Chapter 17 - Additional Aspects of Aqueous Equilibria

In the last chapter we talked about acid and base solutions, in particular weak acid and base solutions. That discussion was fine for laboratory work, but it falls short of describing the more general nature of solutions. Many real solutions contain several species in addition to the solute and solvent. We'll talk about three types of equilibria in this chapter: buffers, slightly soluble salts, and complex ions.

17.1 The Common Ion Effect

Consider a solution of a weak acid, say acetic acid (CH₃CO₂H, HOAc).

\[
\text{HOAc} \rightleftharpoons \text{H}^+ + \text{OAc}^- 
\]

What happens to the equilibrium if we add some NaOAc? Le Châtelier's principle tells us the equilibrium will shift left to remove some of the added ion. What is the effect on pH when this happens? There are fewer hydrogen ions present, so the pH goes up. This should come as no surprise, since we just added a base to the solution. This simple observation can help avoid mistakes when working problems. Try to write out a Le Châtelier's principle argument for the change in pH.

Ex: What is the pH of a solution that is initially 0.500 M in both HOAc and NaOAc?

\[
\begin{align*}
[\text{HOAc}]_i &= 0.500 \text{ M} \\
[\text{HOAc}]_e &= 0.500 - x \text{ M} \\
[\text{H}^+]_i &= 0 \text{ M} \\
[\text{H}^+]_e &= x \text{ M} \\
[\text{OAc}^-]_i &= 0.500 \text{ M} \\
[\text{OAc}^-]_e &= 0.500 + x \text{ M} \\
K_a &= \frac{x(0.500 + x)}{0.500 - x} = 1.8 \times 10^{-5} \\
\text{Since } 0.500 > 100K_a & \text{ we can assume x is negligible in the calculation}
\end{align*}
\]
\[ 1.8 \times 10^{-5} = \frac{x(0.500)}{0.500} \]

\[ x = 1.8 \times 10^{-5} \]

thus \([H^+]) = 1.8 \times 10^{-5} \quad \text{M} \quad \text{pH} = 4.74

This is the same pH obtained for a solution that is 0.300 \(M\) in \(\text{HOAc}\) and \(\text{NaOAc}\) (Ex. 17.1, p. 662). We will see later that, in general for a weak acid, if \([HA] = [A^-]\), then \([H^+] = K_a\).

Mixing an acid and its conjugate base (e.g. acetic acid and sodium acetate as described above) can generate these kinds of solutions or they may be generated by either adding some strong base (e.g. sodium hydroxide) to a weak acid solution or by adding a strong acid to a weak base solution. We will explore this further when we reach titrations in Section 17.3.

\[
\text{HOAc}_{(aq)} + \frac{1}{2} \text{NaOH}_{(aq)} \rightarrow \frac{1}{2} \text{HOAc}_{(aq)} + \frac{1}{2} \text{NaOAc}_{(aq)}
\]

Example 17.2 (p. 663) demonstrates the following rule: **If a solution contains both a strong acid and a weak acid, the pH is determined only by the concentration of the strong acid.** The strong acid dissociates completely and the hydrogen ions released retard the dissociation of the weak acid. This makes the weak acid a negligible contributor to the hydrogen ion concentration. It is widely, and incorrectly, believed that orange juice can cause an upset stomach because of its acidity. While many people have trouble tolerating orange juice, a calculation like that in Problem 17.2 shows that a change in pH is not the cause of the distress.

All of the discussion above applies to basic solutions as well. All you have to do is switch the word “base” for “acid” and “\(K_b\)” for “\(K_a\).”

### 17.2 Buffered Solutions

Solutions that resist a change in pH are called **buffers**. These solutions contain both a weak
acid (to consume $\text{OH}^-$) and a weak base (to consume $\text{H}^+$). Most commonly they are a conjugate acid/base pair (e.g. acetic acid/sodium acetate). They undergo small pH changes when small amounts of strong acid or base are added.

It turns out the math is a little simpler for buffered solutions, than for weak acids or bases dissolved in water. Because significant amounts of both an acid and its conjugate base are present, ionization is suppressed. Again, let’s use acetic acid/sodium acetate.

$$\text{HOAc} \rightleftharpoons \text{H}^+ + \text{OAc}^-$$

In the case of pure acetic acid: $[\text{HOAc}]_e = [\text{HOAc}]_i - x$,

$$[\text{H}^+]_e = [\text{OAc}^-]_e = x$$

In contrast, in a buffer the concentrations look like this: $[\text{HOAc}]_e = [\text{HOAc}]_i + x$

$$[\text{OAc}^-]_e = [\text{OAc}^-]_i - x$$

$$[\text{H}^+]_e = x$$

But according to Le Châtelier's principle, the addition of $\text{OAc}^-$ retards the ionization of $\text{HOAc}$. This results in an $x$ that can be neglected in both its subtraction from $[\text{HOAc}]_i$ and addition to $[\text{OAc}^-]_i$. (This may be clearer while looking at the problem on p. 10 of the Chapter 16 notes.)

The result is $[\text{HOAc}]_e = [\text{HOAc}]_i$ and $[\text{OAc}^-]_e = [\text{OAc}^-]_i$ for a buffer solution.

Consider the hypothetical acid HA: $\text{HA} \rightleftharpoons \text{H}^+ + \text{A}^-$

$$K_a = \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]}$$

and assume there is an appreciable amount of both HA and A$^-$ present in solution so we can neglect ionization.

$$K_a = \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]}$$
\[ [H^+] = K_a \frac{[HA]}{[A^-]} \]

now take the negative logarithm of each side:

\[-\log[H^+] = -\log(K_a \frac{[HA]}{[A^-]}) \]

\[ \text{pH} = -\log K_a - \log \frac{[HA]}{[A^-]} \]

\[ \text{pH} = pK_a + \log \frac{[A^-]}{[HA]} \]

In general:

\[ \text{pH} = pK_a + \log \frac{\text{base}}{\text{acid}} \]

This is called the Henderson-Hasselbach equation. It is very convenient if one works a lot of buffer problems, although it isn’t necessary. One may still work the problem as for a weak acid and I’ll work it both ways in the next example. For a pH change of 1 unit, 90% of the original weak acid or base must be consumed. (Prove this to yourself.)

One common mistake using the equation is forgetting which goes in the numerator, the acid or the base. Here’s a simple way to remember: Adding a base increases pH and pH will only increase if the base goes in the numerator.

**Addition of Strong Acids or Bases to Buffers**

It is probably best to address this subject through an example so we’ll go over one here.

Ex: A buffer solution is made containing 0.50 moles of acetic acid and 0.50 moles of sodium acetate. The volume totals 1.0 L. What is it’s pH? After adding 0.10 moles of hydroxide ion? 0.40 moles of hydroxide ion (total)?
Short method

\[
\text{[HOAc]}_i = \frac{0.50 \text{ mol}_{\text{HOAc}}}{L} = 0.50 \text{ M}
\]

\[
\text{[OAc}^-]_i = \frac{0.50 \text{ mol}_{\text{OAc}^-}}{L} = 0.50 \text{ M}
\]

\[pK_a = \log (1.8 \times 10^{-5}) = 4.74\]

a) \[\text{pH} = 4.74 + \log \frac{0.50 \text{ M}_{\text{OAc}^-}}{0.50 \text{ M}_{\text{HOAc}}} = 4.74\]

b) \[\text{mol}_{\text{HOAc}} = 0.50 \text{ mol}_{\text{HOAc}} - 0.10 \text{ mol}_{\text{OH}^-}\]

\[= 0.40 \text{ mol}\]

\[
\text{[HOAc]} = \frac{0.40 \text{ mol}_{\text{HOAc}}}{L} = 0.40 \text{ M}
\]

\[\text{mol}_{\text{OAc}^-} = 0.50 \text{ mol}_{\text{HOAc}} + 0.10 \text{ mol}_{\text{OH}^-}\]

\[= 0.60 \text{ mol}\]

\[1.8 \times 10^{-5} = \frac{(x)(0.60 + x)}{(0.40 - x)}\]

Long method

\[
\text{[HOAc]}_i = \frac{0.50 \text{ mol}_{\text{HOAc}}}{L} = 0.50 \text{ M}
\]

\[
\text{[OAc}^-]_i = \frac{0.50 \text{ mol}_{\text{OAc}^-}}{L} = 0.50 \text{ M}
\]

\[pK_a = \log (1.8 \times 10^{-5}) = 4.74\]

a) \[\text{pH} = 4.74 + \log \frac{0.50 \text{ M}_{\text{OAc}^-}}{0.50 \text{ M}_{\text{HOAc}}} = 4.74\]

b) \[\text{mol}_{\text{HOAc}} = 0.50 \text{ mol}_{\text{HOAc}} - 0.10 \text{ mol}_{\text{OH}^-}\]

\[= 0.40 \text{ mol}\]

\[
\text{[HOAc]} = \frac{0.40 \text{ mol}_{\text{HOAc}}}{L} = 0.40 \text{ M}
\]

\[\text{[OAc}^-]_e = 0.60 + x \text{ M}\]

\[1.8 \times 10^{-5} = \frac{(x)(0.60 + x)}{(0.40 - x)}\]

\[x = [\text{H}^+] = 1.2 \times 10^{-5} \text{ M}\]

\[\text{pH} = -\log(1.2 \times 10^{-5}) = 4.92\]

If no buffer had been present (i.e. pure water), the pH would have been 13.00.
c) This is worked the same as (b). The final pH is 5.69 (80% of the original acid is consumed here.)

The capacity of a buffer is the amount of strong acid or base that can be added without a significant change in pH. This definition may sound nebulous, but what constitutes “significant change” depends on the situation. For example, if blood pH changes only ±0.05 pH units (see p. 651) from its expected value a medical condition will develop. A change of 0.5 units usually results in death. In more typical chemical reactions, maintaining a pH range of 0.1 pH units is typically unnecessary, so “significant” carries a different meaning. What is always true is that the more buffering agent present in solution, the higher the buffer capacity. Thus, 1 L of a buffer solution that is 1.0 \text{ M} in both weak acid and weak base will have more capacity than 1 L of a buffer solution that is 0.1 \text{ M} in both acid and base.

17.3 Acid-Base Titrations

You should review the section on titrations at the end of Chapter 4 (p. 140) before going on. You will be doing several titrations in CHM 218 and you need to be familiar with the theory and calculations before going into the laboratory.

Recall that a titration is a procedure in which a solution of known concentration is reacted with a known volume of a solution of unknown concentration in order to measure the latter’s concentration. Historically, the end of reaction was signified with an organic dye that changed color when the reaction was complete. Today, pH meters allow the endpoints to be determined with greater precision.

**Strong Acid-Strong Base Titrations**

Consider the titration of a known concentration of the strong base NaOH (e.g. 0.10 \text{ M}) into a
solution of an unknown concentration of the strong acid HCl. The most convenient method of following a titration is to make a plot of the volume of added titrant vs. pH. Initially, the pH of the initial acid solution is quite low (for a 0.10 M HCl solution, pH = 1.00). The pH will increase slowly at the beginning. When the number of added moles of base begins to approach the number of moles of acid in the unknown solution the rate of pH increase will accelerate. Typically, within a few tenths of a milliliter of the equivalence point pH will change several units. (The equivalence point occurs when the moles of titrant equal the moles of unknown.) The pH will continue to increase rapidly for a short distance before beginning to level off below the pH of the base solution (remember it is diluted by the water in the acid solution so the final solution will never achieve a pH of 13.00). This experiment is shown graphically below.

Before going further, here’s a question to think about: How do we know when the equivalence point occurs? In real life, we don’t calculate the curve, an experiment is performed in which we measure pH as a function of added acid or base. Today we use a pH meter, but that wasn’t available a hundred years ago. Before pH meters (and even today when only the endpoint is needed) organic dyes (indicators) were used to signal when the titration was complete. These dyes dramatically changed color on going from a protonated to deprotonated form. For example, phenolphthalein changes from colorless ($C_{20}H_{14}O_3$) to bright pink ($C_{20}H_{13}O_3^-$) at a pH of 8.2 – 10. It is interesting to note that phenolphthalein is used to determine the endpoints of strong acid
and base titrations even though their endpoints occur at pH = 7. Here are two questions for you:

1. Why is it all right to use phenolphthalein here? and
2. One hundred years ago, how did they know to use phenolphthalein instead of methyl orange (pH change from 3.2 – 4.4 red = acid form, yellow = base form) for strong acid/base titrations. Find the answers below.

We should now calculate some of the points on the displayed titration curve (Figure 17.6, p. 672). The initial point is simply the pH of a 0.100 M hydrochloric acid solution. Let’s look at the addition of 10 mL of 0.100 M sodium hydroxide solution and 49.9 mL. Try calculating the pH after adding 49.99 and 49.99 mL of the sodium hydroxide solution on your own.

We begin by determining the number of moles of acid in the original solution:

\[
mol_{H^+}(\text{initial}) = (0.0500 \text{ L}_{\text{soln}}) \left( \frac{0.100 \text{ mol}_{\text{HCl}}}{L_{\text{soln}}} \right) \left( \frac{1 \text{ mol}_{H^+}}{1 \text{ mol}_{\text{HCl}}} \right) = 0.00500 \text{ mol}_{H^+}
\]

Now write out the balanced equation and determine the number of moles of base added:

\[
\text{HCl}_{(aq)} + \text{NaOH}_{(aq)} \rightarrow \text{H}_2\text{O}_{(l)} + \text{NaCl}_{(aq)}
\]

\[
mol_{\text{OH}^-} = (0.0100 \text{ L}_{\text{soln}}) \left( \frac{0.100 \text{ mol}_{\text{NaOH}}}{L_{\text{soln}}} \right) \left( \frac{1 \text{ mol}_{\text{OH}^-}}{1 \text{ mol}_{\text{NaOH}}} \right) = 0.00100 \text{ mol}_{\text{OH}^-}
\]

The amount of acid remaining in solution equals the difference between these numbers, then calculate concentration, and finally pH.

\[
mol_{H^+}(\text{end}) = 0.00500 \text{ mol}_{H^+} - 0.00100 \text{ mol}_{\text{OH}^-} = 0.00400 \text{ mol}_{H^+}
\]

\[
[H^+] = \frac{0.00400 \text{ mol}_{H^+}}{0.0600 \text{ L}_{\text{soln}}} = 0.0667 \text{ M}
\]

\[
pH = -\log(0.0667) = 1.18
\]

In an exactly analogous manner, the pH of the solution after adding 49.9 mL of sodium hydroxide solution is 4.00. It might strike you as really odd that the pH increases so dramatically on addition of such small amounts. After all, the first 10 mL of base increases pH by 0.18 units,
but the 0.9 mL increase from 49.0 mL to 49.9 mL results in a 1.00 unit increase (see book for the 49 mL value). Remember the pH scale is logarithmic. As the titration approaches equivalence, [H⁺] approaches zero. Thus, very small amounts of base cause a large percentage change in remaining acid concentration.

Before answering the two questions raised on the previous page, we need to go over a definition. The endpoint of a titration is the volume of titrant which causes the indicator to change color. In principle, this can lead to a difference between the volume read at the endpoint and that required for the equivalence point. If you repeat the calculations above for 50.001 mL and 50.01 mL of added base you’ll see that it takes a negligibly small amount of base to trigger the indicator and so we can use the endpoint volume as the equivalence point volume. Phenolphthalein works because even though it doesn’t change color until pH ≅ 8.5, the titration curve is almost vertical here. Only a small fraction of a drop moves pH from 7 to 8.5. Methyl orange, on the other, hand will require several mL of titrant to effect the color change. One requirement for an indicator is that the color change occurs rapidly. They knew that the dyes worked because they could use authentic samples of an acid and its conjugate base to track color changes.

**Weak Acid/Base-Strong Base/Acid Titrations**

There are two significant differences between these titrations and those where both components are strong. The first is the appearance of the curve. Because the acid or base being titrated is weak, the vertical portion of the curve is compressed somewhat (see below). The second difference is that the final pH is lower than 7.00 for a strong acid/weak base titration and higher than 7.00 for a strong base/weak acid titration. This is because the products of a strong base/weak acid titration are water and the conjugate base of the weak acid. Remember that this
conjugate base will also be a weak base. Your book uses the word neutralization here. In this context, neutralizing the weak acid means completely removing its proton, not that the solution has a neutral pH. The calculations are more involved because one must determine the equilibrium value each time. Fortunately, the Henderson-Hasselbach equation can be used for these titrations.

Finally, the weaker the acid or base, the less pronounced is the break in the titration curve until at a $K_a$ or $K_b$ of much smaller than $10^{-7}$, it becomes difficult to see where it occurs (see Figure 17.11, p. 658). Everything said so far about weak acids applies in reverse to weak bases.

Read “Titrations of Polyprotic Acids” on your own.

17.4 Solubility Equilibria

So far, all of the equilibria we have discussed in the past two chapters have been homogeneous equilibria. We will now explore heterogeneous equilibria. Recall that all ionic compounds are strong electrolytes, but some have low solubilities. These slightly soluble salts establish an equilibrium with the solution. For the most of the rest of this section we will use magnesium hydroxide as an example.

\[ \text{Mg(OH)}_2 (s) \rightleftharpoons \text{Mg}^{2+} (aq) + 2 \text{OH}^- (aq) \]
The equilibrium constant for this type of equilibrium bears a special name, the solubility product constant, $K_{sp}$. In this case:

$$K_{sp} = [\text{Mg}^{2+}][\text{OH}^-]^2$$

Remember the parent magnesium hydroxide does not appear in the equilibrium because it is in a different phase (see Chapter 15.3). Unlike acid and base solutions where everything is soluble, $K_{sp}$ is used to determine the solubility of the salt under a variety of conditions. We’ll look at several over the next few pages. At this point it is important for you to recall that solubility refers to the mass of solute that will dissolve in a given volume of solvent (frequently g/L). Molar solubility is molarity, $M$. Solubility and the solubility product constant are related, but not necessarily linearly. Thus, it is incorrect to say that because the $K_{sp}$ of some salt is smaller than that of another, it is necessarily less soluble. We’ll come back to this shortly.

Ex. What is the $K_{sp}$ of magnesium hydroxide if a saturated solution contains $1.65 \times 10^{-4}$ mol of $\text{Mg}^{2+}$ ions per liter of solution?

$$K_{sp} = [\text{Mg}^{2+}][\text{OH}^-]^2$$

if $$[\text{Mg}^{2+}] = \frac{1.65 \times 10^{-4} \text{ mol M}_{\text{Mg}^{2+}}}{1.00 \text{ L}} = 1.65 \times 10^{-4} \text{ M}$$

then $$[\text{OH}^-] = (1.65 \times 10^{-4} \text{ mol M}_{\text{Mg}^{2+}}) \left(\frac{1 \text{ mol M}_{\text{Mg(OH)2}}}{1 \text{ mol M}_{\text{Mg}^{2+}}}\right) \left(\frac{2 \text{ mol OH}^-}{1 \text{ mol M}_{\text{Mg(OH)2}}}\right) \left(\frac{1}{1.00 \text{ L}}\right) = 3.30 \times 10^{-4} \text{ M}$$

$$K_{sp} = (1.65 \times 10^{-4})(3.30 \times 10^{-4})^2 = 1.80 \times 10^{-11}$$

Now let’s look at the same problem in reverse.

Ex. What is the molar solubility of a saturated magnesium hydroxide solution?

$$K_{sp} = [\text{Mg}^{2+}][\text{OH}^-]^2 = 1.80 \times 10^{-11}$$
Let $[\text{Mg}^{2+}] = x$, then $[\text{OH}^-] = 2x$ (from stoichiometry)

$x(2x)^2 = 1.80 \times 10^{-11}$

$4x^3 = 1.80 \times 10^{-11}$

$x = 1.65 \times 10^{-4}$

$[\text{Mg(OH)}_2] = \frac{1.65 \times 10^{-4}}{\text{mol}_\text{Mg}^2+} \cdot \frac{1}{\text{mol}_\text{Mg}^2+} = 1.65 \times 10^{-4} M$

It is a very common mistake to forget to multiply the hydroxide “x” by 2 or to square the “2x”, but it there is twice as much hydroxide as magnesium ion and it must be taken account of in both places.

Ex. What is the solubility of magnesium hydroxide?

$\text{solubility} = \frac{1.65 \times 10^{-4} \text{mol}_\text{Mg(OH)}_2}{\text{L}_\text{soln}} \cdot \frac{58.32 \text{g}_\text{Mg(OH)}_2}{\text{mol}_\text{Mg(OH)}_2} = 0.00962 \text{ g/L}$

17.5 Factors That Affect Solubility

There are a number of factors that affect the solubility of slightly soluble salts. They can range from a simple application of Le Châtelier’s principle to properties inherent to the salt in question. We begin with the first case.

The Common Ion Effect

It has long been known (indeed it predates Le Châtelier’s principle) that adding a salt that contains an ion present in the slightly soluble salt depresses the salt’s solubility. This is just what you’d expect based on Le Châtelier’s principle. (Skip “A Closer Look” on p. 682.)

Ex. What is the molar solubility of magnesium hydroxide in a solution which is 1.0 $M$ in magnesium chloride?
\[ [\text{Mg}^{2+}] = 1.0 + x \, M \quad [\text{OH}^-] = 2x \, M \]

\[ 1.8 \times 10^{-11} = (1.0 + x)(2x)^2 \]

We can now make an assumption similar to that done for weak acid/base equilibria.

Since \( 1.0 \gg K_{\text{sp}} \), we will assume \( x \) is negligible in the calculation.

\[ 1.8 \times 10^{-11} = (1.0)(2x)^2 \]

\( x = 2.1 \times 10^{-6} \) (the assumption is correct)

\[ [\text{Mg(OH)}_2] = \left( \frac{2.1 \times 10^{-6} \, \text{mol}_{\text{Mg}^{2+}}}{\text{L}_{\text{soln}}} \right) \left( \frac{1 \, \text{mol}_{\text{Mg(OH)}_2}}{1 \, \text{mol}_{\text{Mg}^{2+}}} \right) = 2.1 \times 10^{-6} \, M \]

This is much less than the \( 1.65 \times 10^{-4} \, M \) found when magnesium hydroxide is dissolved in pure water.

**Solubility and pH**

Now in addition to being a salt, magnesium hydroxide is also a base. Therefore, you’d expect that if we raised the pH of the water we were dissolving the \( \text{Mg(OH)}_2 \) into, the latter would be less soluble (another Le Châtelier’s principle effect). As a reference point, saturated \( \text{Mg(OH)}_2 \) has a pH of 10.52.

**Ex.** What is the molar solubility of magnesium hydroxide at pH = 11.00? at pH = 10.00?

pH = 11.00 \( \Rightarrow \) pOH = 14.00 – 11.00 = 3.00 \( \Rightarrow \) \([\text{OH}^-]\) = antilog(-3.00) = 1.00 \( \times 10^{-3} \, M\)

\[ 1.8 \times 10^{-11} = [\text{Mg}^{2+}](1.00 \times 10^{-3})^2 \]

\[ [\text{Mg}^{2+}] = 1.8 \times 10^{-5} \, M \]

\[ [\text{Mg(OH)}_2] = \left( \frac{1.8 \times 10^{-5} \, \text{mol}_{\text{Mg}^{2+}}}{\text{L}_{\text{soln}}} \right) \left( \frac{1 \, \text{mol}_{\text{Mg(OH)}_2}}{1 \, \text{mol}_{\text{Mg}^{2+}}} \right) = 1.8 \times 10^{-5} \, M \]

pH = 10.00 \( \Rightarrow \) pOH = 14.00 – 10.00 = 4.00 \( \Rightarrow \) \([\text{OH}^-]\) = antilog(-4.00) = 1.00 \( \times 10^{-4} \, M\)
1.8 \times 10^{-11} = [\text{Mg}^{2+}](1.00 \times 10^{-4})^2

[\text{Mg}^{2+}] = 1.8 \times 10^{-3} \text{ M}

\[ [\text{Mg(OH)}_2] = \left( \frac{1.8 \times 10^{-3} \text{ mol}_{\text{Mg}^{2+}}}{L_{\text{soln}}} \right) \left( \frac{1 \text{ mol}_{\text{Mg(OH)}_2}}{1 \text{ mol}_{\text{Mg}^{2+}}} \right) = 1.8 \times 10^{-3} \text{ M} \]

This calculation shows us that the solubility of magnesium hydroxide drops changes rapidly changing pH. (Not surprisingly, lowering the pH raises the solubility of Mg(OH)$_2$.)

pH can still have an effect even when the common ion effect plays no role. Consider the solubility of silver(I) cyanide in acidic solution.

\[
\text{AgCN}_s \rightleftharpoons \text{Ag}^{+}_{(aq)} + \text{CN}^-_{(aq)} \quad K_{sp} = 1.2 \times 10^{-16}
\]

\[
\text{H}^+_{(aq)} + \text{CN}^-_{(aq)} \rightleftharpoons \text{HCN}_{(aq)} \quad K = 2.0 \times 10^9 \quad (\text{this is } 1/K_a)
\]

\[
\text{AgCN}_s + \text{H}^+_{(aq)} \rightleftharpoons \text{Ag}^{+}_{(aq)} + \text{HCN}_{(aq)} \quad K = 2.4 \times 10^{-7}
\]

\[
2.4 \times 10^{-7} = \frac{[\text{Ag}^+] [\text{HCN}]}{[\text{H}^+]}\]

We see from the above equilibrium expression that silver(I) cyanide becomes more soluble as pH decreases. This is reasonable because there are two different species competing to bind with the cyanide ion: Ag$^+$ and H$^+$. Silver(I) ions bind more strongly than do hydrogen ions, but as the concentration of hydrogen ions increases, they tie up more and more of the cyanide ions by weight of numbers.

In general, the solubilities of slightly soluble salts that contain the conjugate base of a weak acid increases as pH decreases (the hydrogen ions convert some of the anion to the weak acid).

Formation of Complex Ions

We learned in Chapter 16 that metal ions are Lewis acids. Water, halide ions, cyanide ions, and ammonia are just a few of many Lewis bases. Different metal ions show different levels of
affinity for different Lewis bases. In the presence of halide ions, silver(I) forms a very stable lattice and precipitates from solution as AgX (X = F\(^-\), Cl\(^-\), Br\(^-\), I\(^-\); we’ll discuss this more in the next section). In contrast, in the presence of ammonia, silver(I) quickly binds to two ammonia molecules to form a “complex ion.” The term “complex” refers to the contrast with the “simple” elemental ion, Ag\(^+\). A complex ion consists of a metal ion to which more than one Lewis base is covalently bound.

\[
\text{Ag}^{+}(\text{aq}) + 2 \text{NH}_3 \rightleftharpoons \text{Ag(NH}_3)_2^{+}(\text{aq})
\]

\[
K_f = \frac{[\text{Ag(NH}_3)_2^{+}]}{[\text{Ag}^{+}][\text{NH}_3]^2} = 1.7 \times 10^7
\]

where \(K_f\) is the “formation constant.” Formation constants can be quite large as can be seen in Table 17.1 (p. 687) meaning that on mixing a soluble salt with the appropriate Lewis base, the complex ion forms readily. Such equilibria can also be used to dissolve slightly soluble salts.

Ex: How much silver(I) chloride will dissolve in 1.0 L of a solution that is 0.10 \(M\) in NH\(_3\) at equilibrium? What is the free silver(I) ion concentration?

\[
\text{AgCl} (\text{s}) \rightleftharpoons \text{Ag}^{+}(\text{aq}) + \text{Cl}^{-}(\text{aq}) \quad K_{sp} = 1.8 \times 10^{-10}
\]

\[
\text{Ag}^{+}(\text{aq}) + 2 \text{NH}_3 \rightleftharpoons \text{Ag(NH}_3)_2^{+}(\text{aq}) \quad K_f = 1.7 \times 10^7
\]

\[
\text{AgCl} (s) + 2 \text{NH}_3 \rightleftharpoons \text{Ag(NH}_3)_2^{+}(\text{aq}) + \text{Cl}^{-}(\text{aq}) \quad K = 3.1 \times 10^{-3}
\]

a) \(\text{mol}_{\text{AgCl}}(\text{dissolved}) = \text{mol}_{\text{Cl}^{-}}(\text{in solution})\)

\[
K = 3.1 \times 10^{-3} = \frac{[\text{Ag(NH}_3)_2^{+}][\text{Cl}^{-}]}{[\text{NH}_3]^2}
\]

Let \([\text{Ag(NH}_3)_2^{+}]_e = [\text{Cl}^{-}]_e = x\)

\[
3.1 \times 10^{-3} = \frac{x^2}{(0.10)^2}
\]

We use Cl\(^-\) because while most of the Ag\(^+\) is bound in the complex, some exists as free ion.
\[ x = 5.6 \times 10^{-3} \]

\[
\text{mass}_{\text{AgCl}} = (1.0 \text{ L}_{\text{soln}}) \left( \frac{5.6 \times 10^{-3} \text{ mol}_{\text{Cl}^-}}{1 \text{ mol}_{\text{AgCl}}} \right) \left( \frac{143.3 \text{ g}_{\text{AgCl}}}{1 \text{ mol}_{\text{AgCl}}} \right) = 0.80 \text{ g}_{\text{AgCl}}
\]

b) \[ K_{\text{sp}} = 1.8 \times 10^{-10} = [\text{Ag}^+](5.6 \times 10^{-3}) \]

\[ [\text{Ag}^+] = 3.2 \times 10^{-8} \text{ M} \]

Saturated silver(I) chloride solution has \([\text{Ag}^+] = 1.3 \times 10^{-5} \text{ M}\), so 99.8% of the silver(I) ion released into solution is tied up as a complex ion.

**Amphoterism**

Many metal hydroxides and oxides are slightly soluble in neutral water, but are surprisingly soluble in both acidic and basic solutions. These substances are called *amphoteric*. Since they are metal hydroxides and oxides their solubility in acidic solutions probably comes as no surprise. Hydrogen ions protonate the hydroxide and oxide ions to water, leaving the metal ions free in solution.

\[
\text{MOH} + \text{H}^+ \rightarrow \text{M}^+ + \text{H}_2\text{O}
\]

\[
\text{M}_2\text{O} + 2 \text{H}^+ \rightarrow 2 \text{M}^+ + \text{H}_2\text{O}
\]

In basic solution, one or more hydroxide ions acts as a Lewis base and coordinates to the metal ion forming a soluble complex ion.

In general:

\[
\text{M(OH)}_n(\text{s}) + \text{OH}^-_{(aq)} \rightleftharpoons \text{M(OH)}_{n+1}^{-}_{(aq)}
\]

So why does this happen and why to only certain metal oxides and hydroxides? There are two parts to this answer: one electronic, the other structural. First, for a substance to be amphoteric, the metal ion must bind to oxide/hydroxide much more strongly than to water. Generally the interaction of oxides and hydroxides will be stronger because of electrostatic
attraction. If the cation interacts with water at a comparable level as oxide/hydroxide, the compound will dissolve (e.g. NaOH). Metal ions with large charges or small sizes are more apt to yield amphoteric oxides and hydroxides. The other feature is structural. If metal ions develop Lewis acid/base interactions with neighboring ions, they can crosslink, making a large structure that is difficult to dissolve. Oxide and hydroxide have multiple lone pairs of electrons. It can now bind to several metal ions (i.e. crosslinking). When a solution hydroxide replaces the bridging interactions, monomeric complexes form and they are generally soluble.

17.6 Precipitation and Separation of Ions

Since some salts are only slightly soluble in water, it serves to reason that if one mixes solutions containing ions that are components of a slightly soluble salt, there is a good chance that the salt will precipitate from solution. Going back to Chapter 15, we know that if $Q > K_{sp}$ a salt will precipitate (more concentrated solutions will yield a larger value and higher probability of precipitation.) This feature has important practical considerations. Many expensive metals are isolated by precipitation of their salts. We’ll go over a couple of examples here.

Ex: If 25.0 mL of a $2.0 \times 10^{-3} \ M$ magnesium chloride solution mixes with 15.0 mL of a $1.0 \times 10^{-3} \ M$ barium hydroxide solution, will a precipitate form?

We first need the concentrations of the magnesium and hydroxide ions.

$$V_T = 25.0 \text{ mL} + 15.0 \text{ mL} = 40.0 \text{ mL (or 0.0400 L)}$$

$$\text{mol}_{\text{Mg}^{2+}} = (0.0250 \text{ L soln}) \left( \frac{2.0 \times 10^{-3} \text{ mol}_{\text{MgCl}_2}}{\text{L soln}} \right) \left( \frac{1 \text{ mol}_{\text{Mg}^{2+}}}{1 \text{ mol}_{\text{MgCl}_2}} \right) = 5.0 \times 10^{-5} \text{ mol}_{\text{Mg}^{2+}}$$

$$[\text{Mg}^{2+}] = \frac{5.0 \times 10^{-5} \text{ mol}_{\text{Mg}^{2+}}}{0.0400 \text{ L soln}} = 1.25 \times 10^{-3} \text{ M}$$

It is important to remember that you must add the volumes of the solutions and recalculate the concentrations.
\[ \text{mol}_{\text{OH}^-} = (0.0150 \text{ L}_{\text{soln}}) \left( \frac{1.0 \times 10^{-3} \text{ mol}_{\text{Ba(OH)2}}}{\text{L}_{\text{soln}}} \right) \left( \frac{2 \text{ mol}_{\text{OH}^-}}{1 \text{ mol}_{\text{Ba(OH)2}}} \right) = 3.0 \times 10^{-5} \text{ mol}_{\text{OH}^-} \]

\[ [\text{OH}^-] = \frac{3.0 \times 10^{-5} \text{ mol}_{\text{Mg}^2+}}{0.0400 \text{ L}_{\text{soln}}} = 7.5 \times 10^{-4} \text{ M} \]

\[ Q = [\text{Mg}^{2+}][\text{OH}^-]^2 = (1.25 \times 10^{-3})(7.5 \times 10^{-4})^2 = 7.0 \times 10^{-10} \]

Since \( Q > K_{\text{sp}} \), magnesium hydroxide does precipitate. It will continue to do so, until the ion concentrations drop to a concentration where \( Q = K_{\text{sp}} \).

Ex. Suppose you had a solution that was 0.10 M each in copper(I), gold(I), and silver(I) ions. Could they be efficiently separated and how?

The solubility product constants of their chlorides are \( K_{\text{sp}(\text{CuCl})} = 1.2 \times 10^{-6}, K_{\text{sp}(\text{AgCl})} = 1.8 \times 10^{-10}, K_{\text{sp}(\text{AuCl})} = 2.0 \times 10^{-13} \). These are each separated by 3–4 orders of magnitude and are worth a try.

The general equilibrium is: \( \text{MCl(s)} \rightleftharpoons \text{M}^{+}(\text{aq}) + \text{Cl}^- (\text{aq}) \quad K_{\text{sp}} = [\text{M}^+][\text{Cl}^-] \)

If \([\text{M}^+][\text{Cl}^-] < K_{\text{sp}}\) for a compound then no salt will precipitate. We want to add chloride ion to the solution until just before the second ion begins to precipitate. Gold(I) chloride will precipitate first (all solubility product formulae are qualitatively the same and AuCl has the smallest \( K_{\text{sp}} \)). Thus, we need to find out how much chloride ion will just begin to precipitate silver(I) chloride.

\[ \text{AgCl: } (0.10)[\text{Cl}^-] = 1.8 \times 10^{-10} \]

\[ [\text{Cl}^-] = 1.8 \times 10^{-9} \text{ M} \]

As long as \([\text{Cl}^-] > 1.8 \times 10^{-9} \text{ M}\), no silver(I) chloride will precipitate. But, how much of the
gold will have been removed from solution at this point.

\[ \text{AuCl: } [\text{Au}^+] (1.8 \times 10^{-9}) = 2.0 \times 10^{-13} \]

\[ [\text{Au}^+] = 1.4 \times 10^{-4} M \]

Recall the initial concentration of gold(I) was 0.10 \( M \), so 99.9% of the gold is removed from solution prior to the commencement of silver(I) chloride precipitation.

Likewise for copper(I) chloride, \([\text{Cl}^-] = 1.2 \times 10^{-5} M\) and \([\text{Ag}^+] = 1.5 \times 10^{-5} M\), so 99.98% of the silver precipitates before copper(I) chloride begins to come out of solution. Thus, this is a pretty good method of separating coinage metal ions from solution and from each other.

17.7 Qualitative Analysis for Metallic Elements

This topic was first introduced in Section 4.2, p. 118, which provides a short review. Frequently we are more interested in whether a particular ion is present in some minimum amount than exactly how much is there. For this purpose a series of tests has been developed. The process of determining if a particular ion is present in a solution is called qualitative analysis. Figure 17.22 gives a full set of rules if you want to learn them. You must learn the rules below. To use them, you would add one of the anions in (2). If a precipitate formed you would know \( \text{Ag}^+, \text{Pb}^{2+}, \) or \( \text{Hg}_2^{2+} \) was present. If no precipitate formed, then add one of the anions from (3) and so forth. These rules include a few oversimplifications, but they will work in most situations and are easier to remember than the more comprehensive list in the book.

1) All ionic compounds containing alkali metal cations, \( \text{NH}_4^+, \text{NO}_3^- \), and acetate are soluble.

2) \( \text{Cl}^-, \text{Br}^-, \) and \( \text{I}^- \) salts are soluble (except with \( \text{Ag}^+, \text{Pb}^{2+}, \text{Hg}_2^{2+} \)).

3) Except for (1) carbonate and phosphate salts are insoluble.
4) Except for (1) and Group IIA, sulfides and hydroxides are insoluble.

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