Manipulating the Equilibrium Law

The equilibrium law is written directly from the balanced chemical equation. On paper, chemical equations are easily manipulated. We can reverse the direction of the reaction by writing the reactants as products and the products as reactants. The coefficients of an equation can all be multiplied or divided by a constant factor. Equations can be added and subtracted. Each of these operations results in a different equilibrium law and a different value for the equilibrium constant.

Reversing a Chemical Equation

The chemical equation with the corresponding K_c

$$O_2(g) + 2SO_2(g) \rightleftharpoons 2SO_3(g) \quad K_c = \frac{[SO_3]^2}{[O_2] \times [SO_2]^2} \qquad (10.14)$$

can be written in the reverse direction as

$$2SO_3(g) \rightleftharpoons O_2(g) + 2SO_2(g) \quad K_c' = \frac{[O_2] \times [SO_2]^2}{[SO_3]^2} \qquad (10.15)$$

The two equilibrium constants, K_c and K_c', are inversely related to each other:

$$K_c = \frac{1}{K_c'} \qquad (10.16)$$

If a chemical reaction is reversed, the value of the new equilibrium constant will be the inverse of the original equilibrium constant.

Multiplying or Dividing Coefficients by a Constant

Taking the same reaction, Equation 10.14, of sulfur dioxide with oxygen:

$$O2(g) + 2SO_2(g) \rightleftharpoons 2SO_3(g) \quad K_c = \frac{[SO_3]^2}{[O_2] \times [SO_2]^2}$$

we can multiply each of the coefficients by 3 to obtain another balanced equation:

$$3O_2(g) + 6SO_2(g) \rightleftharpoons 6SO_3(g) \quad K_c' = \frac{[SO_3]^6}{[O_2]^3 \times [SO_2]^6} \qquad (10.17)$$

The relationship between K_c and K_c' can be shown since

$$\frac{[SO_3]^6}{[O_2]^3\,[SO_2]^6} = \left(\frac{[SO_3]^2}{[O_2]\,[SO_2]^2}\right)\left(\frac{[SO_3]^2}{[O_2][SO_2]^2}\right)\left(\frac{[SO_3]^2}{[O_2]\,[SO_2]^2}\right)$$

$$= \left(\frac{[SO_3]^2}{[O_2]\,[SO_2]^2}\right)^3 \qquad (10.18)$$

$$K_c' = K_cK_cK_c = K^3 \qquad (10.19)$$

We see that the original equilibrium constant is raised to the power equal to the factor used in the multiplication.

Dividing an equation by 2 is the same as multiplying the equation by ½. Therefore, when an equation is divided by 2, the new equilibrium constant, K_c', is the square root of the original K_c:

$$K_c' = K_c^{1/2} = \sqrt{K_c} \qquad (10.20)$$

Finally, reversing a reaction may also be considered mathematically the same as multiplying it by −1. The result is that

$$K_c' = K_c^{-1} = \frac{1}{K_c} \qquad (10.21)$$

which agrees with Equation 10.16.

Adding Chemical Reactions

Chemical reactions are added by adding all reactants and all products in two equations and writing them as one equation. For example:

$$2S(g) + 2O_2(g) \rightleftharpoons 2SO_2(g) \quad K_1 = \frac{[SO_2]^2}{[S]^2 \times [O_2]^2} \qquad (10.22)$$

$$O_2(g) + 2SO_2(g) \rightleftharpoons 2SO_3(g) \quad K_2 = \frac{[SO_3]^2}{[O_2] \times [SO_2]^2} \qquad (10.23)$$

Adding these two equations and canceling the $2SO_2(g)$, which are identical on both sides, yields

$$2S(g) + 3O_2(g) \rightleftharpoons 2SO_3(g) \quad K_{overall} = \frac{[SO_3]^2}{[S]^2 \times [O_2]^3} \qquad (10.24)$$

Mathematically we find that

$$K_{overall} = K_1 \times K_2 \qquad (10.25)$$

When equations are added, the overall equilibrium constant will be the product of the equilibrium constants of the reactions that were added.

Exercise 10.2

Given the following two reactions and their equilibrium constants:

$$Ag^+(aq) + Cl^-(aq) \rightleftharpoons AgCl(s) \qquad K_c = 1.0 \times 10^{10} \quad (a)$$

$$Ag^+(aq) + 2\,NH_3(aq) \rightleftharpoons Ag(NH_3)_2^+(aq) \qquad K_c = 1.6 \times 10^{7} \quad (b)$$

what is the equilibrium constant of the reaction

$$AgCl(s) + 2NH_3(aq) \rightleftharpoons Ag(NH_3)_2^+(aq) + Cl^-(aq) \qquad K_{overall} = ? \quad (c)$$

Show how reactions (a) and (b) are added to obtain reaction (c).

Solution

To add the given equations, it is necessary to reverse equation (a) to make $AgCl(s)$ a reactant and Cl^- a product as required in the overall reaction:

$$AgCl(s) \rightleftharpoons Ag^+(aq) + Cl^-(aq) \qquad K_c = 1/1.0 \times 10^{10} = 1.0 \times 10^{-10} \quad (d)$$

The equilibrium constant is inverted, as shown, when a reaction is reversed. Equation (d) is added to equation (b), and the $Ag^+(aq)$ ions cancel. When reactions are added, the equilibrium constants are multiplied:

$$K_{overall} = (1.0 \times 10^{-10})(1.6 \times 10^{7}) = 1.6 \times 10^{-3}$$