13.5: Some Special Types of Equilibria

Learning Objective

- Identify several special chemical equilibria and construct their K_a expressions.

In one sense, all chemical equilibria are treated the same. However, there are several classes of reactions that are noteworthy because of either the identities of the reactants and products, or the form of the K_{eq} expression.

Weak Acids and Bases

In Chapter 12 - Acids and Bases, we noted how some acids and bases are strong and some are weak. If an acid or base is strong, it is ionized 100% in H_2O. HCl(aq) is an example of a strong acid:

$$HCl(aq) \xrightarrow{100\%} H^+(aq) + Cl^-(aq)$$

However, if an acid or base is weak, it may dissolve in H_2O, but does not ionize completely. This means that there is an equilibrium between the unionized acid or base and the ionized form. $HC_2H_3O_2$ is an example of a weak acid:

$$HC_2H_3O_2(aq) \rightleftharpoons H^+(aq) + C_2H_3O_2^-(aq)$$

$HC_2H_3O_2$ is soluble in H_2O (in fact, it is the acid in vinegar), so the reactant concentration will appear in the equilibrium constant expression. But not all the molecules separate into ions. This is the case for all weak acids and bases.

An **acid dissociation constant**, K_a, is the equilibrium constant for the dissociation of a weak acid into ions. Note the *a* subscript on the *K*; it implies that the substance is acting as an acid. The larger K_a is, the stronger the acid is. Table 13.5.1 - Acid Dissociation Constants for Some Weak Acids, lists several acid dissociation constants. Keep in mind that they are just equilibrium constants.

Table, two columns and 7 rows. The first column on the right has different acids in the rows underneath. The second column on the right side has the acid dissociation content for the corresponding acid in the rows underneath.

Acid	K_a
$HC_2H_3O_2$	1.8×10^{-5}
$HClO_2$	1.1×10^{-2}
$H_2PO_4^-$	6.2×10^{-8}
HCN	6.2×10^{-10}
HF	6.3×10^{-4}
HNO_2	5.6×10^{-4}
H_3PO_4	7.5×10^{-3}

Table 13.5.1 Acid Dissociation Constants for Some Weak Acids

Note also that the acid dissociation constant refers to *one* H^+ ion coming off of the initial reactant. Thus the acid dissociation constant for H_3PO_4 refers to this equilibrium:

$$H_3PO_4(aq) \rightleftharpoons H^+(aq) + H_2PO_4^-(aq) \qquad K_a = 7.5 \times 10^{-3}$$

The $H_2PO_4^-$ ion, called the dihydrogen phosphate ion, is also a weak acid with its own acid dissociation constant:

$$H_2PO_4^-(aq) \rightleftharpoons H^+(aq) + HPO_4^{2-}(aq) \qquad K_a = 6.2 \times 10^{-8}$$

Thus, for so-called *polyprotic* acids, each H^+ ion comes off in sequence; each H^+ ion that ionizes does so with its own characteristic K_a.

Example 13.5.1

Write the equilibrium equation and the K_a expression for HSO_4^- acting as a weak acid.

Solution

HSO_4^- acts as a weak acid by separating into an H^+ ion and an SO_4^{2-} ion:

$$HSO_4^-(aq) \rightleftharpoons H^+(aq) + SO_4^{2-}(aq)$$

The K_a is written just like any other equilibrium constant, in terms of the concentrations of products divided by concentrations of reactants:

$$K_a = \frac{[H^+][SO_4^2-]}{[HSO_4^-]}$$

Exercise 13.5.1

Write the equilibrium equation and the K_a expression for HPO_4^{2-} acting as a weak acid.

Answer

$$HPO_4^{2-}(aq) \rightleftharpoons H^+(aq) + PO_4^{3-}(aq) \qquad K_a = \frac{[H^+][PO_4^{3-}]}{[HPO_4^{2-}]}$$

Autoionization of water

In Chapter 12, "Acids and Bases," we introduced the autoionization of water—the idea that water can act as a proton donor and proton acceptor simultaneously. Because water is not a strong acid (Table 12.5.1 - Strong Acids and Bases), it must be a weak acid, which means that its behavior as an acid must be described as an equilibrium. That equilibrium is as follows:

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

The equilibrium constant includes $[H_3O^+]$ and $[OH^-]$ but not $[H_2O(\ell)]$ because it is a pure liquid. Hence the expression *does not have any terms in its denominator*:

$K = [H_3O^+][OH^-] \equiv K_w = 1.0 \times 10^{-14}$

This is the same K_w that was introduced in Chapter 12 and the same 1.0×10^{-14} that appears in the relationship between the K_a and the K_b of a conjugate acid-base pair. In fact, we can rewrite this relationship as follows:

$K_a \times K_b = K_w$

Insoluble Compounds

In Chapter 4, section 4.3: "Types of Chemical Reactions - Single and Double Displacement Reactions," the concept of soluble and insoluble compounds was introduced. Solubility rules were presented that allow a person to predict whether certain simple ionic compounds will or will not dissolve.

Describing a substance as soluble or insoluble is a bit misleading because virtually all substances are soluble; they are just soluble to different extents. In particular, for ionic compounds, what we typically describe as an *insoluble* compound can actually be ever so slightly soluble; an equilibrium is quickly established between the solid compound and the ions that do form in solution. Thus, the hypothetical compound MX does in fact dissolve but only very slightly. That means we can write an equilibrium for it:

$$MX(s) \rightleftharpoons M^+(aq) + X^-(aq)$$

The equilibrium constant for a compound normally considered insoluble is called a **solubility product constant** and is labeled K_{sp} (with the subscript *sp*, meaning "solubility product"). Because the reactant is a solid, its concentration does not appear in the K_{sp}

expression, so like K_w, expressions for K_{sp} do not have denominators. For example, the chemical equation and the expression for the K_{sp} for AgCl, normally considered insoluble, are as follows:

$$AgCl(s) \rightleftharpoons Ag^+(aq) + Cl^-(aq) \qquad K_{sp} = [Ag^+][Cl^-]$$

Table 13.5.2- Solubility Product Constants for Slightly Soluble Ionic Compounds, lists some values of the K_{sp} for slightly soluble ionic compounds.

Table, two columns and 8 rows. The first column on the right has different compounds in the rows underneath. The second column on the right side has the acid dissociation content for the corresponding compounds in the rows underneath.

Compound	K_{sp}
$BaSO_4$	1.1×10^{-10}
$Ca(OH)_2$	5.0×10^{-6}
$Ca_3(PO_4)_2$	2.1×10^{-33}
$Mg(OH)_2$	5.6×10^{-12}
HgI_2	2.9×10^{-29}
AgCl	1.8×10^{-10}
AgI	8.5×10^{-17}
Ag_2SO_4	1.5×10^{-5}

Table 13.5.2 Solubility Product Constants for Slightly Soluble Ionic Compounds.

Example 13.5.4

Write the K_{sp} expression for $Ca_3(PO_4)_2$.

Solution

Recall that when an ionic compound dissolves, it separates into its individual ions. For $Ca_3(PO_4)_2$, the ionization reaction is as follows:

$$Ca_3(PO_4)_2(s) \rightleftharpoons 3Ca^{2+}(aq) + 2PO_4^{3-}(aq)$$

Hence the K_{sp} expression is

$K_{sp} = [Ca^{2+}]^3[PO_4^{3-}]^2$

Exercise 13.5.4

Write the K_{sp} expression Ag_2SO_4.

Answer

$K_{sp} = [Ag^+]^2[SO_4^{2-}]$

Food and Drink Application: Solids in Your Wine Bottle

People who drink wine from bottles (as opposed to boxes) will occasionally notice some insoluble materials in the wine, either crusting the bottle, stuck to the cork, or suspended in the liquid wine itself. The accompanying figure shows a cork encrusted with colored crystals. What are these crystals?

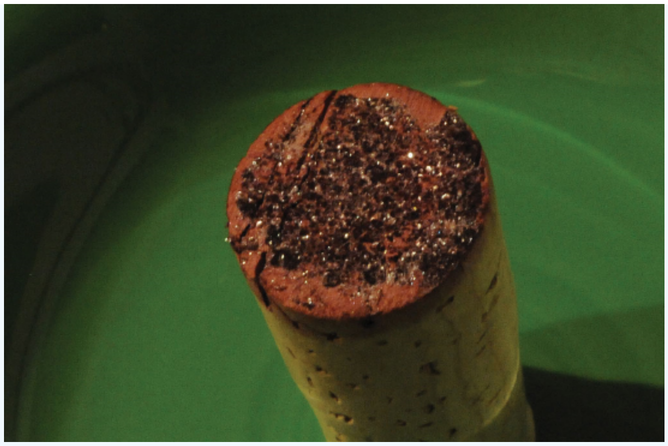

Figure 13.5.1 Wine Cork. The red crystals on the top of the wine cork are from insoluble compounds that are not soluble in the wine. Source: Photo courtesy of Paul A. Hernandez, flickr(opens in new window).

One of the acids in wine is tartaric acid ($H_2C_4H_4O_6$). Like the other acids in wine (citric and malic acids, among others), tartaric acid imparts a slight tartness to the wine. Tartaric acid is rather soluble in H_2O, dissolving over 130 g of the acid in only 100 g of H_2O. However, the potassium salt of singly ionized tartaric acid, potassium hydrogen tartrate ($KHC_4H_4O_6$; also known as potassium bitartrate and better known in the kitchen as cream of tartar), has a solubility of only 6 g per 100 g of H_2O. Thus, over time, wine stored at cool temperatures will slowly precipitate potassium hydrogen tartrate. The crystals precipitate in the wine or grow on the insides of the wine bottle and, if the bottle is stored on its side, on the bottom of the cork. The color of the crystals comes from pigments in the wine; pure potassium hydrogen tartrate is clear in its crystalline form, but in powder form it is white.

The crystals are harmless to ingest; indeed, cream of tartar is used as an ingredient in cooking. However, most wine drinkers do not like to chew their wine, so if tartrate crystals are present in a wine, the wine is usually filtered or decanted to remove the crystals. Tartrate crystals are almost exclusively in red wines; white and rose wines do not have as much tartaric acid in them.

Key Takeaway

- Equilibrium constants exist for certain groups of equilibria, such as weak acids, weak bases, the autoionization of water, and slightly soluble salts.
