

CHAPTER NINETEEN

Ionic Equilibria in Aqueous Systems

19.1 EQUILIBRIA OF ACID-BASE BUFFER SYSTEMS

- An **acid-base buffer** is a solution that lessens the impact on pH from the addition of acid or base.
- A buffer solution contains an acidic component that can react with the added OH^- ion and a basic component that can react with added H_3O^+ ion.
- Most commonly, the components of a buffer are the conjugate acid-base pair of a weak acid, for example, a mixture of acetic acid (CH_3COOH) and acetate ion (CH_3COO^-).

Figure 19.1 shows that a small amount of H_3O^+ or OH^- added to an unbuffered solution (or just water) changes the pH by several units. This change is several orders of magnitude larger than the change that results from the same addition to a buffered solution, shown in Figure 19.2.

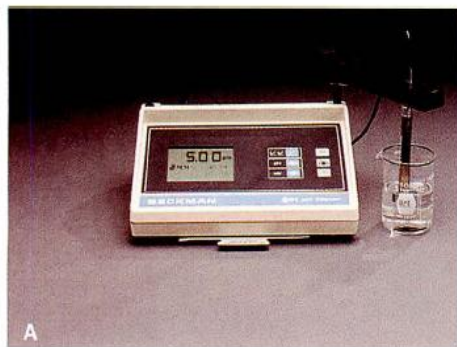


Figure 19.1 The effect of addition of acid or base to an unbuffered solution. **A**, A 100-mL sample of dilute HCl is adjusted to pH 5.00.

B, After the addition of 1 mL of 1 M HCl (left) or of 1 M NaOH (right), the pH changes by several units.

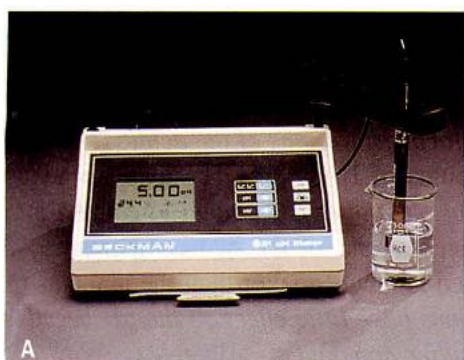


Figure 19.2 The effect of addition of acid or base to a buffered solution. **A**, A 100-mL sample of a buffered solution, made by mixing 1 M CH_3COOH with 1 M CH_3COONa , is adjusted to pH 5.00.

B, After the addition of 1 mL of 1 M HCl (left) or of 1 M NaOH (right), the pH change is negligibly small. Compare these changes with those in Figure 19.1.

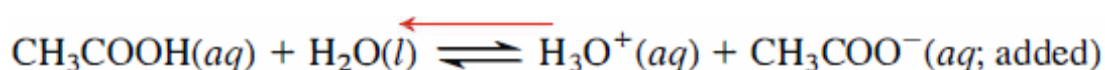
How a Buffer Works: The Common-Ion Effect

- Buffers work through a phenomenon known as **the common-ion effect**.

As an example of this effect, consider acetic acid which dissociates only slightly in water:



From Le Chatelier's principle, if some CH_3COO^- ion is added (from the soluble sodium acetate), the equilibrium position shifts to the left; thus, $[\text{H}_3\text{O}^+]$ decreases:



Similarly, if we dissolve acetic acid in a sodium acetate solution, the acetate ion already present in the solution acts to suppress as much acid from dissociating,

which lowers $[\text{H}_3\text{O}^+]$. Acetate ion is called the **common ion** in this case because it is "common" to both the acetic acid and sodium acetate solutions.

- The common-ion effect occurs when a given ion is added to an equilibrium mixture that already contains that ion, and the position of equilibrium shifts away from forming more of it.

Table 19.1 The Effect of Added Acetate Ion on the Dissociation of Acetic Acid

$[\text{CH}_3\text{COOH}]_{\text{init}}$	$[\text{CH}_3\text{COO}^-]_{\text{added}}$	% Dissociation*	pH
0.10	0.00	1.3	2.89
0.10	0.050	0.036	4.44
0.10	0.10	0.018	4.74
0.10	0.15	0.012	4.92

$$*\% \text{ Dissociation} = \frac{[\text{CH}_3\text{COOH}]_{\text{dissoc}}}{[\text{CH}_3\text{COOH}]_{\text{init}}} \times 100$$

The Essential Feature of a Buffer

How does a buffer solution resist pH changes when H_3O^+ or OH^- is added?

- The essential feature of a buffer is that it consists of high concentrations of the acidic (HA) and basic (A^-) components. When small amounts of H_3O^+ or OH^- ions are added to the buffer, they cause a small amount of one buffer component to convert into the other, which changes the relative concentrations of the two components.
- As long as the amount of H_3O^+ or OH^- added is much smaller than the amounts of HA and A^- present originally, the added ions have little effect on the pH because they are consumed by one or the other buffer component: a large excess of A^- ions react with any added H_3O^+ , and a large excess of HA molecules react with any added OH^- .

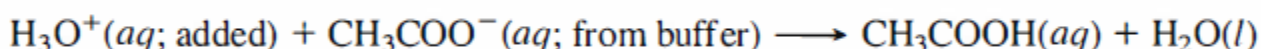
Consider a buffer of CH_3COOH and CH_3COO^- . The expression for HA dissociation at equilibrium is:

$$K_a = \frac{[\text{CH}_3\text{COO}^-][\text{H}_3\text{O}^+]}{[\text{CH}_3\text{COOH}]}$$

$$[\text{H}_3\text{O}^+] = K_a \times \frac{[\text{CH}_3\text{COOH}]}{[\text{CH}_3\text{COO}^-]}$$

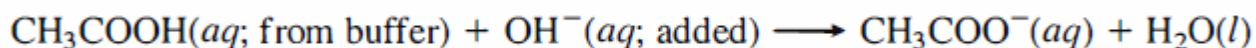
Note that because K_a is constant, the $[\text{H}_3\text{O}^+]$ of the solution depends directly on the buffer-component concentration ratio, $[\text{CH}_3\text{COOH}]/[\text{CH}_3\text{COO}^-]$.

- When we add a small amount of strong acid:



As a result, $[\text{CH}_3\text{COO}^-]$ goes down by that amount and $[\text{CH}_3\text{COOH}]$ goes up by that amount.

- Adding a small amount of strong base produces the opposite result:



The buffer-component concentration ratio decreases, which decreases $[\text{H}_3\text{O}^+]$, but once again, the change is very slight.

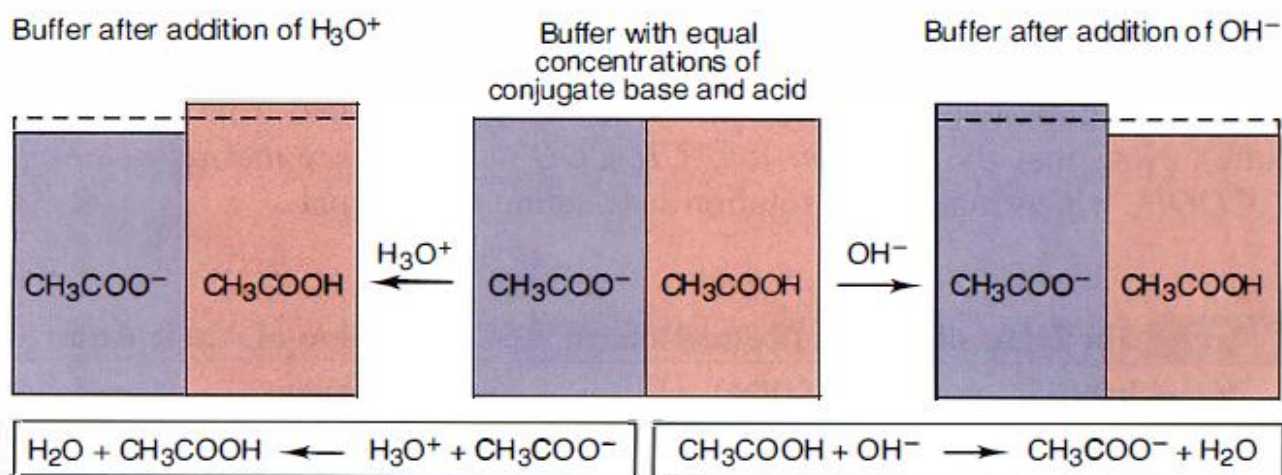


Figure 19.3 How a buffer works. A buffer consists of high concentrations of a conjugate acid-base pair, in this case, acetic acid (CH_3COOH) and acetate ion (CH_3COO^-). When a small amount of H_3O^+ is added (*left*), that same amount of CH_3COO^- combines with it, which increases the amount of CH_3COOH slightly. Similarly, when a small amount of OH^- is added (*right*), that amount of CH_3COOH combines with it, which increases the amount of CH_3COO^- slightly. In both cases, the relative changes in amounts of the buffer components are small, so their concentration ratio, and therefore the pH, changes very little.

SAMPLE PROBLEM 19.1 Calculating the Effect of Added H_3O^+ or OH^- on Buffer pH

Problem Calculate the pH:

(a) Of a buffer solution consisting of 0.50 M CH_3COOH and 0.50 M CH_3COONa

(b) After adding 0.020 mol of solid NaOH to 1.0 L of the buffer solution in part (a)

(c) After adding 0.020 mol of HCl to 1.0 L of the buffer solution in part (a)

K_a of $\text{CH}_3\text{COOH} = 1.8 \times 10^{-5}$. (Assume the additions cause negligible volume changes.)

Plan In each case, we know, or can find, $[\text{CH}_3\text{COOH}]_{\text{init}}$ and $[\text{CH}_3\text{COO}^-]_{\text{init}}$ and the K_a of CH_3COOH (1.8×10^{-5}), and we need to find $[\text{H}_3\text{O}^+]$ at equilibrium and convert it to pH. In (a), we use the given concentrations of buffer components (each 0.50 M) as the initial values. As in earlier problems, we assume that x , the $[\text{CH}_3\text{COOH}]$ that dissociates, which equals $[\text{H}_3\text{O}^+]$, is so small relative to $[\text{CH}_3\text{COOH}]_{\text{init}}$ that it can be neglected. We set up a reaction table, solve for x , and check the assumption. In (b) and (c), we assume that the added OH^- or H_3O^+ reacts completely with the buffer components to yield new $[\text{CH}_3\text{COOH}]_{\text{init}}$ and $[\text{CH}_3\text{COO}^-]_{\text{init}}$, which then dissociate to an unknown extent. We set up two reaction tables. The first summarizes the stoichiometry of adding strong base (0.020 mol) or acid (0.020 mol). The second summarizes the dissociation of the new HA concentrations, so we proceed as in part (a) to find the new $[\text{H}_3\text{O}^+]$.

Solution (a) The original pH: $[\text{H}_3\text{O}^+]$ in the original buffer.

Setting up a reaction table with $x = [\text{CH}_3\text{COOH}]_{\text{dissoc}} = [\text{H}_3\text{O}^+]$ (as in Chapter 18, we assume that $[\text{H}_3\text{O}^+]$ from H_2O is negligible and disregard it):

Concentration (M)	$\text{CH}_3\text{COOH}(aq)$	+	$\text{H}_2\text{O}(l)$	$\rightleftharpoons$	$\text{CH}_3\text{COO}^-(aq)$	+	$\text{H}_3\text{O}^+(aq)$
Initial	0.50		—		0.50		0
Change	$-x$		—		$+x$		$+x$
Equilibrium	$0.50 - x$		—		$0.50 + x$		x

Making the assumption and finding the equilibrium $[\text{CH}_3\text{COOH}]$ and $[\text{CH}_3\text{COO}^-]$: With K_a small, x is small, so we assume

$$[\text{CH}_3\text{COOH}] = 0.50 M - x \approx 0.50 M \quad \text{and} \quad [\text{CH}_3\text{COO}^-] = 0.50 M + x \approx 0.50 M$$

Solving for x ($[\text{H}_3\text{O}^+]$ at equilibrium):

$$x = [\text{H}_3\text{O}^+] = K_a \times \frac{[\text{CH}_3\text{COOH}]}{[\text{CH}_3\text{COO}^-]} \approx (1.8 \times 10^{-5}) \times \frac{0.50}{0.50} = 1.8 \times 10^{-5} M$$

Checking the assumption:

$$\frac{1.8 \times 10^{-5} M}{0.50 M} \times 100 = 3.6 \times 10^{-3} \% < 5\%$$

The assumption is justified, and we will use the same assumption in parts (b) and (c).

Calculating pH:

$$\text{pH} = -\log [\text{H}_3\text{O}^+] = -\log (1.8 \times 10^{-5}) = 4.74$$

(b) The pH after adding base (0.020 mol of NaOH to 1.0 L of buffer). Finding $[\text{OH}^-]_{\text{added}}$:

$$[\text{OH}^-]_{\text{added}} = \frac{0.020 \text{ mol OH}^-}{1.0 \text{ L soln}} = 0.020 \text{ M OH}^-$$

Setting up a reaction table for the *stoichiometry* of adding OH^- to CH_3COOH :

Concentration (M)	$\text{CH}_3\text{COOH(aq)}$	+	$\text{OH}^-(\text{aq})$	$\longrightarrow$	$\text{CH}_3\text{COO}^-(\text{aq})$	+	$\text{H}_2\text{O(aq)}$
Before addition	0.50		—		0.50		—
Addition	—		0.020		—		—
After addition	0.48		0		0.52		—

Setting up a reaction table for the *acid dissociation*, using these new initial concentrations. As in part (a), $x = [\text{CH}_3\text{COOH}]_{\text{dissoc}} = [\text{H}_3\text{O}^+]$:

Concentration (M)	$\text{CH}_3\text{COOH(aq)}$	+	$\text{H}_2\text{O(l)}$	$\rightleftharpoons$	$\text{CH}_3\text{COO}^-(\text{aq})$	+	$\text{H}_3\text{O}^+(\text{aq})$
Initial	0.48		—		0.52		0
Change	$-x$		—		$+x$		$+x$
Equilibrium	$0.48 - x$		—		$0.52 + x$		x

Making the assumption that x is small, and solving for x :

$$[\text{CH}_3\text{COOH}] = 0.48 \text{ M} - x \approx 0.48 \text{ M} \quad \text{and} \quad [\text{CH}_3\text{COO}^-] = 0.52 \text{ M} + x \approx 0.52 \text{ M}$$

$$x = [\text{H}_3\text{O}^+] = K_a \times \frac{[\text{CH}_3\text{COOH}]}{[\text{CH}_3\text{COO}^-]} \approx (1.8 \times 10^{-5}) \times \frac{0.48}{0.52} = 1.7 \times 10^{-5} \text{ M}$$

Calculating the pH:

$$\text{pH} = -\log [\text{H}_3\text{O}^+] = -\log (1.7 \times 10^{-5}) = 4.77$$

The addition of strong base increased the concentration of the basic buffer component at the expense of the acidic buffer component. Note especially that the pH *increased only slightly*, from 4.74 to 4.77.

(c) The pH after adding acid (0.020 mol of HCl to 1.0 L of buffer). Finding $[\text{H}_3\text{O}^+]_{\text{added}}$:

$$[\text{H}_3\text{O}^+]_{\text{added}} = \frac{0.020 \text{ mol H}_3\text{O}^+}{1.0 \text{ L soln}} = 0.020 \text{ M H}_3\text{O}^+$$

Now we proceed as in part (b), by first setting up a reaction table for the *stoichiometry* of adding H_3O^+ to CH_3COO^- :

Concentration (M)	$\text{CH}_3\text{COO}^-(\text{aq})$	+	$\text{H}_3\text{O}^+(\text{aq})$	$\longrightarrow$	$\text{CH}_3\text{COOH(aq)}$	+	$\text{H}_2\text{O(l)}$
Before addition	0.50		—		0.50		—
Addition	—		0.020		—		—
After addition	0.48		0		0.52		—

The reaction table for the acid dissociation, with $x = [\text{CH}_3\text{COOH}]_{\text{dissoc}} = [\text{H}_3\text{O}^+]$ is

Concentration (M)	$\text{CH}_3\text{COOH}(aq)$	+	$\text{H}_2\text{O}(l)$	$\rightleftharpoons$	$\text{CH}_3\text{COO}^-(aq)$	+	$\text{H}_3\text{O}^+(aq)$
Initial	0.52		—		0.48		0
Change	$-x$		—		$+x$		$+x$
Equilibrium	$0.52 - x$		—		$0.48 + x$		x

Making the assumption that x is small, and solving for x :

$$[\text{CH}_3\text{COOH}] = 0.52 \text{ M} - x \approx 0.52 \text{ M} \quad \text{and} \quad [\text{CH}_3\text{COO}^-] = 0.48 \text{ M} + x \approx 0.48 \text{ M}$$

$$x = [\text{H}_3\text{O}^+] = K_a \times \frac{[\text{CH}_3\text{COOH}]}{[\text{CH}_3\text{COO}^-]} \approx (1.8 \times 10^{-5}) \times \frac{0.52}{0.48} = 2.0 \times 10^{-5} \text{ M}$$

Calculating the pH:

$$\text{pH} = -\log [\text{H}_3\text{O}^+] = -\log (2.0 \times 10^{-5}) = 4.70$$

The addition of strong acid increased the concentration of the acidic buffer component at the expense of the basic buffer component and *lowered* the pH only slightly, from 4.74 to 4.70.

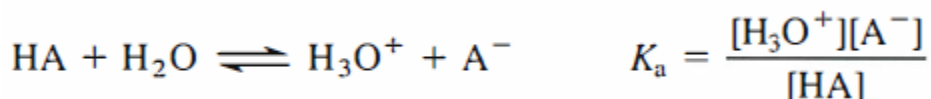
Check The changes in $[\text{CH}_3\text{COOH}]$ and $[\text{CH}_3\text{COO}^-]$ occur in opposite directions in parts (b) and (c), which makes sense. The additions were of equal amounts, so the pH increase in (b) should equal the pH decrease in (c), within rounding.

Comment In part (a), we justified our assumption that x can be neglected. Therefore, in parts (b) and (c), we could have used the “After addition” values from the last line of the stoichiometry tables directly for the ratio of buffer components; that would have allowed us to dispense with a reaction table for the dissociation. In subsequent problems in this chapter, we will follow this simplified approach.

FOLLOW-UP PROBLEM 19.1 Calculate the pH of a buffer consisting of 0.50 M HF and 0.45 M F^- (a) before and (b) after addition of 0.40 g of NaOH to 1.0 L of the buffer (K_a of HF = 6.8×10^{-4}).

The Henderson-Hasselbalch Equation

For any weak acid, HA, the dissociation equation and K_a expression are



$$[\text{H}_3\text{O}^+] = K_a \times \frac{[\text{HA}]}{[\text{A}^-]}$$

$$-\log [\text{H}_3\text{O}^+] = -\log K_a - \log \left(\frac{[\text{HA}]}{[\text{A}^-]} \right)$$

$$\text{pH} = \text{p}K_a + \log \left(\frac{[\text{A}^-]}{[\text{HA}]}\right)$$

Generalizing the previous equation for any conjugate acid-base pair gives the **Henderson-Hasselbalch equation**:

$$\text{pH} = \text{p}K_a + \log \left(\frac{[\text{base}]}{[\text{acid}]}\right)$$

This relationship is very useful for two reasons. First, it allows us to solve directly for pH instead of having to calculate $[\text{H}_3\text{O}^+]$ first. For instance, by applying the Henderson-Hasselbalch equation in part (b) of Sample Problem 19.1, we could have found the pH of the buffer after the addition of NaOH as follows:

$$\text{pH} = \text{p}K_a + \log \left(\frac{[\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]}\right) = 4.74 + \log \left(\frac{0.52}{0.48}\right) = 4.77$$

Second, it allows us to prepare a buffer of a desired pH just by mixing the appropriate amounts of A^- and HA.

Buffer Capacity and Buffer Range

- **Buffer capacity** is a measure of this ability to resist pH change, and depends on both the absolute and relative component concentrations.
- In absolute terms, the more concentrated the components of a buffer, the greater the buffer capacity. A buffer made of equal volumes of 1.0 M CH_3COOH and 1.0 M CH_3COO^- has the same pH (4.74) as a buffer made of equal volumes of 0.10 M CH_3COOH and 0.10 M CH_3COO^- , but the more concentrated buffer has a much larger capacity for resisting a pH change.
- Buffer capacity is also affected by the relative concentrations of the buffer components. *For a given addition of acid or base, the buffer-component concentration ratio changes less when the concentrations are similar than when they are different.*

Suppose that a buffer has $[\text{HA}] = [\text{A}^-] = 1.000 \text{ M}$. When we add 0.010 mol of OH^- to 1.00 L of buffer, $[\text{A}^-]$ becomes 1.010 M and $[\text{HA}]$ becomes 0.990 M:

$$\frac{[A^-]_{\text{init}}}{[HA]_{\text{init}}} = \frac{1.000\text{ M}}{1.000\text{ M}} = 1.000$$

$$\frac{[A^-]_{\text{final}}}{[HA]_{\text{final}}} = \frac{1.010\text{ M}}{0.990\text{ M}} = 1.02$$

$$\text{Percent change} = \frac{1.02 - 1.000}{1.000} \times 100 = 2\%$$

Now suppose that the component concentrations are $[HA] = 0.250\text{ M}$ and $[A^-] = 1.750\text{ M}$. The same addition of 0.010 mol of OH^- to 1.00 L of buffer gives $[HA] = 0.240\text{ M}$ and $[A^-] = 1.760\text{ M}$, so the ratios are:

$$\frac{[A^-]_{\text{init}}}{[HA]_{\text{init}}} = \frac{1.750\text{ M}}{0.250\text{ M}} = 7.00$$

$$\frac{[A^-]_{\text{final}}}{[HA]_{\text{final}}} = \frac{1.760\text{ M}}{0.240\text{ M}} = 7.33$$

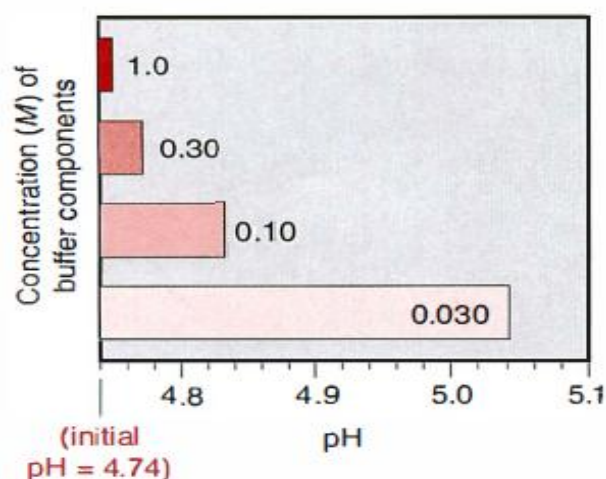
$$\text{Percent change} = \frac{7.33 - 7.00}{7.00} \times 100 = 4.7\%$$

It follows that a buffer has the highest capacity when the component concentrations are equal, that is, when $[A^-]/[HA] = 1$:

$$\text{pH} = \text{p}K_a + \log \left(\frac{[A^-]}{[HA]} \right) = \text{p}K_a + \log 1 = \text{p}K_a + 0 = \text{p}K_a$$

Note this important result: *for a given concentration, a buffer whose pH is equal to or near the $\text{p}K_a$ of its acid component has the highest buffer capacity.*

Figure 19.4 The relation between buffer capacity and pH change. The four bars in the graph represent $\text{CH}_3\text{COOH}-\text{CH}_3\text{COO}^-$ buffers with the same initial pH (4.74) but different component concentrations (labeled on or near each bar). When a given amount of strong base is added to each buffer, the pH increases. The length of the bar corresponds to the pH increase. Note that the more concentrated the buffer, the greater its capacity, and the smaller the pH change.



- The **buffer range** is the pH range over which the buffer acts effectively, and it is related to the relative component concentrations. *The further the buffer component concentration ratio is from 1, the less effective the buffering action* (that is, the lower the buffer capacity). In practice, if the $[A^-]/[HA]$ ratio is greater than 10 or less than 0.1, buffering action is poor. **Buffers have a usable range within ± 1 pH unit of the pK_a of the acid component:**

$$pH = pK_a + \log\left(\frac{10}{1}\right) = pK_a + 1 \quad \text{and} \quad pH = pK_a + \log\left(\frac{1}{10}\right) = pK_a - 1$$

Preparing a Buffer

Several steps are required to prepare a buffer:

1. Decide on the conjugate acid-base pair. The choice is determined mostly by the desired pH which should be close to the pK_a of the acid.
2. Find the ratio of $[A^-]/[HA]$ that gives the desired pH, using the Henderson-Hasselbalch equation. Note that, because HA is a weak acid, and thus dissociates very little, the equilibrium concentrations are approximately equal to the initial concentrations; that is,

$$pH = pK_a + \log\left(\frac{[A^-]}{[HA]}\right) \approx pK_a + \log\left(\frac{[A^-]_{init}}{[HA]_{init}}\right)$$

3. Choose the buffer concentration and calculate the amounts to mix. Remember that the higher the concentration, the greater the buffer capacity. For most laboratory applications, concentrations from 0.05 M to 0.5 M are suitable.
4. Mix the amounts together and adjust the buffer pH to the desired value. Add small amounts of strong acid or strong base, while monitoring the solution with a pH meter.

SAMPLE PROBLEM 19.2 Preparing a Buffer

Problem An environmental chemist needs a carbonate buffer of pH 10.00 to study the effects of the acid rain on limestone-rich soils. How many grams of Na_2CO_3 must she add to 1.5 L of freshly prepared 0.20 M NaHCO_3 to make the buffer? K_a of HCO_3^- is 4.7×10^{-11} .

Plan The conjugate pair is already chosen, HCO_3^- (acid) and CO_3^{2-} (base), as are the volume (1.5 L) and concentration (0.20 M) of HCO_3^- , so we must find the buffer-component concentration ratio that gives pH 10.00 and the mass of Na_2CO_3 to dissolve. We find the amount (mol) of NaHCO_3 and use the ratio to find the amount (mol) of Na_2CO_3 , which we convert to mass (g) using the molar mass.

Solution Solving for the buffer-component concentration ratio:

$$\text{pH} = \text{p}K_a + \log \left(\frac{[\text{CO}_3^{2-}]}{[\text{HCO}_3^-]} \right) \quad \text{or} \quad 10.00 = 10.33 + \log \left(\frac{[\text{CO}_3^{2-}]}{[\text{HCO}_3^-]} \right)$$

$$\log \left(\frac{[\text{CO}_3^{2-}]}{[\text{HCO}_3^-]} \right) = -0.33 \quad \text{so} \quad \frac{[\text{CO}_3^{2-}]}{[\text{HCO}_3^-]} = 0.47$$

Calculating the amount (mol) and mass (g) of Na_2CO_3 that will give the needed 0.47:1.0 ratio:

$$\text{Amount (mol) of NaHCO}_3 = 1.5 \text{ L} \times \frac{0.20 \text{ M NaHCO}_3}{1.0 \text{ L soln}} = 0.30 \text{ mol NaHCO}_3$$

$$\begin{aligned} \text{Amount (mol) of Na}_2\text{CO}_3 &= 0.30 \text{ mol NaHCO}_3 \times \frac{0.47 \text{ mol Na}_2\text{CO}_3}{1 \text{ mol NaHCO}_3} \\ &= 0.14 \text{ mol Na}_2\text{CO}_3 \end{aligned}$$

$$\text{Mass (g) of Na}_2\text{CO}_3 = 0.14 \text{ mol Na}_2\text{CO}_3 \times \frac{105.99 \text{ g Na}_2\text{CO}_3}{1 \text{ mol Na}_2\text{CO}_3} = 15 \text{ g Na}_2\text{CO}_3$$

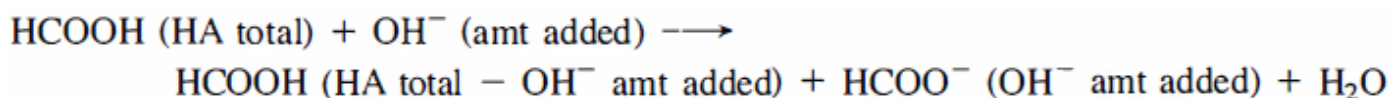
We dissolve 15 g of Na_2CO_3 into approximately 1.3 L of 0.20 M NaHCO_3 and add 0.20 M NaHCO_3 to make 1.5 L. Using a pH meter, we adjust the pH to 10.00 with strong acid or base.

Check For a useful buffer range, the concentration of the acidic component, $[\text{HCO}_3^-]$, must be within a factor of 10 of the concentration of the basic component, $[\text{CO}_3^{2-}]$. We have 0.30 mol of HCO_3^- and 0.14 mol of CO_3^{2-} ; $0.30:0.14 = 2.1$, which seems fine. Make sure the relative amounts of components seem reasonable: we want a pH lower than the $\text{p}K_a$ of HCO_3^- (10.33), so it makes sense that we have more of the acidic than the basic species.

Comment In the follow-up problem, we use an alternative calculation that does not rely on the Henderson-Hasselbalch equation.

FOLLOW-UP PROBLEM 19.2 How would you prepare a benzoic acid–benzoate buffer with pH = 4.25, starting with 5.0 L of 0.050 M sodium benzoate ($\text{C}_6\text{H}_5\text{COONa}$) solution and adding the acidic component? K_a of benzoic acid ($\text{C}_6\text{H}_5\text{COOH}$) is 6.3×10^{-5} .

Another way to prepare a buffer is to form one of the components during the final mixing step by partial neutralization of the other component. For example, suppose you need a HCOOH-HCOO^- buffer. You can prepare it by mixing appropriate amounts of HCOOH solution and NaOH solution. As the OH^- ions react with the HCOOH molecules, neutralization of part of the total HCOOH present produces the HCOO^- needed:



This method is based on the same chemical process that occurs when a weak acid is titrated with a strong base, as you'll see in the next section.

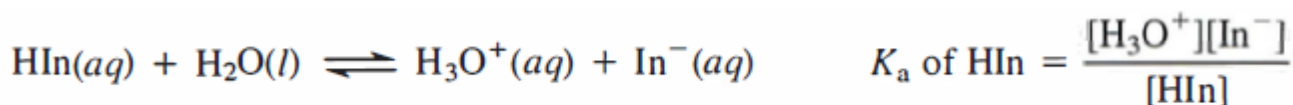
19.2 ACID-BASE TITRATION CURVES

In Chapter 4, we discussed the acid-base titration as an analytical method. Let's re-examine it, this time tracking the change in pH with an acid-base titration curve, a plot of pH vs. volume of titrant added.

Monitoring pH with Acid-Base Indicators

- **An acid-base indicator** is a weak organic acid (HIn) that has a different color than its conjugate base (In^-), with the color change occurring over a specific and relatively narrow pH range.

Selecting an indicator requires that you know the approximate pH of the titration end point, which in turn requires that you know which ionic species are present. Because the indicator molecule is a weak acid, the ratio of the two forms is governed by the $[\text{H}_3\text{O}^+]$ of the test solution:



Therefore,

$$\frac{[\text{HIn}]}{[\text{In}^-]} = \frac{[\text{H}_3\text{O}^+]}{K_a}$$

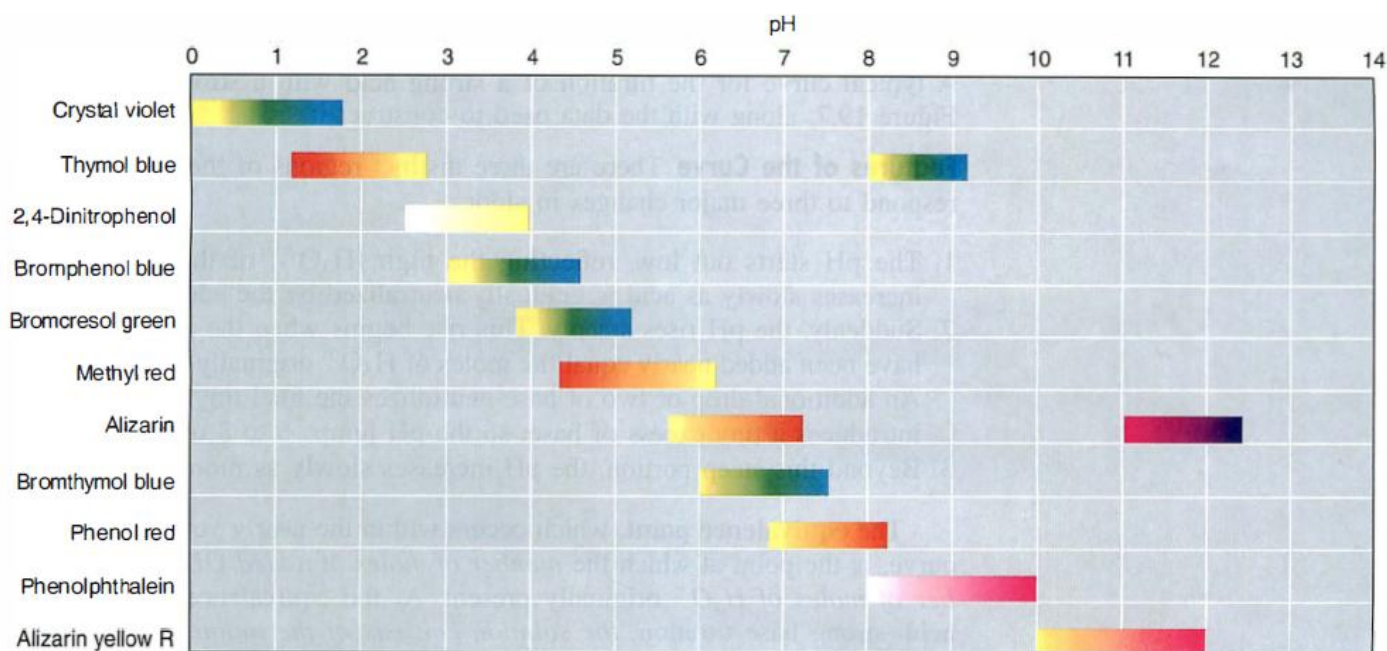


Figure 19.5 Colors and approximate pH range of some common acid-base indicators. Most have a range of about 2 pH units, in keeping with the useful buffer range of 2 pH units ($\text{pK}_a \pm 1$). (The pH range depends to some extent on the solvent used to prepare the indicator.)

Typically, the experimenter will see the HIn color if the $[\text{HIn}]/[\text{In}^-]$ ratio is 10:1 or greater and the In^- color if the $[\text{HIn}]/[\text{In}^-]$ ratio is 1:10 or less. Between these extremes, the colors of the two forms merge into an intermediate hue. Therefore, an indicator changes color over a range of about 2 pH units. For example, bromthymol blue has a pH range of about 6.0 to 7.6 and, as Figure 19.6 shows, it is yellow below that range, blue above it, and greenish in between.



Figure 19.6 The color change of the indicator bromthymol blue. The acidic form of bromthymol blue is yellow (*left*) and the basic form is blue (*right*). Over the pH range in which the indicator is changing, both forms are present, so the mixture appears greenish (*center*).

Strong Acid -Strong Base Titration Curves

A typical curve for the titration of a strong acid with a strong base appears in Figure 19.7, along with the data used to construct it.

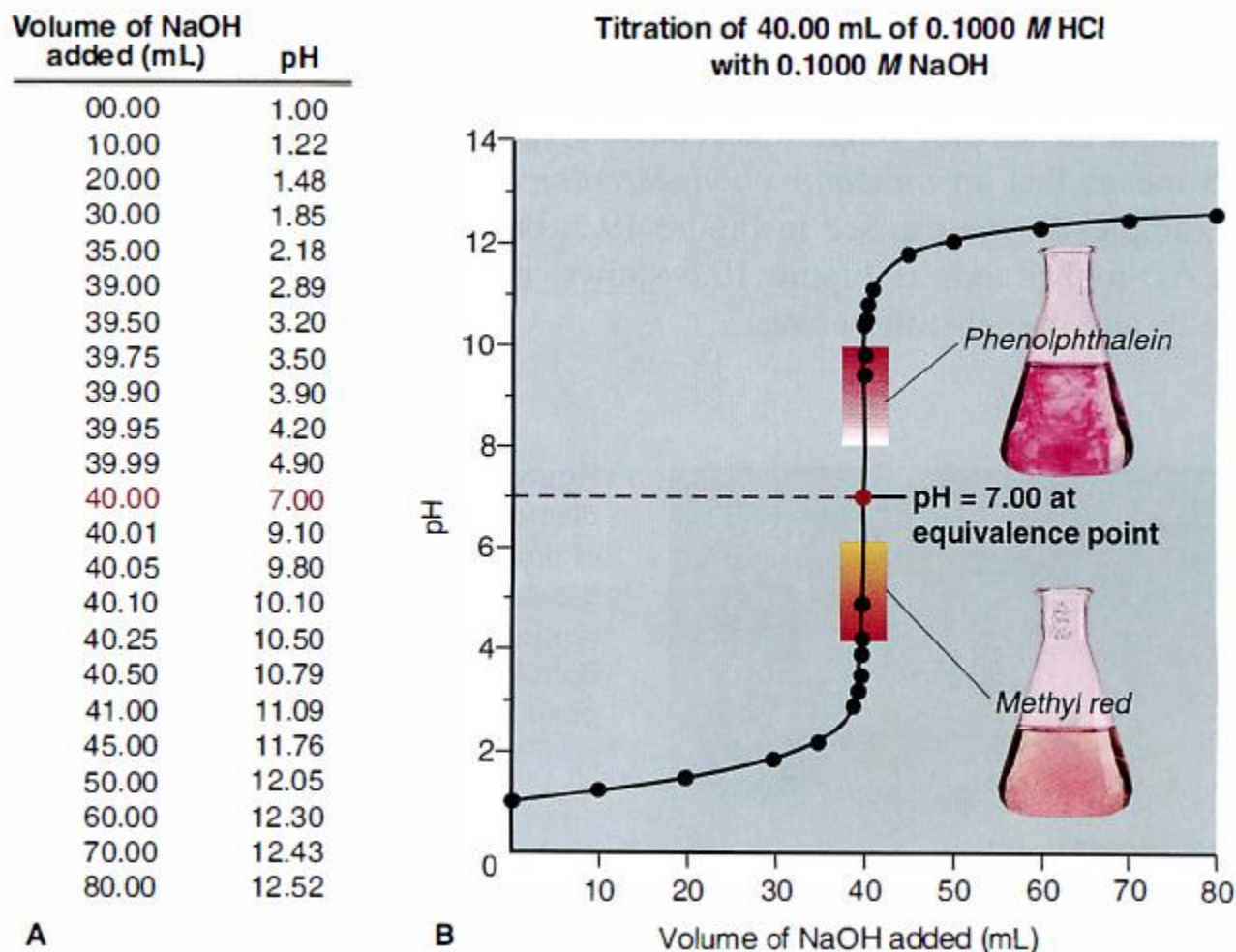


Figure 19.7 Curve for a strong acid-strong base titration. A, Data obtained from the titration of 40.00 mL of 0.1000 M HCl with 0.1000 M NaOH. B, Acid-base titration curve from data in part A. The pH increases gradually at first. When the amount (mol) of OH^- added is slightly less than the amount (mol) of H_3O^+ originally present, a large pH change accompanies a small addition of OH^- . The equivalence point occurs when amount (mol) of OH^- added = amount (mol) of H_3O^+ originally present. Note that, for a strong acid-strong base titration, pH = 7.00 at the equivalence point. Added before the titration begins, either methyl red or phenolphthalein is a suitable indicator in this case because each changes color on the steep portion of the curve, as shown by the color strips. Photos showing the color changes from 1-2 drops of indicator appear nearby. Beyond this point, added OH^- causes a gradual pH increase again.

Features of the Curve There are three distinct regions of the curve, which correspond to three major changes in slope:

1. The pH starts out low, reflecting the high $[\text{H}_3\text{O}^+]$ of the strong acid, and increases slowly as acid is gradually neutralized by the added base.
2. Suddenly, the pH rises steeply. This rise begins when the moles of OH^- that have been added nearly equal the moles of H_3O^+ originally present in the acid. An additional drop or two of base neutralizes the final tiny excess of acid and introduces a tiny excess of base, so the pH jumps 6 to 8 units.
3. Beyond this steep portion, the pH increases slowly as more base is added.

The equivalence point is the point at which the number of moles of added OH^- equals the number of moles of H_3O^+ originally present.

At the equivalence point of a strong acid-strong base titration, the solution consists of the anion of the strong acid and the cation of the strong base. These ions do not react with water, so the solution is neutral: $\text{pH} = 7.00$.

The end point of the titration occurs when the indicator changes color. *We choose an indicator with an end point close to the equivalence point, one that changes color in the pH range on the steep vertical portion of the curve.*

e.g. Methyl red changes from red at pH 4.2 to yellow at pH 6.3, whereas phenolphthalein changes from colorless at pH 8.3 to pink at pH 10.0. Even though neither color change occurs at the equivalence point (pH 7.00), both occur on the vertical portion of the curve, where a single drop of base causes a large pH change: when methyl red turns yellow, or when phenolphthalein turns pink, we know we are within a drop or two of the equivalence point.

Calculating the pH By knowing the chemical species present during the titration, we can calculate the pH at various points along the way:

1. Original solution of strong HA

Because a strong acid is completely dissociated, $[\text{HCl}] = [\text{H}_3\text{O}^+] = 0.1000 \text{ M}$.

$$\text{pH} = -\log [\text{H}_3\text{O}^+] = -\log (0.1000) = 1.00$$

2. Before the equivalence point.

As soon as we start adding base, two changes occur that affect the pH calculations:

(1) some acid is neutralized, and (2) the volume of solution increases.

For example, after adding 20.00 mL of 0.1000 M NaOH:

- Find the moles of H_3O^+ remaining;

$$\begin{array}{rcl} \text{Initial moles of } \text{H}_3\text{O}^+ & = & 0.04000 \text{ L} \times 0.1000 \text{ M} = 0.004000 \text{ mol } \text{H}_3\text{O}^+ \\ - \text{Moles of } \text{OH}^- \text{ added} & = & 0.02000 \text{ L} \times 0.1000 \text{ M} = 0.002000 \text{ mol } \text{OH}^- \\ \hline \text{Moles of } \text{H}_3\text{O}^+ \text{ remaining} & = & 0.002000 \text{ mol } \text{H}_3\text{O}^+ \end{array}$$

- Calculate $[\text{H}_3\text{O}^+]$, taking the total volume into account.

$$\begin{aligned} [\text{H}_3\text{O}^+] &= \frac{\text{amount (mol) of } \text{H}_3\text{O}^+ \text{ remaining}}{\text{original volume of acid} + \text{volume of added base}} \\ &= \frac{0.002000 \text{ mol } \text{H}_3\text{O}^+}{0.04000 \text{ L} + 0.02000 \text{ L}} = 0.03333 \text{ M} \quad \text{pH} = 1.48 \end{aligned}$$

3. At the equivalence point.

After 40.00 mL of 0.1000 M NaOH has been added, the equivalence point is reached. All the H_3O^+ from the acid has been neutralized, and the solution contains Na^+ and Cl^- , *neither of which reacts with water*.

Because of the autoionization of water, however,

$$[\text{H}_3\text{O}^+] = 1.0 \times 10^{-7} \text{ M}, \text{ pH} = 7.00$$

4. After the equivalence point.

From the equivalence point on, the pH calculation is based on the moles of excess OH^- present. For example, after adding 50.00 mL of NaOH, we have:

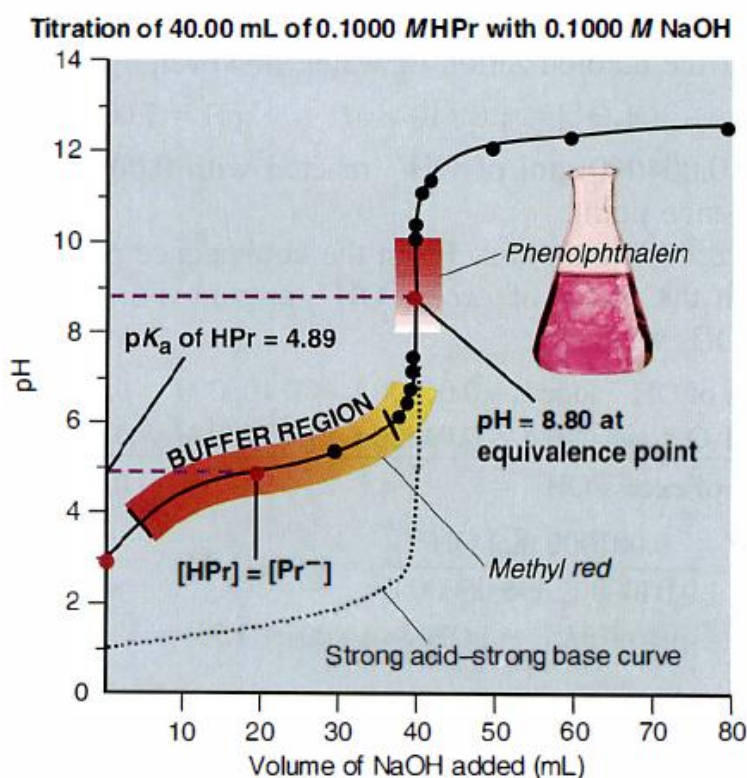
$$\begin{array}{rcl}
 \text{Total moles of OH}^- \text{ added} & = & 0.05000 \text{ L} \times 0.1000 \text{ M} = 0.005000 \text{ mol OH}^- \\
 - \text{Moles of H}_3\text{O}^+ \text{ consumed} & = & 0.04000 \text{ L} \times 0.1000 \text{ M} = 0.004000 \text{ mol H}_3\text{O}^+ \\
 \hline
 \text{Moles of excess OH}^- & = & 0.001000 \text{ mol OH}^- \\
 \\
 [\text{OH}^-] & = & \frac{0.001000 \text{ mol OH}^-}{0.04000 \text{ L} + 0.05000 \text{ L}} = 0.01111 \text{ M} \quad \text{pOH} = 1.95 \\
 \text{pH} & = & \text{p}K_w - \text{pOH} = 14.00 - 1.95 = 12.05
 \end{array}$$

Weak Acid-Strong Base Titration Curves

Figure 19.8 shows the curve obtained when we use 0.1000 M NaOH to titrate 40.00 mL of 0.1000 M propanoic acid, a weak organic acid ($\text{CH}_3\text{CH}_2\text{COOH}$; $K_a = 1.3 \times 10^{-5}$). (We abbreviate the acid as HPr and the conjugate base, $\text{CH}_3\text{CH}_2\text{COO}^-$, as Pr^- .)

Figure 19.8

Curve for a weak acid-strong base titration. The curve for the titration of 40.00 mL of 0.1000 M $\text{CH}_3\text{CH}_2\text{COOH}$ (HPr) with 0.1000 M NaOH is compared with that for the strong acid HCl (dotted curve portion). Phenolphthalein (photo) is a suitable indicator here.



Features of the Curve

When we compare this weak acid-strong base titration curve with the strong acid-strong base titration curve, four key regions appear, and the first three differ from the strong acid case:

1. The initial pH is higher.

Because the weak acid (HPr) dissociates slightly, less H_3O^+ is present than with the strong acid.

2. A gradually rising portion of the curve, called the buffer region, appears before the steep rise to the equivalence point.

As HPr reacts with the strong base, more and more conjugate base (Pr^-) forms, which creates an HPr-Pr buffer. At the midpoint of the buffer region, half the original HPr has reacted, so $[\text{HPr}] = [\text{Pr}^-]$, or $[\text{Pr}^-]/[\text{HPr}] = 1$. Therefore, the pH equals the pK_a :

$$\text{pH} = \text{pK}_a + \log \left(\frac{[\text{Pr}^-]}{[\text{HPr}]}\right) = \text{pK}_a + \log 1 = \text{pK}_a + 0 = \text{pK}_a$$

3. The pH at the equivalence point **is greater than 7.00**. The solution contains the strong-base cation Na^+ , which does not react with water, and the weak acid anion Pr^- , which acts as a weak base to accept a proton from H_2O and yield OH^- .

4. Beyond the equivalence point, the pH increases slowly as excess OH^- is added.

Our choice of indicator is more limited here than for a strong acid-strong base titration because the steep rise occurs over a smaller pH range. Phenolphthalein is suitable because its color change lies within this range (Figure 19.8).

Calculating the pH

There are four key regions of the titration curve:

1. Solution of HA

Before base is added,

$x = [\text{HPr}]_{\text{dissoc}}$, assume $[\text{H}_3\text{O}^+] = [\text{HPr}]_{\text{dissoc}} \ll [\text{HPr}]_{\text{init}}$, and solve for x :

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{Pr}^-]}{[\text{HPr}]} \approx \frac{x^2}{[\text{HPr}]_{\text{init}}} \quad \text{therefore,} \quad x = [\text{H}_3\text{O}^+] \approx \sqrt{K_a \times [\text{HPr}]_{\text{init}}}$$

2. Solution of HA and added base

As soon as we add NaOH, it reacts with HPr to form Pr^- . This means that up to the equivalence point, we have a mixture of acid and conjugate base, and an HPr- Pr^- buffer solution exists over much of that interval.

$$[\text{H}_3\text{O}^+] = K_a \times \frac{[\text{HPr}]}{[\text{Pr}^-]}$$

3. Equivalent amounts of HA and added base

At the equivalence point, the original amount of HPr has reacted, so the flask contains a solution of Pr^- , a weak base that reacts with water to form OH^- :



Therefore, the solution at the equivalence point is slightly basic, $\text{pH} > 7.00$.

$$(1) [\text{OH}^-] \approx \sqrt{K_b \times [\text{Pr}^-]}, \quad \text{where } K_b = \frac{K_w}{K_a} \quad \text{and} \quad [\text{Pr}^-] = \frac{\text{moles of HPr}_{\text{init}}}{\text{total volume}}$$

$$(2) [\text{H}_3\text{O}^+] = \frac{K_w}{[\text{OH}^-]}$$

Combining them into one step gives

$$[\text{H}_3\text{O}^+] \approx \frac{K_w}{\sqrt{K_b \times [\text{Pr}^-]}}$$

4. Solution of excess added base.

Beyond the equivalence point, we are just adding excess OH^- ion, so the calculation is the same as for the strong acid-strong base titration:

$$[\text{H}_3\text{O}^+] = \frac{K_w}{[\text{OH}^-]}, \quad \text{where } [\text{OH}^-] = \frac{\text{moles of excess OH}^-}{\text{total volume}}$$

SAMPLE PROBLEM 19.3 Finding the pH During a Weak Acid–Strong Base Titration

Problem Calculate the pH during the titration of 40.00 mL of 0.1000 M propanoic acid (HPr; $K_a = 1.3 \times 10^{-5}$) after adding the following volumes of 0.1000 M NaOH:

(a) 0.00 mL (b) 30.00 mL (c) 40.00 mL (d) 50.00 mL

Plan (a) 0.00 mL: No base has been added yet, so this is a weak-acid solution. Thus, we calculate the pH as we did in Section 18.4. (b) 30.00 mL: A mixture of Pr^- and HPr is present. We find the amount (mol) of each, substitute into the K_a expression to solve for

$[\text{H}_3\text{O}^+]$, and convert to pH. (c) 40.00 mL: The amount (mol) of NaOH added equals the initial amount (mol) of HPr, so a solution of Na^+ and the weak base Pr^- exists. We calculate the pH as we did in Section 18.5, except that we need *total* volume to find $[\text{Pr}^-]$. (d) 50.00 mL: Excess NaOH is added, so we calculate the amount (mol) of excess OH^- in the total volume and convert to $[\text{H}_3\text{O}^+]$ and then pH.

Solution (a) 0.00 mL of 0.1000 M NaOH added. Following the approach used in Sample Problem 18.7 and just described in the text, we obtain

$$[\text{H}_3\text{O}^+] \approx \sqrt{K_a \times [\text{HPr}]_{\text{init}}} = \sqrt{(1.3 \times 10^{-5})(0.1000)} = 1.1 \times 10^{-3} \text{ M}$$

$$\text{pH} = 2.96$$

(b) 30.00 mL of 0.1000 M NaOH added. Calculating the ratio of moles of HPr to Pr^- :

$$\text{Original moles of HPr} = 0.04000 \text{ L} \times 0.1000 \text{ M} = 0.004000 \text{ mol HPr}$$

$$\text{Moles of NaOH added} = 0.03000 \text{ L} \times 0.1000 \text{ M} = 0.003000 \text{ mol OH}^-$$

For 1 mol of NaOH that reacts, 1 mol of Pr^- forms, so we construct the following reaction table for the stoichiometry:

Amount (mol)	HPr(aq)	+	$\text{OH}^-(\text{aq})$	$\longrightarrow$	$\text{Pr}^-(\text{aq})$	+	$\text{H}_2\text{O}(\text{l})$
Before addition	0.004000		—		0		—
Addition	—		0.003000		—		—
After addition	0.001000		0		0.003000		—

The last line of this table shows the new initial amounts of HPr and Pr^- that will react to attain a new equilibrium. However, with x very small, we assume that the $[\text{HPr}]/[\text{Pr}^-]$ ratio at equilibrium is essentially equal to the ratio of these new initial amounts (see Comment in Sample Problem 19.1). Thus,

$$\frac{[\text{HPr}]}{[\text{Pr}^-]} = \frac{0.001000 \text{ mol}}{0.003000 \text{ mol}} = 0.3333$$

$$\text{Solving for } [\text{H}_3\text{O}^+]: \quad [\text{H}_3\text{O}^+] = K_a \times \frac{[\text{HPr}]}{[\text{Pr}^-]} = (1.3 \times 10^{-5})(0.3333) = 4.3 \times 10^{-6} \text{ M}$$

$$\text{pH} = 5.37$$

(c) 40.00 mL of 0.1000 M NaOH added. Calculating $[\text{Pr}^-]$ after all HPr has reacted:

$$[\text{Pr}^-] = \frac{0.004000 \text{ mol}}{0.04000 \text{ L} + 0.04000 \text{ L}} = 0.05000 \text{ M}$$

Calculating K_b :

$$K_b = \frac{K_w}{K_a} = \frac{1.0 \times 10^{-14}}{1.3 \times 10^{-5}} = 7.7 \times 10^{-10}$$

Solving for $[\text{H}_3\text{O}^+]$ as described in the text:

$$[\text{H}_3\text{O}^+] \approx \frac{K_w}{\sqrt{K_b \times [\text{Pr}^-]}} = \frac{1.0 \times 10^{-14}}{\sqrt{(7.7 \times 10^{-10})(0.05000)}} = 1.6 \times 10^{-9} \text{ M}$$

$$\text{pH} = 8.80$$

(d) 50.00 mL of 0.1000 M NaOH added.

$$\text{Moles of excess OH}^- = (0.1000 \text{ M})(0.05000 \text{ L} - 0.04000 \text{ L}) = 0.001000 \text{ mol}$$

$$[\text{OH}^-] = \frac{\text{moles of excess OH}^-}{\text{total volume}} = \frac{0.001000 \text{ mol}}{0.09000 \text{ L}} = 0.01111 \text{ M}$$

$$[\text{H}_3\text{O}^+] = \frac{K_w}{[\text{OH}^-]} = \frac{1.0 \times 10^{-14}}{0.01111} = 9.0 \times 10^{-13} \text{ M}$$

$$\text{pH} = 12.05$$

Check As expected from the continuous addition of base, the pH increases through the four stages. Be sure to round off and check the arithmetic along the way.

FOLLOW-UP PROBLEM 19.3 A chemist titrates 20.00 mL of 0.2000 M HBrO ($K_a = 2.3 \times 10^{-9}$) with 0.1000 M NaOH. What is the pH (a) before any base is added; (b) when $[\text{HBrO}] = [\text{BrO}^-]$; (c) at the equivalence point; (d) when the moles of OH^- added are twice the moles of HBrO originally present? (e) Sketch the titration curve.

Weak Base-Strong Acid Titration Curves

The titration curve of a weak base (NH_3) with a strong acid (HCl), shown in Figure 19.9. The regions of the curve have the following features:

1. The initial solution is that of a weak base, so the pH starts out above 7.00.
2. The pH decreases gradually in the buffer region, where significant amounts of base (NH_3) and conjugate acid (NH_4^+) are present. At the midpoint of the buffer region, the pH equals the $\text{p}K_a$ of the ammonium ion.
3. After the buffer region, the curve drops vertically to the equivalence point, at

which all the NH_3 has reacted and the solution contains only NH_4^+ and Cl^- .

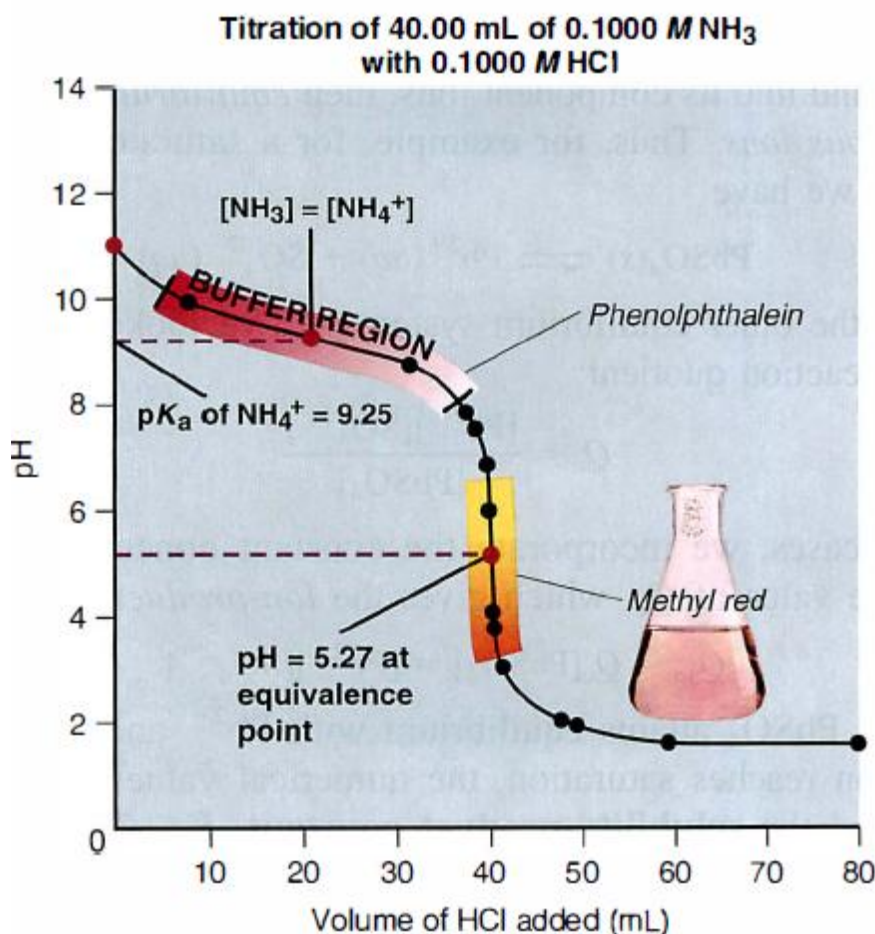
Note that the pH at the equivalence point is below 7.00 because Cl^- does not react with water and NH_4^+ is acidic:



4. Beyond the equivalence point, the pH decreases slowly as excess H_3O^+ is added.

For this titration, methyl red lies on the steep portion of the curve and straddles the equivalence point, so it is a perfect choice.

Figure 19.9 Curve for a weak base-strong acid titration. Titrating 40.00 mL of 0.1000 M NH_3 with a solution of 0.1000 M HCl leads to a curve whose shape is the same as that of the weak acid-strong base curve in Figure 19.8 but inverted. The midpoint of the buffer region occurs when $[\text{NH}_3] = [\text{NH}_4^+]$; the pH at this point equals the pK_a of NH_4^+ . Methyl red (photo) is a suitable indicator here.



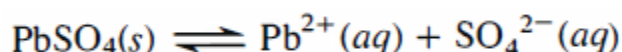
19.3 EQUILIBRIA OF SLIGHTLY SOLUBLE IONIC COMPOUNDS

- In this section, we explore the aqueous equilibria of **slightly soluble ionic compounds**, which up to now we've called "insoluble."
- Slightly soluble ionic compounds have a relatively low solubility, so they reach equilibrium with relatively little solute dissolved. At this point, it would be a good idea for you to review the solubility rules listed in Table 4.1.
- Many slightly soluble salts, particularly those of transition metals and heavy main-group metals, have metal-nonmetal bonds with significant covalent character, and their solutions often contain other species that are partially dissociated or even undissociated.

For example, when lead(II) chloride is thoroughly stirred in water, a small amount dissolves, and the solution contains not only the $\text{Pb}^{2+}(\text{aq})$ and $\text{Cl}^{-}(\text{aq})$ ions expected from complete dissociation, but also undissociated $\text{PbCl}_2(\text{aq})$ molecules and $\text{PbCl}^{+}(\text{aq})$ ions.

The Ion-Product Expression (Q_{sp}) and the Solubility-Product Constant (K_{sp})

Consider, for example, for a saturated solution of lead(II) sulfate in water,



As with all the other equilibrium systems we've looked at, this one can be expressed by a reaction quotient:

$$Q_{\text{c}} = \frac{[\text{Pb}^{2+}][\text{SO}_4^{2-}]}{[\text{PbSO}_4]}$$

As in previous cases, we incorporate the constant concentration of the solid, $[\text{PbSO}_4]$, into the value of Q_{c} , which gives the ion-product expression, Q_{sp} :

$$Q_{\text{sp}} = Q_{\text{c}}[\text{PbSO}_4] = [\text{Pb}^{2+}][\text{SO}_4^{2-}]$$

And, when solid PbSO_4 attains equilibrium with Pb^{2+} and SO_4^{2-} ions, Q_{sp} becomes equivalent to the **solubility-product constant**, K_{sp} .

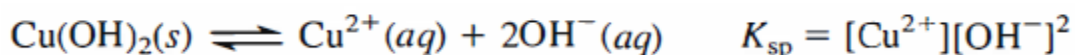
The K_{sp} for $PbSO_4$ at $25^\circ C$, for example, is 1.6×10^{-8} . A given K_{sp} value depends only on the temperature, not on the individual ion concentrations.

In general, for a saturated solution of a slightly soluble ionic compound, M_pX_q , composed of the ions M^{n+} and X^{z-} , the equilibrium condition is:

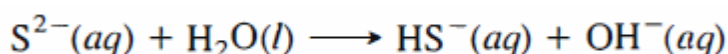
$$Q_{sp} = [M^{n+}]^p [X^{z-}]^q = K_{sp}$$

Examples,

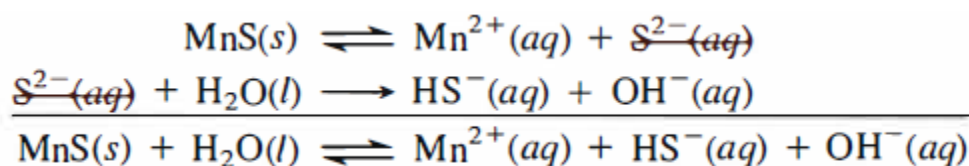
- The equation and ion-product expression that describe a saturated solution of $Cu(OH)_2$ are



- Insoluble metal sulfides present a slightly different case. The sulfide ion, S^{2-} , is so basic that it is not stable in water and reacts completely to form the hydrogen sulfide ion (HS^{-}) and the hydroxide ion (OH^{-}):



For instance, when manganese(II) sulfide is shaken with water, the solution contains Mn^{2+} , HS^{-} , and OH^{-} ions. Although the sulfide ion does not exist as such in water, you can imagine the dissolution process as the sum of two steps, with S^{2-} occurring as an intermediate that is consumed immediately:



$$K_{sp} = [Mn^{2+}][HS^{-}][OH^{-}]$$

SAMPLE PROBLEM 19.4

Writing Ion-Product Expressions for Slightly Soluble Ionic Compounds

Problem Write the ion-product expression for each of the following compounds:

(a) Magnesium carbonate

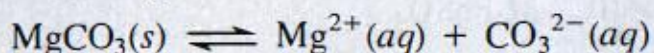
(b) Iron(II) hydroxide

(c) Calcium phosphate

(d) Silver sulfide

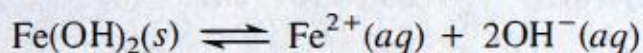
Plan We write an equation that describes a saturated solution and then write the ion-product expression, K_{sp} , according to Equation 19.2, noting the sulfide in part (d).

Solution (a) Magnesium carbonate:



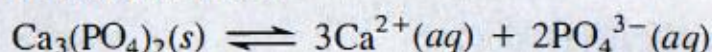
$$K_{sp} = [\text{Mg}^{2+}][\text{CO}_3^{2-}]$$

(b) Iron(II) hydroxide:



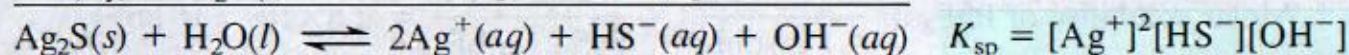
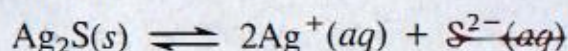
$$K_{sp} = [\text{Fe}^{2+}][\text{OH}^-]^2$$

(c) Calcium phosphate:



$$K_{sp} = [\text{Ca}^{2+}]^3[\text{PO}_4^{3-}]^2$$

(d) Silver sulfide:



Check Except for part (d), you can check by reversing the process to see if you obtain the formula of the compound from K_{sp} .

Comment In part (d), we include H_2O as reactant to obtain a balanced equation.

FOLLOW-UP PROBLEM 19.4 Write the ion-product expression for each of the following compounds:

(a) Calcium sulfate

(b) Chromium(III) carbonate

(c) Magnesium hydroxide

(d) Arsenic(III) sulfide

Table 19.2 Solubility-Product Constants (K_{sp}) of Selected Ionic Compounds at 25°C

Name, Formula	K_{sp}
Aluminum hydroxide, Al(OH)_3	3×10^{-34}
Cobalt(II) carbonate, CoCO_3	1.0×10^{-10}
Iron(II) hydroxide, Fe(OH)_2	4.1×10^{-15}
Lead(II) fluoride, PbF_2	3.6×10^{-8}
Lead(II) sulfate, PbSO_4	1.6×10^{-8}
Mercury(I) iodide, Hg_2I_2	4.7×10^{-29}
Silver sulfide, Ag_2S	8×10^{-48}
Zinc iodate, $\text{Zn(IO}_3)_2$	3.9×10^{-6}

The value of K_{sp} indicates how far to the right the dissolution proceeds at equilibrium (saturation). Table 19.2 presents some representative K_{sp} values. (Appendix C includes a much more extensive list.)

Calculations Involving the Solubility-Product Constant

Determining K_{sp} from Solubility

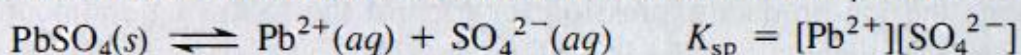
- Most Solubility values are given in units of grams of solute dissolved in 100 grams of H_2O . Because the mass of compound in solution is small, a negligible error is introduced if we assume that "100 g of water" is equal to "100 mL of solution."
- Solubility can also be expressed as **molar solubility**, the amount (mol) of solute dissolved per liter of solution (that is, the molarity of the solute).

SAMPLE PROBLEM 19.5 Determining K_{sp} from Solubility

Problem (a) Lead(II) sulfate ($PbSO_4$) is a key component in lead-acid car batteries. Its solubility in water at $25^\circ C$ is 4.25×10^{-3} g/100 mL solution. What is the K_{sp} of $PbSO_4$? (b) When lead(II) fluoride (PbF_2) is shaken with pure water at $25^\circ C$, the solubility is found to be 0.64 g/L. Calculate the K_{sp} of PbF_2 .

Plan We are given the solubilities in various units and must find K_{sp} . For each compound, we write an equation for its dissolution to see the number of moles of each ion, and then write the ion-product expression. We convert the solubility to molar solubility, find the molarity of each ion, and substitute into the ion-product expression to calculate K_{sp} .

Solution (a) For $PbSO_4$. Writing the equation and ion-product (K_{sp}) expression:



Converting solubility to molar solubility:

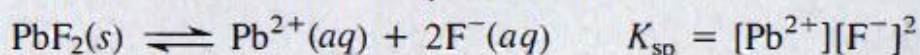
$$\begin{aligned} \text{Molar solubility of } PbSO_4 &= \frac{0.00425 \text{ g } PbSO_4}{100 \text{ mL soln}} \times \frac{1000 \text{ mL}}{1 \text{ L}} \times \frac{1 \text{ mol } PbSO_4}{303.3 \text{ g } PbSO_4} \\ &= 1.40 \times 10^{-4} \text{ M } PbSO_4 \end{aligned}$$

Determining molarities of the ions: Because 1 mol of Pb^{2+} and 1 mol of SO_4^{2-} form when 1 mol of $PbSO_4$ dissolves, $[Pb^{2+}] = [SO_4^{2-}] = 1.40 \times 10^{-4} \text{ M}$.

Calculating K_{sp} :

$$K_{sp} = [Pb^{2+}][SO_4^{2-}] = (1.40 \times 10^{-4})^2 = 1.96 \times 10^{-8}$$

(b) For PbF_2 . Writing the equation and K_{sp} expression:



Converting solubility to molar solubility:

$$\text{Molar solubility of PbF}_2 = \frac{0.64 \text{ g PbF}_2}{1 \text{ L soln}} \times \frac{1 \text{ mol PbF}_2}{245.2 \text{ g PbF}_2} = 2.6 \times 10^{-3} \text{ M PbF}_2$$

Determining molarities of the ions: 1 mol of Pb^{2+} and 2 mol of F^- form when 1 mol of PbF_2 dissolves, so we have

$$[\text{Pb}^{2+}] = 2.6 \times 10^{-3} \text{ M} \quad \text{and} \quad [\text{F}^-] = 2(2.6 \times 10^{-3} \text{ M}) = 5.2 \times 10^{-3} \text{ M}$$

Calculating K_{sp} :

$$K_{\text{sp}} = [\text{Pb}^{2+}][\text{F}^-]^2 = (2.6 \times 10^{-3})(5.2 \times 10^{-3})^2 = 7.0 \times 10^{-8}$$

Check The low solubilities are consistent with K_{sp} values being small. In (a), the molar solubility seems about right: $\sim \frac{4 \times 10^{-2} \text{ g/L}}{3 \times 10^2 \text{ g/mol}} \approx 1.3 \times 10^{-4} \text{ M}$. Squaring this number gives 1.7×10^{-8} , close to the calculated K_{sp} . In (b), we check the final step: $\sim (3 \times 10^{-3})(5 \times 10^{-3})^2 = 7.5 \times 10^{-8}$, close to the calculated K_{sp} .

Comment 1. In part (b), the formula PbF_2 means that $[\text{F}^-]$ is twice $[\text{Pb}^{2+}]$. Then we square this value of $[\text{F}^-]$. Always follow the ion-product expression explicitly.

2. The tabulated K_{sp} values for these compounds (Table 19.2) are lower than our calculated values. For PbF_2 , for instance, the tabulated value is 3.6×10^{-8} , but we calculated 7.0×10^{-8} from solubility data. The discrepancy arises because we assumed that the PbF_2 in solution dissociates completely to Pb^{2+} and F^- . Here is an example of the complexity pointed out at the beginning of this section. Actually, about a third of the PbF_2 dissolves as $\text{PbF}^+(aq)$ and a small amount as undissociated $\text{PbF}_2(aq)$. The solubility (0.64 g/L) is determined experimentally and includes these other species, which we did not include in our simple calculation. This is why we treat such calculated K_{sp} values as approximations.

FOLLOW-UP PROBLEM 19.5 When powdered fluorite (CaF_2) is shaken with pure water at 18°C , $1.5 \times 10^{-4} \text{ g}$ dissolves for every 10.0 mL of solution. Calculate the K_{sp} of CaF_2 at 18°C .

Determining Solubility from K_{sp}

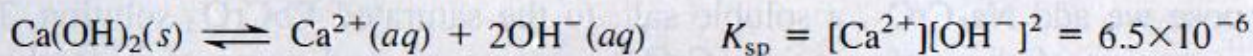
The reverse of the previous type of problem involves finding the solubility of a compound based on its formula and K_{sp} value.

SAMPLE PROBLEM 19.6 Determining Solubility from K_{sp}

Problem Calcium hydroxide (slaked lime) is a major component of mortar, plaster, and cement, and solutions of $\text{Ca}(\text{OH})_2$ are used in industry as a cheap, strong base. Calculate the solubility of $\text{Ca}(\text{OH})_2$ in water if the K_{sp} is 6.5×10^{-6} .

Plan We write the dissolution equation and the ion-product expression. We know K_{sp} (6.5×10^{-6}); to find molar solubility (S), we set up a reaction table that expresses $[Ca^{2+}]$ and $[OH^-]$ in terms of S , substitute into the ion-product expression, and solve for S .

Solution Writing the equation and ion-product expression:



Setting up a reaction table, with S = molar solubility:

Concentration (M)	$Ca(OH)_2(s)$	$\rightleftharpoons$	$Ca^{2+}(aq)$	+	$2OH^-(aq)$
Initial	—		0		0
Change	—		$+S$		$+2S$
Equilibrium	—		S		$2S$

Substituting into the ion-product expression and solving for S :

$$K_{sp} = [Ca^{2+}][OH^-]^2 = (S)(2S)^2 = (S)(4S^2) = 4S^3 = 6.5 \times 10^{-6}$$

$$S = \sqrt[3]{\frac{6.5 \times 10^{-6}}{4}} = 1.2 \times 10^{-2} M$$

Check We expect a low solubility from a slightly soluble salt. If we reverse the calculation, we should obtain the given K_{sp} : $4(1.2 \times 10^{-2})^3 = 6.9 \times 10^{-6}$, close to 6.5×10^{-6} .

Comment 1. Note that we did not double and *then* square $[OH^-]$. $2S$ is the $[OH^-]$, so we just squared it, as the ion-product expression required.

2. Once again, we assumed that the solid dissociates completely. Actually, the solubility is increased to about $2.0 \times 10^{-2} M$ by the presence of $CaOH^+(aq)$ formed in the reaction $Ca(OH)_2(s) \rightleftharpoons CaOH^+(aq) + OH^-(aq)$. Our calculated answer is only approximate because we did not take this other species into account.

FOLLOW-UP PROBLEM 19.6 A suspension of $Mg(OH)_2$ in water is marketed as “milk of magnesia,” which alleviates minor symptoms of indigestion by neutralizing stomach acid. The $[OH^-]$ is too low to harm the mouth and throat, but the suspension dissolves in the acidic stomach juices. What is the molar solubility of $Mg(OH)_2$ ($K_{sp} = 6.3 \times 10^{-10}$) in pure water?

Using K_{sp} Values to Compare Solubilities

The K_{sp} values provide a guide to relative solubility, as long as we compare compounds whose formulas contain the same total number of ions. In such cases, the higher the K_{sp} , the greater the solubility. Table 19.3 shows this point for several compounds. Note that for compounds that form three ions, the relationship holds

whether the cation:anion ratio is 1:2 or 2:1, because the mathematical expression containing S is the same ($4S^3$) in the calculation (see Sample Problem 19.6).

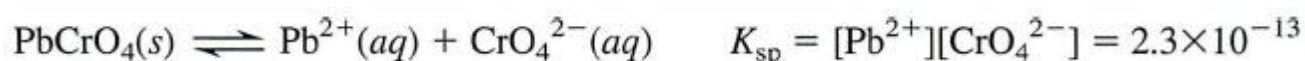
Table 19.3 Relationship Between K_{sp} and Solubility at 25°C

No. of Ions	Formula	Cation:Anion	K_{sp}	Solubility (M)
2	MgCO ₃	1:1	3.5×10^{-8}	1.9×10^{-4}
2	PbSO ₄	1:1	1.6×10^{-8}	1.3×10^{-4}
2	BaCrO ₄	1:1	2.1×10^{-10}	1.4×10^{-5}
3	Ca(OH) ₂	1:2	6.5×10^{-6}	1.2×10^{-2}
3	BaF ₂	1:2	1.5×10^{-6}	7.2×10^{-3}
3	CaF ₂	1:2	3.2×10^{-11}	2.0×10^{-4}
3	Ag ₂ CrO ₄	2:1	2.6×10^{-12}	8.7×10^{-5}

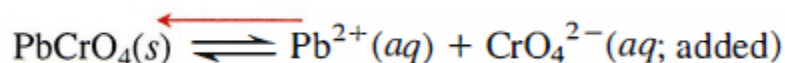
The Effect of a Common Ion on Solubility

The presence of a common ion **decreases the solubility** of a slightly soluble ionic compound.

Let's examine the equilibrium condition for a saturated solution of lead(II) chromate:



- Suppose we add Na₂CrO₄, a soluble salt, to the saturated PbCrO₄ solution. The concentration of the **common ion**, CrO₄²⁻, increases, and some of it combines with Pb²⁺ ion to form more solid PbCrO₄ (Figure 19.10). The overall effect is a shift in the position of equilibrium to the left:



- We also obtain this result by adding a soluble lead(II) salt, such as Pb(NO₃)₂. The added Pb²⁺ ion combines with some CrO₄²⁻ (aq), thereby lowering the amount of dissolved PbCrO₄. In this case Pb²⁺ ion is the **common ion**.

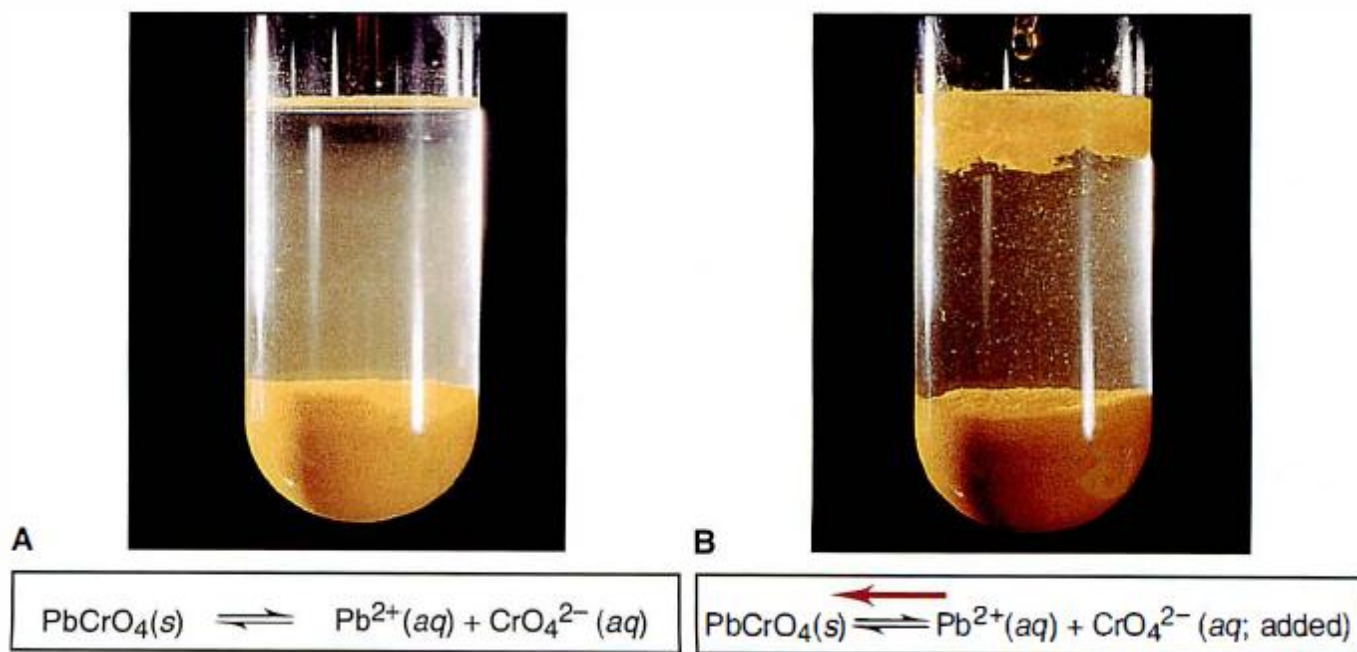


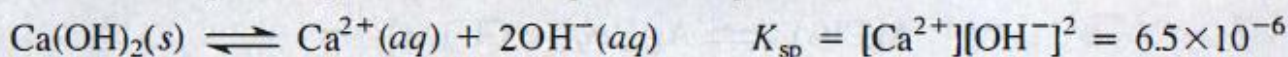
Figure 19.10 The effect of a common ion on solubility. When a common ion is added to a saturated solution of an ionic compound, the solubility is lowered and more of the compound precipitates. A, Lead(II) chromate, a slightly soluble salt, forms a saturated aqueous solution. B, When Na_2CrO_4 solution is added, the amount of $\text{PbCrO}_4(s)$ increases. Thus, PbCrO_4 is less soluble in the presence of the common ion CrO_4^{2-} .

SAMPLE PROBLEM 19.7 Calculating the Effect of a Common Ion on Solubility

Problem In Sample Problem 19.6, we calculated the solubility of $\text{Ca}(\text{OH})_2$ in water. What is its solubility in 0.10 M $\text{Ca}(\text{NO}_3)_2$? K_{sp} of $\text{Ca}(\text{OH})_2$ is 6.5×10^{-6} .

Plan Addition of Ca^{2+} , the common ion, should lower the solubility. We write the equation and ion-product expression and set up a reaction table, with $[\text{Ca}^{2+}]_{\text{init}}$ coming from $\text{Ca}(\text{NO}_3)_2$ and S equal to $[\text{Ca}^{2+}]_{\text{from Ca}(\text{OH})_2}$. To simplify the math, we assume that, because K_{sp} is low, S is so small relative to $[\text{Ca}^{2+}]_{\text{init}}$ that it can be neglected. Then we solve for S and check the assumption.

Solution Writing the equation and ion-product expression:



Setting up the reaction table, with $S = [\text{Ca}^{2+}]_{\text{from Ca}(\text{OH})_2}$:

Concentration (M)	$\text{Ca}(\text{OH})_2(s)$	$\rightleftharpoons$	$\text{Ca}^{2+}(aq)$	+	$2\text{OH}^-(aq)$
Initial	—		0.10		0
Change	—		+S		+2S
Equilibrium	—		$0.10 + S$		2S

Making the assumption: K_{sp} is small, so $S \ll 0.10\text{ M}$; thus, $0.10\text{ M} + S \approx 0.10\text{ M}$. Substituting into the ion-product expression and solving for S :

$$K_{sp} = [\text{Ca}^{2+}][\text{OH}^-]^2 = 6.5 \times 10^{-6} \approx (0.10)(2S)^2$$

Therefore,

$$4S^2 \approx \frac{6.5 \times 10^{-6}}{0.10} \quad \text{so} \quad S \approx \sqrt{\frac{6.5 \times 10^{-6}}{4}} = 4.0 \times 10^{-3}\text{ M}$$

Checking the assumption:

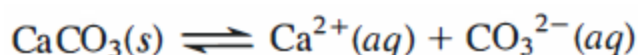
$$\frac{4.0 \times 10^{-3}\text{ M}}{0.10\text{ M}} \times 100 = 4.0\% < 5\%$$

Check In Sample Problem 19.6, the solubility of $\text{Ca}(\text{OH})_2$ was 0.012 M , but here, it is 0.0040 M , so the solubility *decreased* in the presence of added Ca^{2+} , the common ion, as expected.

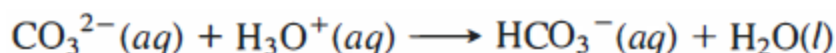
FOLLOW-UP PROBLEM 19.7 To improve the quality of x-ray images used in the diagnosis of intestinal disorders, the patient drinks an aqueous suspension of BaSO_4 before the x-ray procedure. The Ba^{2+} in the suspension is opaque to x-rays, but it is also toxic; thus, the Ba^{2+} concentration is lowered by the addition of dilute Na_2SO_4 . What is the solubility of BaSO_4 ($K_{sp} = 1.1 \times 10^{-10}$) in (a) pure water and in (b) $0.10\text{ M Na}_2\text{SO}_4$?

The Effect of pH on Solubility

The hydronium ion concentration can have a profound effect on the solubility of an ionic compound. In a saturated solution of CaCO_3 , we have

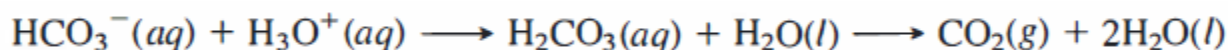


- Adding some strong acid introduces a large amount of H_3O^+ , which immediately reacts with CO_3^{2-} to form the weak acid HCO_3^- :

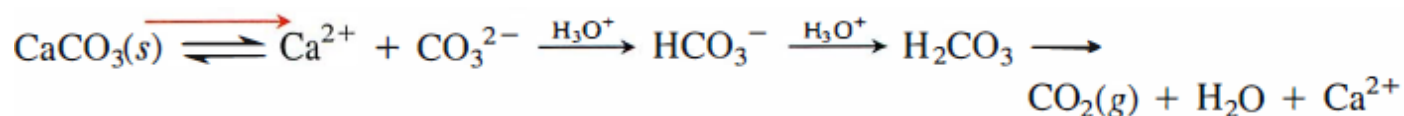


Thus, **more CaCO_3 dissolves**.

- If enough H_3O^+ is added, further reaction occurs to form carbonic acid, which decomposes immediately to H_2O and CO_2 , and the gas escapes the container:

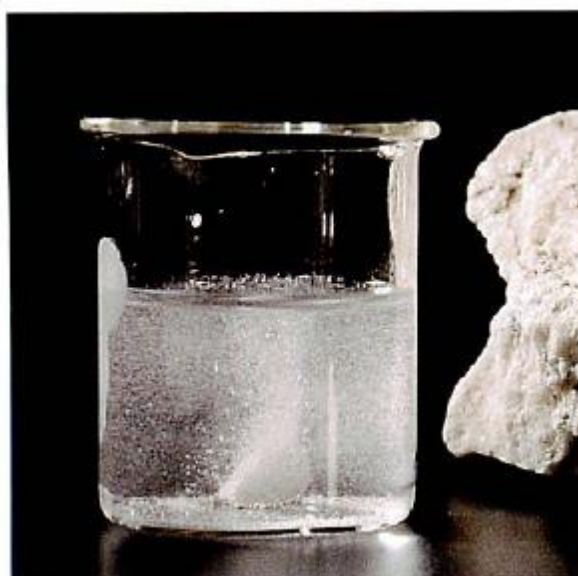


As this sequence of changes shows, the net effect of added H_3O^+ is a shift in the equilibrium position to the right:

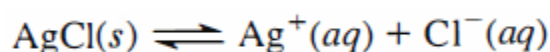


In fact, this example illustrates a qualitative field test for carbonate minerals because the CO_2 bubbles vigorously (Figure 19.11).

Figure 19.11 Test for the presence of a carbonate. When a mineral that contains carbonate ion is treated with strong acid, the added H_3O^+ shifts the equilibrium position of the carbonate solubility. More carbonate dissolves, and the carbonic acid that is formed breaks down to water and gaseous CO_2 .



In contrast, adding H_3O^+ to a saturated solution of a compound with a strong acid anion, such as silver chloride, has no effect on the equilibrium position:



Because Cl^- ion is the conjugate base of a strong acid (HCl), it can coexist in solution with high $[\text{H}_3\text{O}^+]$. The Cl^- does not leave the system, so the equilibrium position is not affected.

SAMPLE PROBLEM 19.8 Predicting the Effect on Solubility of Adding Strong Acid

Problem Write balanced equations to explain whether addition of H_3O^+ from a strong acid affects the solubility of these ionic compounds:

- (a) Lead(II) bromide (b) Copper(II) hydroxide (c) Iron(II) sulfide

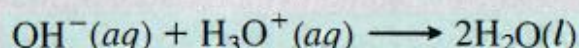
Plan We write the balanced dissolution equation and note the anion: Weak-acid anions react with H_3O^+ and shift the equilibrium position toward more dissolution. Strong-acid anions do not react, so added H_3O^+ has no effect.

Solution (a) $\text{PbBr}_2(s) \rightleftharpoons \text{Pb}^{2+}(aq) + 2\text{Br}^-(aq)$

No effect. Br^- is the anion of HBr , a strong acid, so it does not react with H_3O^+ .

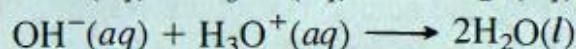
(b) $\text{Cu}(\text{OH})_2(s) \rightleftharpoons \text{Cu}^{2+}(aq) + 2\text{OH}^-(aq)$

Increases solubility. OH^- is the anion of H_2O , a very weak acid, so it reacts with the added H_3O^+ :



(c) $\text{FeS}(s) + \text{H}_2\text{O}(l) \rightleftharpoons \text{Fe}^{2+}(aq) + \text{HS}^-(aq) + \text{OH}^-(aq)$

Increases solubility. We noted earlier that the S^{2-} ion reacts immediately with water to form HS^- and OH^- . The added H_3O^+ reacts with both of these weak-acid anions:



FOLLOW-UP PROBLEM 19.8 Write balanced equations to show how addition of $\text{HNO}_3(aq)$ affects the solubility of these ionic compounds:

(a) Calcium fluoride (b) Zinc sulfide (c) Silver iodide

Predicting the Formation of a Precipitate: Q_{sp} vs. K_{sp}

- $Q_{\text{sp}} = K_{\text{sp}}$: solution is saturated and no change occurs.
- $Q_{\text{sp}} > K_{\text{sp}}$: precipitate forms until solution is saturated.
- $Q_{\text{sp}} < K_{\text{sp}}$: solution is unsaturated and no precipitate forms.

SAMPLE PROBLEM 19.9 Predicting Whether a Precipitate Will Form

Problem A common laboratory method for preparing a precipitate is to mix solutions containing the component ions. Does a precipitate form when 0.100 L of 0.30 M $\text{Ca}(\text{NO}_3)_2$ is mixed with 0.200 L of 0.060 M NaF ?

Plan First, we must decide which slightly soluble salt could form and look up its K_{sp} value in Appendix C. To see whether mixing these solutions will form the precipitate, we find the ion concentrations by calculating the amount (mol) of each ion from its concentration and volume, and then dividing by the *total* volume because one solution dilutes the other. Finally, we write the ion-product expression, calculate Q_{sp} , and compare Q_{sp} with K_{sp} .

Solution The ions present are Ca^{2+} , Na^+ , F^- , and NO_3^- . All sodium and all nitrate salts are soluble (Table 4.1), so the only possibility is CaF_2 ($K_{\text{sp}} = 3.2 \times 10^{-11}$).

Calculating the ion concentrations:

$$\begin{aligned}\text{Moles of } \text{Ca}^{2+} &= 0.30 \text{ M } \text{Ca}^{2+} \times 0.100 \text{ L} \\ &= 0.030 \text{ mol } \text{Ca}^{2+}\end{aligned}$$

$$\begin{aligned}[\text{Ca}^{2+}] &= \frac{0.030 \text{ mol } \text{Ca}^{2+}}{0.100 \text{ L} + 0.200 \text{ L}} \\ &= 0.10 \text{ M } \text{Ca}^{2+}\end{aligned}$$

$$\begin{aligned}\text{Moles of } \text{F}^- &= 0.060 \text{ M } \text{F}^- \times 0.200 \text{ L} \\ &= 0.012 \text{ mol } \text{F}^-\end{aligned}$$

$$\begin{aligned}[\text{F}^-] &= \frac{0.012 \text{ mol } \text{F}^-}{0.100 \text{ L} + 0.200 \text{ L}} \\ &= 0.040 \text{ M } \text{F}^-\end{aligned}$$

Substituting into the ion-product expression and comparing Q_{sp} with K_{sp} :

$$Q_{\text{sp}} = [\text{Ca}^{2+}][\text{F}^-]^2 = (0.10)(0.040)^2 = 1.6 \times 10^{-4}$$

Because $Q_{\text{sp}} > K_{\text{sp}}$, CaF_2 will precipitate until $Q_{\text{sp}} = 3.2 \times 10^{-11}$.

Check Remember to round off and quickly check the math. For example, $Q_{\text{sp}} = (1 \times 10^{-1})(4 \times 10^{-2})^2 = 1.6 \times 10^{-4}$. With K_{sp} so low, CaF_2 must have a low solubility, and given the sizable concentrations being mixed, we would expect CaF_2 to precipitate.

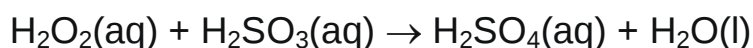
FOLLOW-UP PROBLEM 19.9 As a result of mineral erosion and biological activity, phosphate ion is common in natural waters, where it often precipitates as insoluble salts, such as $\text{Ca}_3(\text{PO}_4)_2$. If $[\text{Ca}^{2+}] = [\text{PO}_4^{3-}] = 1.0 \times 10^{-9} \text{ M}$ in a given river, will $\text{Ca}_3(\text{PO}_4)_2$ precipitate? K_{sp} of $\text{Ca}_3(\text{PO}_4)_2$ is 1.2×10^{-29} .

Applying Ionic Equilibria to the Acid-Rain Problem

Three major substances are involved in acid rain:

1. Sulfurous acid

Sulfur dioxide (SO_2) from the burning of high-sulfur coal forms sulfurous acid in contact with water. Oxidizing air pollutants, such as hydrogen peroxide, convert sulfurous acid to sulfuric acid:



2. Sulfuric acid

Sulfur trioxide (SO_3) forms through the atmospheric oxidation of SO_2 and becomes H_2SO_4 in contact with water.

3. Nitric acid

Nitrogen oxides (denoted NO_x) form when N_2 and O_2 react. NO is produced during combustion in car engines and electric power plants, and then forms NO_2 and HNO_3 . At night, NO_x are converted to N_2O_5 , which hydrolyzes to HNO_3 in water.

Figure 19.12 illustrates some of the main sources of the two strong acids.

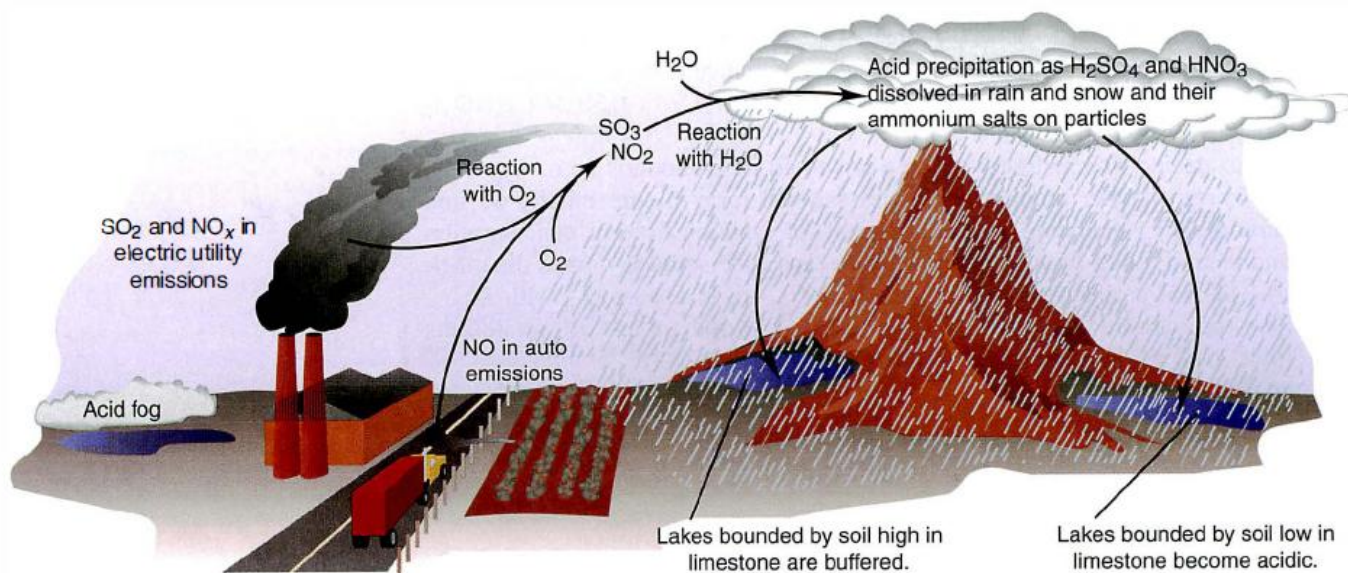
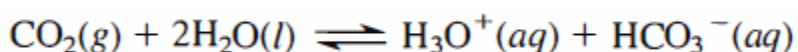


Figure 19.12 Formation of acidic precipitation. A complex interplay of human activities, atmospheric chemistry, and environmental distribution leads to acidic precipitation and its harmful effects. Car exhaust and electrical utility waste gases contain lower oxides of nitrogen and sulfur. These are oxidized in the atmosphere by O_2 (or O_3 , not shown) to higher oxides (NO_2 , SO_3), which react with moisture to form acidic rain, snow, and fog. In contact with acidic precipitation, many lakes become acidified, whereas limestone-bounded lakes form a carbonate buffer that prevents acidification.

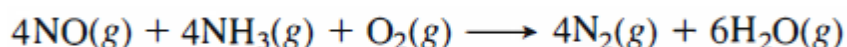
- Unpolluted rainwater is weakly acidic ($\text{pH} = 5.6$) because it contains dissolved CO_2 :



- In contrast, the average pH of rainfall in much of the United States was 4.2 as early as 1984; rain with a pH of 2.7 (about the same as vinegar) has been observed in Sweden and with a pH of 1.8 (between lemon juice and stomach acid) in West Virginia.
- These 10- to 10,000-fold excesses of $[\text{H}_3\text{O}^+]$ are very destructive to fish (many species die at a pH below 5) and to forests.
- Acid rain also dissolves the calcium carbonate in the marble and limestone of buildings and monuments.
- SO_2 is removed from power-plant emissions with limestone or, in a newer method, it is partially reduced to H_2S and then converted to sulfur:



- The catalytic converter in an automobile exhaust system reduces NO_x to N_2 and NH_3 , and in power plants, NO_x is removed from the hot stack gases with ammonia:

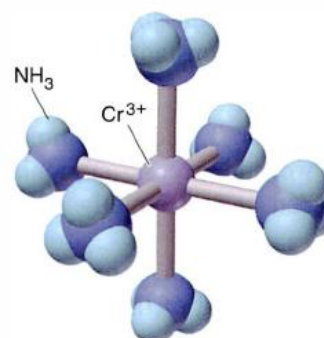


19.4 EQUILIBRIA INVOLVING COMPLEX IONS

A **complex ion** consists of a **central metal ion** covalently bonded to two or more anions or molecules, called **ligands**.

- ionic ligands: e.g. hydroxide, chloride, and cyanide ions
- molecular ligands: e.g. water, carbon monoxide, and ammonia

Figure 19.13 $\text{Cr}(\text{NH}_3)_6^{3+}$, a typical complex ion. A complex ion consists of a central metal ion, such as Cr^{3+} , covalently bonded to a specific number of ligands, such as NH_3 .



As we discussed in Section 18.8, all complex ions are **Lewis adducts**. The *metal ion acts as a Lewis acid* (accepts an electron pair) and *the ligand acts as a Lewis base* (donates an electron pair).

Formation of Complex Ions

Whenever a metal ion enters water, a complex ion forms, with water as the ligand. In many cases, when we treat this hydrated cation with a solution of another ligand, the bound water molecules exchange for the other ligand.

For example;



$$K_c = \frac{[\text{M}(\text{NH}_3)_4^{2+}][\text{H}_2\text{O}]^4}{[\text{M}(\text{H}_2\text{O})_4^{2+}][\text{NH}_3]^4}$$

Once again, because the concentration of water is essentially constant in aqueous reactions, we incorporate it into K_c and obtain the expression for a new equilibrium constant, the **formation constant, K_f** :

$$K_f = \frac{K_c}{[\text{H}_2\text{O}]^4} = \frac{[\text{M}(\text{NH}_3)_4^{2+}]}{[\text{M}(\text{H}_2\text{O})_4^{2+}][\text{NH}_3]^4}$$

At the molecular level (Figure 19.14), the **actual process is stepwise**:



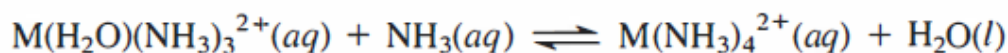
$$K_{f1} = \frac{[\text{M}(\text{H}_2\text{O})_3(\text{NH}_3)^{2+}]}{[\text{M}(\text{H}_2\text{O})_4^{2+}][\text{NH}_3]}$$



$$K_{f2} = \frac{[\text{M}(\text{H}_2\text{O})_2(\text{NH}_3)_2^{2+}]}{[\text{M}(\text{H}_2\text{O})_3(\text{NH}_3)^{2+}][\text{NH}_3]}$$



$$K_{f3} = \frac{[\text{M}(\text{H}_2\text{O})(\text{NH}_3)_3^{2+}]}{[\text{M}(\text{H}_2\text{O})_2(\text{NH}_3)_2^{2+}][\text{NH}_3]}$$



$$K_{f4} = \frac{[\text{M}(\text{NH}_3)_4^{2+}]}{[\text{M}(\text{H}_2\text{O})(\text{NH}_3)_3^{2+}][\text{NH}_3]}$$

The sum of the equations gives the overall equation, so the product of the individual formation constants gives the overall formation constant:

$$K_f = K_{f1} \times K_{f2} \times K_{f3} \times K_{f4}$$

Appendix C shows the formation constants (K_f) of several complex ions; note that all are 10^6 or greater, which means that the equilibria of the formation reactions lie far to the right.

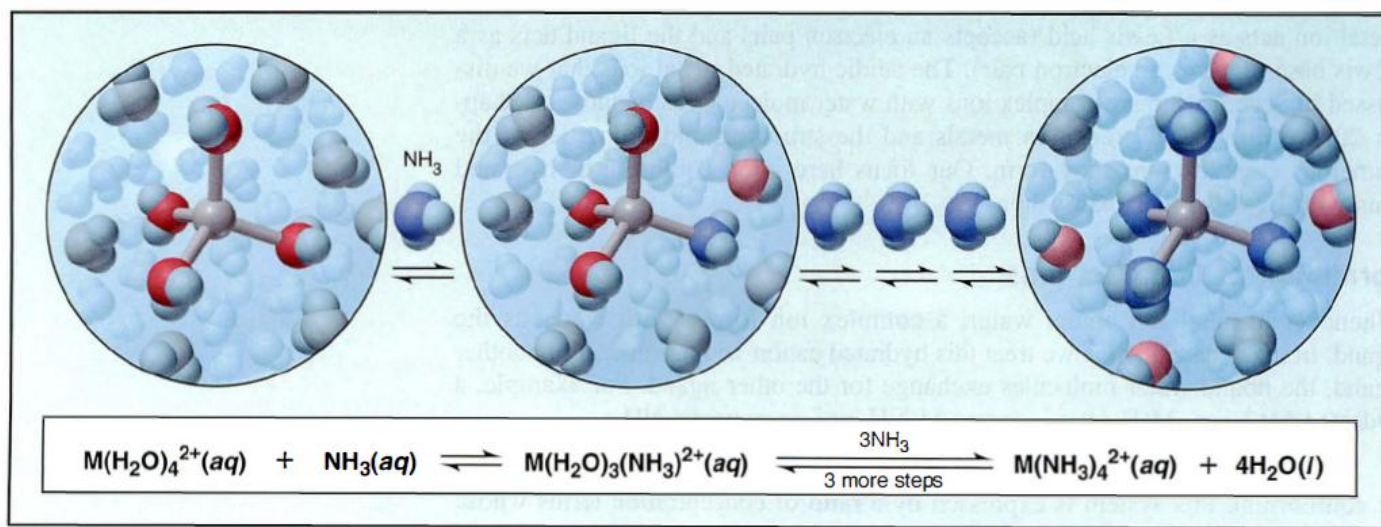
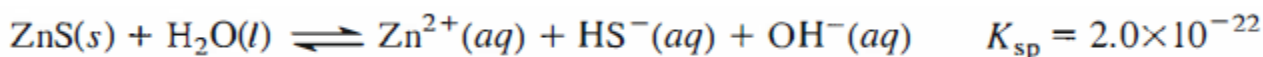


Figure 19.14 The stepwise exchange of NH_3 for H_2O in $\text{M}(\text{H}_2\text{O})_4^{2+}$. The ligands of a complex ion can exchange for other ligands. When ammonia is added to a solution of the hydrated M^{2+} ion, $\text{M}(\text{H}_2\text{O})_4^{2+}$, NH_3 molecules replace the bound H_2O molecules one at a time to form the $\text{M}(\text{NH}_3)_4^{2+}$ ion. The molecular-scale views show the first exchange and the fully ammoniated ion.

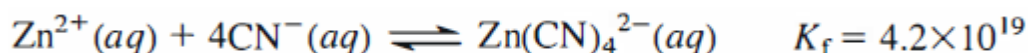
Complex Ions and the Solubility of Precipitates

A ligand **increases the solubility** of a slightly soluble ionic compound if it forms a complex ion with the cation.

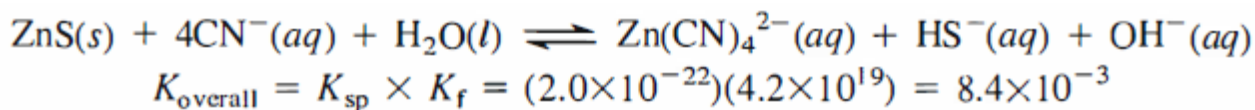
For example, zinc sulfide is very slightly soluble:



When we add some 1.0 M NaCN, the CN^{-} ions act as ligands and react with the small amount of $\text{Zn}^{2+}(\text{aq})$ to form the complex ion $\text{Zn}(\text{CN})_4^{2-}$:



To see the effect of complex-ion formation on the solubility of ZnS, we add the equations and, therefore, multiply their equilibrium constants:



The overall equilibrium constant increased by more than a factor of 10^{19} in the presence of the ligand; this reflects the increased amount of ZnS in solution.

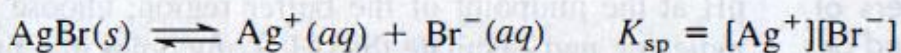
SAMPLE PROBLEM 19.10

Calculating the Effect of Complex-Ion Formation on Solubility

Problem In black-and-white film developing, excess AgBr is removed from the film negative by “hypo,” an aqueous solution of sodium thiosulfate ($\text{Na}_2\text{S}_2\text{O}_3$), which forms the complex ion $\text{Ag}(\text{S}_2\text{O}_3)_2^{3-}$. Calculate the solubility of AgBr in (a) H_2O ; (b) 1.0 M hypo. K_f of $\text{Ag}(\text{S}_2\text{O}_3)_2^{3-}$ is 4.7×10^{13} and K_{sp} of AgBr is 5.0×10^{-13} .

Plan (a) After writing the equation and the ion-product expression, we use the given K_{sp} to solve for S , the molar solubility of AgBr. (b) In hypo, Ag^+ forms a complex ion with $\text{S}_2\text{O}_3^{2-}$, which shifts the equilibrium and dissolves more AgBr. We write the complex-ion equation and add it to the equation for dissolving AgBr to obtain the overall equation for dissolving AgBr in hypo. We multiply K_{sp} by K_f to find K_{overall} . To find the solubility of AgBr in hypo, we set up a reaction table, with $S = [\text{Ag}(\text{S}_2\text{O}_3)_2^{3-}]$, substitute into the expression for K_{overall} , and solve for S .

Solution (a) Solubility in water. Writing the equation for the saturated solution and the ion-product expression:



Solving for solubility (S) directly from the equation: We know that

$$S = [\text{AgBr}]_{\text{dissolved}} = [\text{Ag}^+] = [\text{Br}^-]$$

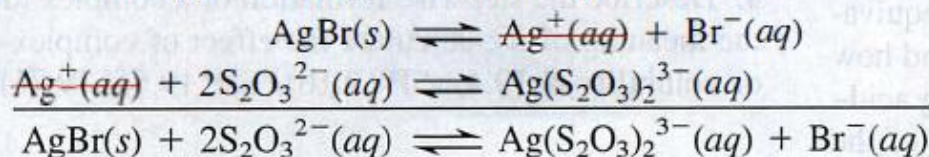
Thus,

$$K_{\text{sp}} = [\text{Ag}^+][\text{Br}^-] = S^2 = 5.0 \times 10^{-13}$$

so

$$S = 7.1 \times 10^{-7} \text{ M}$$

(b) Solubility in 1.0 M hypo. Writing the overall equation:



Calculating K_{overall} :

$$K_{\text{overall}} = \frac{[\text{Ag}(\text{S}_2\text{O}_3)_2^{3-}][\text{Br}^-]}{[\text{S}_2\text{O}_3^{2-}]^2} = K_{\text{sp}} \times K_f = (5.0 \times 10^{-13})(4.7 \times 10^{13}) = 24$$

Setting up a reaction table, with $S = [\text{AgBr}]_{\text{dissolved}} = [\text{Ag}(\text{S}_2\text{O}_3)_2^{3-}]$:

Concentration (M)	$\text{AgBr}(s)$	+	$2\text{S}_2\text{O}_3^{2-}(aq)$	$\rightleftharpoons$	$\text{Ag}(\text{S}_2\text{O}_3)_2^{3-}(aq)$	+	$\text{Br}^-(aq)$
Initial	—		1.0		0		0
Change	—		$-2S$		$+S$		$+S$
Equilibrium	—		$1.0 - 2S$		S		S

Substituting the values into the expression for K_{overall} and solving for S :

$$K_{\text{overall}} = \frac{[\text{Ag}(\text{S}_2\text{O}_3)_2^{3-}][\text{Br}^-]}{[\text{S}_2\text{O}_3^{2-}]^2} = \frac{S^2}{(1.0 M - 2S)^2} = 24$$

Taking the square root of both sides gives

$$\frac{S}{1.0 M - 2S} = \sqrt{24} = 4.9 \quad [\text{Ag}(\text{S}_2\text{O}_3)_2^{3-}] = S = 0.45 M$$

Check (a) From the number of ions in the formula of AgBr , we know that $S = \sqrt{K_{\text{sp}}}$ so the order of magnitude seems right: $\sim \sqrt{10^{-14}} = 10^{-7}$. **(b)** The K_{overall} seems correct: the exponents cancel, and $5 \times 5 = 25$. Most importantly, the answer makes sense because the photographic process requires the remaining AgBr to be washed off the film and the large K_{overall} confirms that. We can check S by rounding and working backward to find K_{overall} : from the reaction table, we find that

$$[\text{S}_2\text{O}_3^{2-}] = 1.0 M - 2S = 1.0 M - 2(0.45 M) = 1.0 M - 0.90 M = 0.1 M$$

so $K_{\text{overall}} \approx (0.45)^2 / (0.1)^2 = 20$, within rounding of the calculated value.

FOLLOW-UP PROBLEM 19.10 How does the solubility of AgBr in $1.0 M \text{NH}_3$ compare with its solubility in hypo? K_f of $\text{Ag}(\text{NH}_3)_2^+$ is 1.7×10^7 .