Ladder diagrams are a useful tool for evaluating chemical reactivity, usually providing a reasonable approximation of a chemical system's composition at equilibrium. If we need a more exact quantitative description of the equilibrium condition, then a ladder diagram is insufficient. In this case we need to find an algebraic solution. In this section we will learn how to set-up and solve equilibrium problems. We will start with a simple problem and work toward more complex problems.

6.7.1 A Simple Problem—Solubility of Pb(IO₃)₂

If we place an insoluble compound such as Pb(IO₃)₂ in deionized water, the solid dissolves until the concentrations of Pb²⁺ and IO₃⁻ satisfy the solubility product for Pb(IO₃)₂. At equilibrium the solution is saturated with Pb(IO₃)₂, which simply means that no more solid can dissolve. How do we determine the equilibrium concentrations of Pb²⁺ and IO₃⁻, and what is the molar solubility of Pb(IO₃)₂ in this saturated solution?

When we first add solid Pb(IO₃)₂ to water, the concentrations of Pb²⁺ and IO₃⁻ are zero and the reaction quotient, Q, is

\[Q=[Pb^{2+}][IO_3^-]^2=0\]

As the solid dissolves, the concentrations of these ions increase, but Q remains smaller than Ksp. We reach equilibrium and "satisfy the solubility product" when

\[Q=K_{sp}\]

We begin by writing the equilibrium reaction and the solubility product expression for Pb(IO₃)₂.

\[\text{Pb(IO}_3\text{)}_2(s)\rightleftharpoons\text{Pb}^{2+}(aq)+2\text{IO}_3^-(aq)\]

\[K_{sp}=[Pb^{2+}][IO_3^-]^2=2.5\times10^{-13}\tag{6.33}\]

As Pb(IO₃)₂ dissolves, two IO₃⁻ ions are produced for each ion of Pb²⁺. If we assume that the change in the molar concentration of Pb²⁺ at equilibrium is x, then the change in the molar concentration of IO₃⁻ is 2x. The following table helps us keep track of the initial concentrations, the change in concentrations, and the equilibrium concentrations of Pb²⁺ and IO₃⁻.

<table>
<thead>
<tr>
<th>Concentrations</th>
<th>Pb(IO₃)₂ (s)</th>
<th>≡</th>
<th>Pb²⁺ (aq)</th>
<th>+</th>
<th>2IO₃⁻ (aq)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial</td>
<td>solid</td>
<td>0</td>
<td>0</td>
<td></td>
<td>0</td>
</tr>
<tr>
<td>Change</td>
<td>solid</td>
<td>+x</td>
<td>+2x</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Equilibrium</td>
<td>solid</td>
<td>x</td>
<td>2x</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Because a solid, such as Pb(IO\textsubscript{3})\textsubscript{2}, does not appear in the solubility product expression, we do not need to keep track of its concentration. Remember, however, that the $K\text{sp}$ value applies only if there is some Pb(IO\textsubscript{3})\textsubscript{2} present at equilibrium.

Substituting the equilibrium concentrations into equation 6.33 and solving gives

$$(x)(2x)^2=4x^3=2.5\times10^{-13}$$

$$x=3.97\times10^{-5}$$

Substituting this value of $x$ back into the equilibrium concentration expressions for Pb\textsuperscript{2+} and IO\textsubscript{3}\textsuperscript{-} gives their concentrations as

$$\text{[Pb\textsuperscript{2+}]}=x=4.0\times10^{-5}\text{ M}$$

$$\text{[\sideset{\_3^{-}}{_{\text{IO}}}]}=2x=7.9\times10^{-5}\text{ M}$$

Because one mole of Pb(IO\textsubscript{3})\textsubscript{2} contains one mole of Pb\textsuperscript{2+}, the molar solubility of Pb(IO\textsubscript{3})\textsubscript{2} is equal to the concentration of Pb\textsuperscript{2+}, or $4.0 \times 10^{-5}$ M.

We can express a compound’s solubility in two ways: molar solubility (mol/L) or mass solubility (g/L). Be sure to express your answer clearly.

Exercise 6.7

Calculate the molar solubility and the mass solubility for Hg\textsubscript{2}Cl\textsubscript{2}, given the following solubility reaction and $K\text{sp}$ value.

$$\text{Hg}_2\text{Cl}_2(s)\rightleftharpoons \text{Hg}_2\textsuperscript{2+}(aq)+2\text{Cl}^{-}(aq)$$

$$K\text{sp}=1.2\times10^{-18}$$

Click here to review your answer to this exercise.

### 6.7.2 A More Complex Problem—The Common Ion Effect

Calculating the solubility of Pb(IO\textsubscript{3})\textsubscript{2} in deionized water is a straightforward problem since the solid’s dissolution is the only source of Pb\textsuperscript{2+} and IO\textsubscript{3}-. But what if we add Pb(IO\textsubscript{3})\textsubscript{2} to a solution of 0.10 M Pb(NO\textsubscript{3})\textsubscript{2}, which provides a second source of Pb\textsuperscript{2+}? Before we set-up and solve this problem algebraically, think about the system’s chemistry and decide whether the solubility of Pb(IO\textsubscript{3})\textsubscript{2} will increase, decrease or remain the same.

Beginning a problem by thinking about the likely answer is a good habit to develop. Knowing what answers are reasonable will help you spot errors in your calculations and give you more confidence that your solution to a problem is correct.

Because the solution already contains a source of Pb\textsuperscript{2+}, we can use Le Châtelier’s principle to predict that the solubility of Pb(IO\textsubscript{3})\textsubscript{2} is smaller than that in our previous problem.

We begin by setting up a table to help us keep track of the concentrations of Pb\textsuperscript{2+} and IO\textsubscript{3} as this system moves toward
and reaches equilibrium.

\[
\begin{array}{c|ccc}
\text{Concentrations} & \text{Pb(IO}_3\text{)}_2 & \rightleftharpoons & \text{Pb}^{2+} \\
\text{(s)} & (aq) & + & 2\text{IO}_3^{-} \\
\hline
\text{Initial} & \text{solid} & 0.10 & 0 \\
\text{Change} & \text{solid} & +x & +2x \\
\text{Equilibrium} & \text{solid} & 0.10 + x & 2x \\
\end{array}
\]

Substituting the equilibrium concentrations into equation 6.33

\[
(0.10 + x)(2x)^2 = 2.5 \times 10^{-13}
\]

and multiplying out the terms on the equation’s left side leaves us with

\[
4x^3 + 0.40x^2 = 2.5 \times 10^{-13}
\]  

This is a more difficult equation to solve than that for the solubility of Pb(IO_3)_2 in deionized water, and its solution is not immediately obvious. We can find a rigorous solution to equation 6.34 using available computer software packages and spreadsheets, some of which are described in Section 6.J.

Note

There are several approaches to solving cubic equations, but none are computationally easy.

How might we solve equation 6.34 if we do not have access to a computer? One approach is to use our understanding of chemistry to simplify the problem. From Le Châtelier’s principle we know that a large initial concentration of Pb^{2+} significantly decreases the solubility of Pb(IO_3)_2. One reasonable assumption is that the equilibrium concentration of Pb^{2+} is very close to its initial concentration. If this assumption is correct, then the following approximation is reasonable

\[
\text{[Pb}^{2+}\text{]} = 0.10 + x \approx 0.10 \text{ M}
\]

Substituting our approximation into equation 6.33 and solving for \(x\) gives

\[
(0.1)(2x)^2 = 2.5 \times 10^{-13}
\]

\[
0.4x^2 = 2.5 \times 10^{-13}
\]

\[
x = 7.91 \times 10^{-7}
\]

Before accepting this answer, we must verify that our approximation is reasonable. The difference between the calculated concentration of Pb^{2+}, 0.10 + x M, and our assumption that it is 0.10 M is 7.9 \times 10^{-7}, or 7.9 \times 10^{-4}\% of the assumed concentration. This is a negligible error.
\[
\text{Note}
\]
\[
\begin{align}
\text{error} &= \dfrac{(0.10+x)-0.10}{0.10}\times100 \\
&= \dfrac{7.91\times10^{-7}}{0.10}\times100 \\
&= 7.91\times10^{-4}\% 
\end{align}
\]

Accepting the result of our calculation, we find that the equilibrium concentrations of Pb\(^{2+}\) and IO\(_3^–\) are
\[
\text{[Pb}^{2+}\text{]}=0.10+x\approx\text{0.10 M}
\]
\[
\text{[IO}_3\text{]}=2x=1.6\times10^{-6}\text{ M}
\]

The molar solubility of Pb(IO\(_3\)\(_2\)) is equal to the additional concentration of Pb\(^{2+}\) in solution, or 7.9 \times 10^{-4} \text{ mol/L}. As expected, Pb(IO\(_3\)\(_2\)) is less soluble in the presence of a solution that already contains one of its ions. This is known as the **common ion effect**.

As outlined in the following example, if an approximation leads to an unacceptably large error we can extend the process of making and evaluating approximations.

**Example 6.10**

Calculate the solubility of Pb(IO\(_3\)\(_2\)) in 1.0 \times 10^{-4} \text{ M Pb(NO}_3\text{)\(_2\).}

**Solution**

Letting \(x\) equal the change in the concentration of Pb\(^{2+}\), the equilibrium concentrations of Pb\(^{2+}\) and IO\(_3^–\) are
\[
\text{[Pb}^{2+}\text{]}=1.0\times10^{-4}+x\approx1.0\times10^{-4}\text{ M}
\]
\[
\text{[IO}_3\text{]}=2x=2.5\times10^{-5}\text{ M}
\]

Substituting these concentrations into equation 6.33 leaves us with
\[
(1.0\times10^{-4}+x)(2x)^2=2.5\times10^{-13}
\]

To solve this equation for \(x\), we make the following assumption
\[
\text{[Pb}^{2+}\text{]}=1.0\times10^{-4}+x\approx1.0\times10^{-4}\text{ M}
\]

obtaining a value for \(x\) of 2.50\times10^{-4}. Substituting back, gives the calculated concentration of Pb\(^{2+}\) at equilibrium as
\[
\text{[Pb}^{2+}\text{]}=1.0\times10^{-4}+2.50\times10^{-4}=1.25\times10^{-4}\text{ M}
\]
a value that differs by 25% from our assumption that the equilibrium concentration is 1.0\times10^{-4} \text{ M}. This error seems unreasonably large. Rather than shouting in frustration, we make a new assumption. Our first assumption—that the concentration of Pb\(^{2+}\) is 1.0\times10^{-4} \text{ M—was too small. The calculated concentration of 1.25\times10^{-4} \text{ M, therefore, is probably
a bit too large. For our second approximation, let’s assume that

\[
\text{[Pb}^{2+}\text{]} = 1.0 \times 10^{-4} + x \approx 1.25 \times 10^{-4}
\]

Substituting into equation 6.33 and solving for \(x\) gives its value as \(2.24 \times 10^{-5}\). The resulting concentration of \(\text{Pb}^{2+}\) is

\[
\text{[Pb}^{2+}\text{]} = 1.0 \times 10^{-4} + 2.24 \times 10^{-5} = 1.22 \times 10^{-4} \text{ M}
\]

which differs from our assumption of \(1.25 \times 10^{-4}\) M by 2.4%. Because the original concentration of \(\text{Pb}^{2+}\) is given to two significant figure, this is a more reasonable error. Our final solution, to two significant figures, is

\[
\text{[Pb}^{2+}\text{]} = 1.2 \times 10^{-4} \text{ M} \hspace{7mm} \text{[IO}_3^-\text{]} = 4.5 \times 10^{-5} \text{ M}
\]

and the molar solubility of \(\text{Pb(IO}_3)_2\) is \(2.2 \times 10^{-5}\) mol/L. This iterative approach to solving an equation is known as the **method of successive approximations**.

Practice Exercise 6.8
Calculate the molar solubility for \(\text{Hg}_2\text{Cl}_2\) in 0.10 M NaCl and compare your answer to its molar solubility in deionized water (see Practice Exercise 6.7).

Click here to review your answer to this exercise.

### 6.7.3 A Systematic Approach to Solving Equilibrium Problems

Calculating the solubility of \(\text{Pb(IO}_3)_2\) in a solution of \(\text{Pb(NO}_3)_2\) is more complicated than calculating its solubility in deionized water. The calculation, however, is still relatively easy to organize, and the simplifying assumption fairly obvious. This problem is reasonably straightforward because it involves only one equilibrium reaction and one equilibrium constant.

Determining the equilibrium composition of a system with multiple equilibrium reactions is more complicated. In this section we introduce a systematic approach to setting-up and solving equilibrium problems. As shown in Table 6.1, this approach involves four steps.

<table>
<thead>
<tr>
<th>Table 6.1 Systematic Approach to Solving Equilibrium Problems</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Step 1:</strong> Write all relevant equilibrium reactions and equilibrium constant expressions.</td>
</tr>
<tr>
<td><strong>Step 2:</strong> Count the unique species appearing in the equilibrium constant expressions; these are your unknowns. You have enough information to solve the problem if the number of unknowns equals the number of equilibrium constant expressions. If not, add a mass balance equation and/or a charge balance equation. Continue adding equations until the number of equations equals the number of unknowns.</td>
</tr>
<tr>
<td><strong>Step 3:</strong> Combine your equations and solve for one unknown. Whenever possible, simplify the algebra by making appropriate assumptions. If you make an assumption, set a limit for its error. This decision influences your evaluation of the assumption.</td>
</tr>
<tr>
<td><strong>Step 4:</strong> Check your assumptions. If any assumption proves invalid, return to the previous step and continue solving. The problem is complete when you have an answer that does not violate any of your assumptions.</td>
</tr>
</tbody>
</table>
In addition to equilibrium constant expressions, two other equations are important to the systematic approach for solving equilibrium problems. The first of these is a **mass balance equation**, which is simply a statement that matter is conserved during a chemical reaction. In a solution of a acetic acid, for example, the combined concentrations of the conjugate weak acid, CH$_3$COOH, and the conjugate weak base, CH$_3$COO$^-$, must equal acetic acid’s initial concentration, CCH$_3$COOH.

\[C_{\text{CH}_3\text{COOH}}=\text{[CH}_3\text{COOH]+[CH}_3\text{COO}^-]\]

**Note**

You may recall from **Chapter 2** that this is the difference between a formal concentration and a molar concentration. The variable C represents a formal concentration.

The second equation is a **charge balance equation**, which requires that total charge from the cations equal the total charge from the anions. Mathematically, the charge balance equation is

\[\sum_{i}|(z^+)_i|C^{z+}_i=\sum_{j}|(z^-)_j|A^{z-}_j\]

where \([C^+]_i\) and \([A^-]_j\) are, respectively, the concentrations of the \(i\)th cation and the \(j\)th anion, and \(|(z^+)_i|\) and \(|(z^-)_j|\) are the absolute values of the \(i\)th cation’s charge and the \(j\)th anion’s charge. Every ion in solution, even if it does not appear in an equilibrium reaction, must appear in the charge balance equation. For example, the charge balance equation for an aqueous solution of Ca(NO$_3$)$_2$ is

\[2\times[\text{Ca}^{2+}]+[\text{H}_3\text{O}^+]=[\text{OH}^-]+2\times[\text{NO}_3^-]\]

**Note**

We use absolute values because we are balancing the concentration of charge and concentrations cannot be negative.

There are situations where it is impossible to write a charge balance equation because we do not have enough information about the solution’s composition. For example, suppose we fix a solution’s pH using a buffer. If the buffer’s composition is not specified, then a charge balance equation cannot be written.

**Example 6.11**

Write mass balance equations and a charge balance equation for a 0.10 M solution of NaHCO$_3$.

**Solution**

It is easier to keep track of the species in solution if we write down the reactions controlling the solution’s composition. These reactions are the dissolution of a soluble salt

\[\text{NaHCO}_3(s)\rightarrow\text{Na}^+(aq)+\text{HCO}_3^-(aq)\]

and the acid–base dissociation reactions of HCO$_3^-$ and H$_2$O

\[\text{HCO}_3^-+\text{H}_2\text{O}(l)\rightleftharpoons\text{H}_3\text{O}^++\text{CO}_3^{2-}\]
\[
\text{H}_3\text{O}^+(aq) + \text{CO}_3^{2-}(aq) \rightleftharpoons \text{\sideset{}{_{3}^{-}}{HCO}} (aq) + \text{H}_2\text{O}(l)
\]
\[
\text{2H}_2\text{O}(l) \rightleftharpoons \text{H}_3\text{O}^+(aq) + \text{OH}^-(aq)
\]

The mass balance equations are
\[
0.10 \text{ M} = [\text{H}_2\text{CO}_3] + [\text{\sideset{}{_{3}^{-}}{HCO}}] + [\text{CO}_3^{2-}]
\]
\[
0.10 \text{ M} = [\text{Na}^+]
\]

and the charge balance equation is
\[
[\text{Na}^+] + [\text{H}_3\text{O}^+] = [\text{OH}^-] + [\text{\sideset{}{_{3}^{-}}{HCO}}] + 2 \times [\text{CO}_3^{2-}]
\]

Practice Exercise 6.9

Write appropriate mass balance and charge balance equations for a solution containing 0.10 M KH$_2$PO$_4$ and 0.050 M Na$_2$HPO$_4$.

Click here to review your answer to this exercise.

### 6.7.4 pH of a Monoprotic Weak Acid

To illustrate the systematic approach to solving equilibrium problems, let’s calculate the pH of 1.0 M HF. (Step 1: Write all relevant equilibrium reactions and equilibrium constant expressions.) Two equilibrium reactions affect the pH. The first, and most obvious, is the acid dissociation reaction for HF
\[
\text{HF}(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{H}_3\text{O}^+(aq) + \text{F}^-(aq)
\]
for which the equilibrium constant expression is
\[
K_a = \frac{[\text{H}_3\text{O}^+][\text{F}^-]}{[\text{HF}]} = 6.8 \times 10^{-4} \tag{6.35}
\]

The second equilibrium reaction is the dissociation of water, which is an obvious yet easily neglected reaction
\[
\text{2H}_2\text{O}(l) \rightleftharpoons \text{H}_3\text{O}^+(aq) + \text{OH}^-(aq)
\]
\[
K_w = [\text{H}_3\text{O}^+][\text{OH}^-] = 1.00 \times 10^{-14} \tag{6.36}
\]

Note

Step 2: Count the unique species appearing in the equilibrium constant expressions; these are your unknowns. You have enough information to solve the problem if the number of unknowns equals the number of equilibrium constant expressions. If not, add a mass balance equation and/or a charge balance equation. Continue adding equations until the
number of equations equals the number of unknowns.

Counting unknowns, we find four: $[HF]$, $[F^-]$, $[H_3O^+]$, and $[OH^-]$. To solve this problem we need two additional equations. These equations are a mass balance equation on hydrofluoric acid

$$\text{C}_{\text{HF}} = [HF] + [F^-] \tag{6.37}$$

and a charge balance equation

$$\text{[H}_3\text{O}^+\text{]} = [OH^-] + [F^-] \tag{6.38}$$

With four equations and four unknowns, we are ready to solve the problem. Before doing so, let’s simplify the algebra by making two assumptions.

Note

Step 3: Combine your equations and solve for one unknown. Whenever possible, simplify the algebra by making appropriate assumptions. If you make an assumption, set a limit for its error. This decision influences your evaluation the assumption.

**Assumption One.** Because HF is a weak acid, the solution must be acidic. For an acidic solution it is reasonable to assume that

$$[H_3O^+] >> [OH^-]$$

which simplifies the charge balance equation to

$$[H_3O^+] = [F^-] \tag{6.39}$$

**Assumption Two.** Because HF is a weak acid, very little dissociation occurs. Most of the HF remains in its conjugate weak acid form and it is reasonable to assume that

$$[HF] >> [F^-]$$

which simplifies the mass balance equation to

$$\text{C}_{\text{HF}} = [HF] \tag{6.40}$$

For this exercise let’s accept an assumption if it introduces an error of less than ±5%.

Substituting equation 6.39 and equation 6.40 into equation 6.35, and solving for the concentration of $H_3O^+$ gives us

$$K_a = \frac{[H_3O^+][H_3O^+]}{[HF]} = \frac{[H_3O^+]^2}{[HF]} = 6.8 \times 10^{-4}$$

$$[H_3O^+] = \sqrt{K_a C_{\text{HF}}} = \sqrt{(6.8 \times 10^{-4})(1.0)} = 2.6 \times 10^{-2}$$
Note

Step 4: Check your assumptions. If any assumption proves invalid, return to the previous step and continue solving. The problem is complete when you have an answer that does not violate any of your assumptions.

Before accepting this answer, we must verify our assumptions. The first assumption is that $[\text{OH}^-]$ is significantly smaller than $[\text{H}_3\text{O}^+]$. Using equation 6.36, we find that

$$[\text{OH}^-] = \dfrac{K_w}{[\text{H}_3\text{O}^+]} = \dfrac{1.00 \times 10^{-14}}{2.6 \times 10^{-2}} = 3.8 \times 10^{-13}$$

Clearly this assumption is acceptable. The second assumption is that $[\text{F}^-]$ is significantly smaller than $[\text{HF}]$. From equation 6.39 we have

$$[\text{F}^-] = 2.6 \times 10^{-2} \text{ M}$$

Because $[\text{F}^-]$ is $2.60\%$ of $[\text{HF}]$, this assumption is also acceptable. Given that $[\text{H}_3\text{O}^+]$ is $2.6 \times 10^{-2}$ M, the pH of 1.0 M HF is 1.59.

How does the calculation change if we limit an assumption’s error to less than ±1%? In this case we can no longer assume that $[\text{HF}] \gg [\text{F}^-]$ and we cannot simplify the mass balance equation. Solving the mass balance equation for $[\text{HF}]$

$$[\text{HF}] = C_{\text{HF}} - [\text{F}^-] = C_{\text{HF}} - [\text{H}_3\text{O}^+]$$

and substituting into the $K_a$ expression along with equation 6.39 gives

$$K_a = \dfrac{[\text{H}_3\text{O}^+]^2}{C_{\text{HF}} - [\text{H}_3\text{O}^+]}$$

Rearranging this equation leaves us with a quadratic equation

$$[\text{H}_3\text{O}^+]^2 + K_a[\text{H}_3\text{O}^+] - K_aC_{\text{HF}} = 0$$

which we solve using the quadratic formula

$$x = \dfrac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

where $a$, $b$, and $c$ are the coefficients in the quadratic equation

$$ax^2 + bx + c = 0$$

Solving a quadratic equation gives two roots, only one of which has chemical significance. For our problem, the equation’s roots are

$$x = \dfrac{-6.8 \times 10^{-4} \pm \sqrt{(6.8 \times 10^{-4})^2 - 4(1)(6.8 \times 10^{-2})}}{2(1)}$$

$$x = \dfrac{-6.8 \times 10^{-4} \pm 5.22 \times 10^{-2}}{2}$$
Only the positive root is chemically significant because the negative root gives a negative concentration for $\text{H}_3\text{O}^+$. Thus, $[\text{H}_3\text{O}^+]$ is $2.6 \times 10^{-2}$ M and the pH is 1.59.

You can extend this approach to calculating the pH of a monoprotic weak base by replacing $K_a$ with $K_b$, replacing $C_{HF}$ with the weak base’s concentration, and solving for $[\text{OH}^-]$ in place of $[\text{H}_3\text{O}^+]$.

Practice Exercise 6.10

Calculate the pH of 0.050 M $\text{NH}_3$. State any assumptions you make in solving the problem, limiting the error for any assumption to ±5%. The $K_b$ value for $\text{NH}_3$ is $1.75 \times 10^{-5}$.

Click here to review your answer to this exercise.

6.7.5 pH of a Polyprotic Acid or Base

A more challenging problem is to find the pH of a solution containing a polyprotic weak acid or one of its conjugate species. As an example, consider the amino acid alanine, whose structure is shown in Figure 6.12. The ladder diagram in Figure 6.13 shows alanine’s three acid–base forms and their respective areas of predominance. For simplicity, we identify these species as $\text{H}_2\text{L}^+$, HL, and $\text{L}^-$.

![Figure 6.12 Structure of the amino acid alanine, which has pK_a values of 2.348 and 9.867.](image-url)
pH of 0.10 M Alanine Hydrochloride ($H_2L^+$)

Alanine hydrochloride is a salt of the diprotic weak acid $H_2L^+$ and $Cl^-$. Because $H_2L^+$ has two acid dissociation reactions, a complete systematic solution to this problem is more complicated than that for a monoprotic weak acid. The ladder diagram in Figure 6.13 helps us simplify the problem. Because the areas of predominance for $H_2L^+$ and $L^-$ are so far apart, we can assume that a solution of $H_2L^+$ is not likely to contain significant amounts of $L^-$. As a result, we can treat $H_2L^+$ as though it is a monoprotic weak acid. Calculating the pH of 0.10 M alanine hydrochloride, which is 1.72, is left to the reader as an exercise.
pH of 0.10 M Sodium Alaninate (L⁻)

The alaninate ion is a diprotic weak base. Because L⁻ has two base dissociation reactions, a complete systematic solution to this problem is more complicated than that for a monoprotic weak base. Once again, the ladder diagram in Figure 6.13 helps us simplify the problem. Because the areas of predominance for H₂L⁺ and L⁻ are so far apart, we can assume that a solution of L⁻ is not likely to contain significant amounts of H₂L⁺. As a result, we can treat L⁻ as though it is a monoprotic weak base. Calculating the pH of 0.10 M sodium alaninate, which is 11.42, is left to the reader as an exercise.

pH of 0.1 M Alanine (HL)

Finding the pH of a solution of alanine is more complicated than our previous two examples because we cannot ignore the presence of both H₂L⁺ and L⁻. To calculate the solution’s pH we must consider alanine’s acid dissociation reaction

\[ \text{HL}(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{H}_3\text{O}^+(aq) + \text{L}^-(aq) \]

and its base dissociation reaction

\[ \text{HL}(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{OH}^-(aq) + \text{H}_2\text{L}^+(aq) \]

As always, we must also consider the dissociation of water

\[ \text{2H}_2\text{O}(l) \rightleftharpoons \text{H}_3\text{O}^+(aq) + \text{OH}^-(aq) \]

This leaves us with five unknowns—[H₂L⁺], [HL], [L⁻], [H₃O⁺], and [OH⁻]—for which we need five equations. These equations are \(K_{\text{a2}}\) and \(K_{\text{b2}}\) for alanine

\[ K_{\text{a2}} = \frac{[\text{H}_3\text{O}^+][\text{L}^-]}{[\text{HL}]} \]

\[ K_{\text{b2}} = \frac{K_w}{K_{\text{a1}}} = \frac{[\text{OH}^-][\text{H}_2\text{L}^+]}{[\text{HL}]} \]

the \(K_w\) equation

\[ K_w = [\text{H}_3\text{O}^+][\text{OH}^-] \]

a mass balance equation for alanine

\[ C_{\text{HL}} = [\text{H}_2\text{L}^+]+[\text{HL}]+[\text{L}^-] \]

and a charge balance equation

\[ [\text{H}_2\text{L}^+]+[\text{H}_3\text{O}^+] = [\text{OH}^-]+[\text{L}^-] \]

Because HL is a weak acid and a weak base, it seems reasonable to assume that

\[ [\text{HL}] >> [\text{H}_2\text{L}^+]+[\text{L}^-] \]
which allows us to simplify the mass balance equation to

\[C_{\text{HL}} = [\text{HL}]\]

Next we solve \(K_{b2}\) for \([H_2L^+]\)

\[\frac{[H_2L^+]}{[\text{HL}]} = \frac{[\text{H}_3\text{O}^+]K_{a2}}{K_w} = \frac{C_{\text{HL}}[\text{H}_3\text{O}^+]}{K_{a2}}\]

and \(K_{a2}\) for \([L^-]\)

\[\frac{[L^-]}{[\text{HL}]} = \frac{K_{a2}C_{\text{HL}}}{[\text{H}_3\text{O}^+]} = \frac{K_{a2}C_{\text{HL}}}{K_w} = \frac{K_{a2}C_{\text{HL}}}{K_{a1}C_{\text{HL}}} = \frac{K_{a2}}{K_{a1}}\]

Substituting these equations for \([H_2L^+]\) and \([L^-]\), along with the equation for \(K_w\), into the charge balance equation give us

\[\frac{C_{\text{HL}}[\text{H}_3\text{O}^+]}{K_{a1}} + [\text{H}_3\text{O}^+] = \frac{K_w}{[\text{H}_3\text{O}^+]} + \frac{K_{a2}C_{\text{HL}}}{[\text{H}_3\text{O}^+]},\]

which we simplify to

\[\frac{[\text{H}_3\text{O}^+]}{K_{a1}} + 1 = \frac{1}{[\text{H}_3\text{O}^+]}(K_w + K_{a2}C_{\text{HL}})\]

\[[\text{H}_3\text{O}^+]^2 = \frac{K_{a2}C_{\text{HL}} + K_w}{C_{\text{HL}} + K_{a1}}\]

\[[\text{H}_3\text{O}^+] = \sqrt{\frac{K_{a2}C_{\text{HL}} + K_w}{C_{\text{HL}} + K_{a1}}}\]

We can further simplify this equation if \(K_{a1}K_w < < K_{a1}K_{a2}C_{\text{HL}}\), and if \(K_{a1} < < C_{\text{HL}}\), leaving us with

\[[\text{H}_3\text{O}^+] = \sqrt{K_{a2}C_{\text{HL}}}\]

For a solution of 0.10 M alanine the \([\text{H}_3\text{O}^+]\) is

\[[\text{H}_3\text{O}^+] = \sqrt{(4.487 \times 10^{-10})(1.358 \times 10^{-10})} = 7.807 \times 10^{-7}; \text{M}]\]

or a pH of 6.11.

Practice Exercise 6.11

Verify that each assumption in our solution for the pH of 0.10 M alanine is reasonable, using \(\pm5\%\) as the limit for the acceptable error.

Click here to review your answer to this exercise.
6.7.6 Effect of Complexation on Solubility

One method for increasing a precipitate’s solubility is to add a ligand that forms soluble complexes with one of the precipitate’s ions. For example, the solubility of AgI increases in the presence of NH\(_3\) due to the formation of the soluble Ag(NH\(_3\))\(_2^+\) complex. As a final illustration of the systematic approach to solving equilibrium problems, let’s calculate the molar solubility of AgI in 0.10 M NH\(_3\).

We begin by writing the relevant equilibrium reactions, which includes the solubility of AgI, the acid–base chemistry of NH\(_3\) and H\(_2\)O, and the metal-ligand complexation chemistry between Ag\(^{+}\) and NH\(_3\).

\[
\text{AgI(s)} \rightleftharpoons \text{Ag}^{+}(\text{aq}) + \text{I}^{-}(\text{aq})
\]
\[
\text{NH}_3(\text{aq}) + \text{H}_2\text{O}(l) \rightleftharpoons \text{OH}^{-}(\text{aq}) + \text{NH}_4^{+}(\text{aq})
\]
\[
2\text{H}_2\text{O}(l) \rightleftharpoons \text{H}_3\text{O}^{+}(\text{aq}) + \text{OH}^{-}(\text{aq})
\]
\[
\text{Ag}^{+}(\text{aq}) + 2\text{NH}_3(\text{aq}) \rightleftharpoons \text{Ag(NH}_3)_2^{+}(\text{aq})
\]

This leaves us with seven unknowns—[Ag\(^{+}\)], [I\(^{-}\)], [NH\(_3\)], [NH\(_4\)\(^{+}\)], [OH\(^{-}\)], [H\(_3\)O\(^{+}\)], and [Ag(NH\(_3\))\(_2^+\)]—and a need for seven equations. Four of the equations we need to solve this problem are the equilibrium constant expressions

\[K_{\text{sp}} = \text{[Ag}^{+}\text{][I}^{-}\text{]} = 8.3 \times 10^{-17}\] \tag{6.41}\]
\[K_b = \frac{\text{[NH}_4^{+}\text{][OH}^{-}\text{]}}{\text{[NH}_3\text{]}} = 1.75 \times 10^{-5}\] \tag{6.42}\]
\[K_w = \text{[H}_3\text{O}^{+}\text{][OH}^{-}\text{]} = 1.00 \times 10^{-14}\] \tag{6.43}\]
\[\beta_2 = \frac{\text{[Ag(NH}_3)_2^{+}\]}{\text{[Ag}^{+}\text{][NH}_3^2\text{]}} = 1.7 \times 10^7\] \tag{6.44}\]

We still need three additional equations. The first of these equation is a mass balance for NH\(_3\).

\[C_{\text{NH}_3} = \text{[NH}_3\text{]} + \text{[NH}_4^{+}\text{]} + 2\times\text{[Ag(NH}_3)_2^{+}\]}\] \tag{6.45}\]

In writing this mass balance equation we multiply the concentration of Ag(NH\(_3\))\(_2^+\) by two since there are two moles of NH\(_3\) per mole of Ag(NH\(_3\))\(_2^+\). The second additional equation is a mass balance between iodide and silver. Because AgI is the only source of I\(^{-}\) and Ag\(^{+}\), each iodide in solution must have an associated silver ion, which may be Ag\(^{+}\) or Ag(NH\(_3\))\(_2^+\); thus

\[\text{[I}^{-}\text{]} = \text{[Ag}^{+}\text{]} + \text{[Ag(NH}_3)_2^{+}\]}\] \tag{6.46}\]

Finally, we include a charge balance equation.

\[\text{[Ag}^{+}\text{]} + \text{[Ag(NH}_3)_2^{+}\} + \text{[NH}_4^{+}\text{]} + \text{[H}_3\text{O}^{+}\text{]} = \text{[OH}^{-}\text{]} + \text{[I}^{-}\text{]}\] \tag{6.47}\]

Although the problem looks challenging, three assumptions greatly simplify the algebra.
**Assumption One.** Because the formation of the \( \text{Ag(NH}_3\text{)}_2^+ \) complex is so favorable (\( \beta_2 = 1.7 \times 10^7 \)), there is very little free \( \text{Ag}^+ \) and it is reasonable to assume that

\[
\text{[Ag}^\text{+]} \ll \text{[Ag(NH}_3\text{)}_2^+] \]

**Assumptions Two.** Because \( \text{NH}_3 \) is a weak base we may reasonably assume that most uncomplexed ammonia remains as \( \text{NH}_3 \); thus

\[
\text{[NH}_4\text{+]} \ll \text{[NH}_3\text{]} \]

**Assumption Three.** Because \( K_{sp} \) for \( \text{AgI} \) is significantly smaller than \( \beta_2 \) for \( \text{Ag(NH}_3\text{)}_2^+ \), the solubility of \( \text{AgI} \) is probably small enough that very little ammonia is needed for metal–ligand complexation; thus

\[
\text{[Ag(NH}_3\text{)}_2^+] \ll \text{[NH}_3\text{]} \]

As we use these assumptions to simplify the algebra, let’s set ±5% as the limit for error.

Assumption two and assumption three suggest that the concentration of \( \text{NH}_3 \) is much larger than the concentrations of either \( \text{NH}_4^+ \) or \( \text{Ag(NH}_3\text{)}_2^+ \), allowing us to simplify the mass balance equation for \( \text{NH}_3 \) to

\[
[C_\text{NH}_3] = \text{[NH}_3\text{]} \tag{6.48} \]

Finally, using assumption one, which suggests that the concentration of \( \text{Ag(NH}_3\text{)}_2^+ \) is much larger than the concentration of \( \text{Ag}^+ \), we simplify the mass balance equation for \( \text{I}^- \) to

\[
\text{[I}^-\text{]} = \text{[Ag(NH}_3\text{)}_2^+] \tag{6.49} \]

Now we are ready to combine equations and solve the problem. We begin by solving equation 6.41 for \( \text{[Ag}^+\text{]} \) and substitute it into \( \beta_2 \) (equation 6.44), leaving us with

\[
\beta_2 = \frac{\text{[Ag(NH}_3\text{)}_2^+] \times \text{[I}^-\text{]}}{K_{sp} \times (C_\text{NH}_3)^2} \tag{6.50} \]

Next we substitute equation 6.48 and equation 6.49 into equation 6.50, obtaining

\[
\beta_2 = \frac{\text{[I}^-\text{]}^2}{K_{sp} \times (C_\text{NH}_3)^2} \tag{6.51} \]

Solving equation 6.51 for \( \text{[I}^-\text{]} \) gives

\[
\text{[I}^-\text{]} = \sqrt{\frac{\beta_2 \times K_{sp}}{C_\text{NH}_3}} \times 0.10 = \sqrt{\frac{(1.7 \times 10^7) \times (8.3 \times 10^{-17})}{(0.10) \times (0.10)}} = 3.76 \times 10^{-6} \text{ mol/L} \]

Because one mole of \( \text{AgI} \) produces one mole of \( \text{I}^- \), the molar solubility of \( \text{AgI} \) is the same as the \( \text{[I}^-\text{]} \), or \( 3.8 \times 10^{-6} \text{ mol/L} \).

Before accepting this answer we need to check our assumptions. Substituting \( \text{[I}^-\text{]} \) into equation 6.41, we find that the concentration of \( \text{Ag}^+ \) is
\[\text{[Ag}^+\text{]=}\frac{\text{K}_{\text{sp}}}{\text{[I}^-\text{]}=\frac{8.3\times10^{-17}}{3.76\times10^{-6}}=2.2\times10^{-11}\text{M}]\]

Substituting the concentrations of I\(^-\) and Ag\(^+\) into the mass balance equation for iodide (equation 6.46), gives the concentration of Ag(NH\(_3\))\(_2^+\) as

\[\text{[Ag(NH}_3\text{)_2}^+\text{]=}[\text{I}^-]-[\text{Ag}^+]=3.76\times10^{-6}-2.2\times10^{-11}=3.8\times10^{-6}\text{M}]\]

Our first assumption that [Ag\(^+\)] is significantly smaller than the [Ag(NH\(_3\))\(_2^+\)] is reasonable.

Substituting the concentrations of Ag\(^+\) and Ag(NH\(_3\))\(_2^+\) into equation 6.44 and solving for \([\text{NH}_3]\), gives

\[\text{[NH}_3\text{]=}\sqrt{\frac{\text{[Ag(NH3)2}^+\text{]}\beta_2}} = \sqrt{\frac{3.8\times10^{-6}}{(2.2\times10^{-11})(1.7\times10^7)}} = 0.10\text{ M}\]

From the mass balance equation for NH\(_3\) (equation 6.44) we see that [NH\(_4^+\)] is negligible, verifying our second assumption that [NH\(_4^+\)] is significantly smaller than [NH\(_3\)]. Our third assumption that [Ag(NH\(_3\))\(_2^+\)] is significantly smaller than [NH\(_3\)] also is reasonable.

Note

Did you notice that our solution to this problem did not make use of equation 6.47, the charge balance equation? The reason for this is that we did not try to solve for the concentration of all seven species. If we need to know the complete equilibrium composition of the reaction mixture, then we would need to incorporate the charge balance equation into our solution.

Contributors

David Harvey (DePauw University)