrm{N_2}][\mathrm{H_2}]^3}{[\mathrm{NH_3}]^2} = \frac{(2.0)(1.0)^3}{(3.0)^2} = 0.22$$

As $Q < K = 6.8 \times 10^4$, the reaction proceeds to the right to make more products. For (c) we have

$$Q = \frac{[\mathrm{SO_2}]^2[\mathrm{O_2}]}{[\mathrm{SO_3}]^2} = \frac{(1.00)^2(1.00)}{(0)} = \text{undefined}$$

As $Q > K = 0.230$, the reaction proceeds to the left to make more reactants. For (d) we have

$$Q = \frac{[\mathrm{SO_2}]^2[\mathrm{O_2}]}{[\mathrm{SO_3}]^2} = \frac{(1.00)^2(1.00)}{(1.00)} = 1.00$$

As $Q < K = 16.5$, the reaction proceeds to the right to make more products. For (e) we have

$$Q = \frac{[\mathrm{NOCl}]^2}{[\mathrm{NO}]^2[\mathrm{Cl_2}]} = \frac{(0)^2}{(1.00)^2(1.00)} = 0$$

As $Q < K = 4.6 \times 10^4$, the reaction proceeds to the right to make more products. For (f) we have

$$Q = \frac{[\mathrm{NO}]^2}{[\mathrm{N_2}][\mathrm{O_2}]} = \frac{(10.0)^2}{(5.00)(5.00)} = 4$$

As $Q > K = 0.050$, the reaction proceeds to the left to make more reactants.

13.31: The equilibrium constant for this reaction is $K = [\mathrm{CO_2}]$. For an equilibrium to exist, both solids must be present even though they do not appear in the equilibrium constant expression; thus, if the concentration of CO_2 is less than the equilibrium constant, K, then all $CaCO_3$ will remain.

13.36: For the reaction $\mathrm{N_2}(g) + 2\,\mathrm{H_2}(g) \longrightarrow \mathrm{N_2H_4}(g)$, we can increase the amount of $\mathrm{N_2H_4}(g)$ produced by (1) increasing the amount of N_2 or (2) by increasing the amount of H_2, both of which shift the reaction to the right to remove some of the added material. We also can (3) decrease the volume of the container, which will shift the reaction to the right to decrease the total number of particles in the container. Finally, as the reaction is endothermic, we can (4) increase the temperature, which shifts the reaction to the right to use up some of the additional heat.

13.40: For (a), the equilibrium constant expression is

$$K = \frac{[\mathrm{CH_3OH}]}{[2\,\mathrm{H_2}]^2[\mathrm{CO}]}$$

For (b), adding H_2 pushes the reaction to the right, increasing the concentration of CH_3OH and decreasing the concentration of CO. The concentration of H_2 has a net increase as only some of the added H_2 is converted to CH_3OH.

For (c), removing some of the CO pushes the reaction to the left, decreasing the concentration of CH_3OH and increasing the concentration of H_2. The concentration of CO has a net decrease as some, but not all, of the CO is replaced by the reaction of CH_3OH.

For (d), adding CH_3OH pushes the reaction to the left, increasing the concentrations of H_2 and of CO. The concentration of CH_3OH has a net increase as some, but not all, of the added CH_3COH reacts to form H_2 and CO.

For (e), as the reaction is exothermic, increasing the temperature pushes the reaction to the left to use up some of the added heat. As a result, the concentration of CH_3OH decreases and the concentrations of H_2 and of CO increase.

13.44: Of the three options, only (b) will increase the concentration of NH_4^+. Adding NaOH (option a) pushes the reaction to the left, decreasing the concentration of NH_4^+. Adding NH_4Cl (option c) also pushes the reaction to the left as NH_4Cl is a source of NH_4^+. Adding HCl (option b) pushes the reaction to the right because the HCl reacts with OH^-, decreasing its concentration.

13.46: One approach is to add a soluble salt of Cl^-, such as NaCl. This increases the concentration of Cl^- and pushes the reaction to the right, reducing the concentration of Ag^+. A second approach is to lower the temperature, which pushes this exothermic reaction to the right to produce additional heat.

13.50: For (a), the equilibrium constant is

$$K = \frac{[C]^2}{[\mathrm{A}][\mathrm{B}]^2} = 1000$$

For (b), pick any two species and set their concentrations to a value less than or equal to 1 M and then solve for the third. There are, of course, an infinte number of solutions; here are two: [A] = 0.1 M, [B] = 0.1 M, and [C] = 1.0 M; and [A] = 0.0010 M, [B] = 1.0 M, and [C] = 1.0 M.

13.52: The equilibrium constant is

$$K = \frac{[\mathrm{NH_3}]^2}{[\mathrm{N_2}][\mathrm{H_2}]^3} = \frac{(0.412)^2}{(1.15)(1.35)^3} = 0.060$$

13.54: The reaction is $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$, for which the equilibrium constant expression is

$$K = \frac{[\mathrm{PCl_3}][\mathrm{Cl_2}]}{[\mathrm{PCl_5}]}$$

Given the stoichiometry of the reaction, which is 1:1:1, each mole of PCl_3 and of Cl_2 formed requires the loss of one mole of PCl_5; thus, at equilibrium, we have $0 + 0.40 = 0.40$ mol PCl_3, $0 + 0.40 = 0.40$ mol Cl_2, and $0.72 - 0.40 = 0.32$ mol PCl_5. Substituting into the equilibrium constant expression gives K as

$$K = \frac{[\mathrm{PCl_3}][\mathrm{Cl_2}]}{[\mathrm{PCl_5}]} = \frac{(0.40)(0.40)}{0.32} = 0.50$$

13.64: The equilibrium constant expression for this reaction is

$$K = \frac{[\mathrm{NH_3}]^2}{[\mathrm{N_2}][\mathrm{H_2}]^3} = 0.50$$

We know two of the three equilibrium concentrations; thus, we enter them into the equilibrium constant expression and solve for the remaining concentration.

$$K = \frac{[NH_3]^2}{[1.2][0.24]^3} = 0.50$$

$$[NH_3]^2 = 0.0083$$

$$[NH_3] = \sqrt{0.0083} = 0.091 \text{ M}$$

13.74: The equilibrium constant expression for this reaction is

$$K = \frac{[NO_2]^2}{[N_2O_4]} = 1.07 \times 10^{-5}$$

Let's assume that the initial concentration of N_2O_4 decreases by an amount equal to x; this means that the equilibrium concentration for N_2O_4 is

$$[N_2O_4]_{\text{eq}} = [N_2O_4]_{\text{initial}} - x = 0.129 - x$$

and, given the stoichiometry, the equilibrium concentration for NO_2 increases by $2x$ and is

$$[NO_2]_{\text{eq}} = [NO_2]_{\text{initial}} = 0 + 2x = 2x$$

For (a), we are told to assume that $[N_2O_4]_{\text{eq}} = 0.129 - x \approx 0.129$; thus

$$K = 1.07 \times 10^{-5} = \frac{[NO_2]^2}{[N_2O_4]} = \frac{(2x)^2}{0.129 - x} \approx \frac{4x^2}{0.129}$$

Solving for x gives its value as 5.87×10^{-4}; thus, the equilibrium concentrations are

$$[N_2O_4]_{\text{eq}} = 0.129 - x = 0.129 - 5.87 \times 10^{-4} = 0.128 \text{ M}$$

$$[NO_2]_{\text{eq}} = 2x = (2)(5.87 \times 10^{-4}) = 1.17 \times 10^{-3} \text{ M}$$

For (b), the percent error in the assumption that $0.129 - x \approx 0.129$ is

$$\frac{0.129 - (0.129 - x)}{0.129} \times 100 = \frac{5.78 \times 10^{-4}}{0.129} \times 100 = 0.455\%$$

As this is significantly less than 5%, the assumption is reasonable.