Sample Exercise 17.1 Calculating the pH When a Common Ion is Involved

What is the pH of a solution made by adding 0.30 mol of acetic acid and 0.30 mol of sodium acetate to enough water to make 1.0 L of solution?

Solution

**Analyze:** We are asked to determine the pH of a solution of a weak electrolyte (CH₃COOH) and a strong electrolyte (CH₃COONa) that share a common ion, CH₃COO⁻.

**Plan:** In any problem in which we must determine the pH of a solution containing a mixture of solutes, it is helpful to proceed by a series of logical steps:

1. Consider which solutes are strong electrolytes and which are weak electrolytes, and identify the major species in solution.
2. Identify the important equilibrium that is the source of H⁺ and therefore determines pH.
3. Tabulate the concentrations of ions involved in the equilibrium.
4. Use the equilibrium-constant expression to calculate [H⁺] and then pH.

**Solve:** First, because CH₃COOH is a weak electrolyte and CH₃COONa is a strong electrolyte, the major species in the solution are CH₃COOH (a weak acid), Na⁺ (which is neither acidic nor basic and is therefore a spectator in the acid–base chemistry), and CH₃COO⁻ (which is the conjugate base of CH₃COOH).

Second, [H⁺] and, therefore, the pH are controlled by the dissociation equilibrium of CH₃COOH:

(We have written the equilibrium Using H⁺(aq) rather than H₃O⁺(aq) but both representations of the hydrated hydrogen ion are equally valid.)

\[
\text{CH₃COOH(aq)} \rightleftharpoons \text{H⁺(aq)} + \text{CH₃COO⁻(aq)}
\]
Sample Exercise 17.1 Calculating the pH When a Common Ion is Involved

Solution (Continued)

Third, we tabulate the initial and equilibrium concentrations as we did in solving other equilibrium problems in Chapters 15 and 16:

<table>
<thead>
<tr>
<th></th>
<th>CH₃COOH(aq)</th>
<th>H⁺(aq)</th>
<th>CH₃COO⁻(aq)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial</td>
<td>0.30 M</td>
<td>0</td>
<td>0.30 M</td>
</tr>
<tr>
<td>Change</td>
<td>−x M</td>
<td>+x M</td>
<td>+x M</td>
</tr>
<tr>
<td>Equilibrium</td>
<td>(0.30 − x) M</td>
<td>x M</td>
<td>(0.30 + x) M</td>
</tr>
</tbody>
</table>

The equilibrium concentration of CH₃COO⁻ (the common ion) is the initial concentration that is due to CH₃COONa (0.30 M) plus the change in concentration (x) that is due to the ionization of CH₃COOH.

Now we can use the equilibrium-constant expression:

\[ K_a = 1.8 \times 10^{-5} = \frac{[H^+][CH₃COO^-]}{[CH₃COOH]} \]

(The dissociation constant for CH₃COOH at 25 °C is from Appendix D; addition of CH₃COONa does not change the value of this constant.) Substituting the equilibrium-constant concentrations from our table into the equilibrium expression gives

\[ K_a = 1.8 \times 10^{-5} = \frac{x(0.30 + x)}{0.30 - x} \]
Sample Exercise 17.1 Calculating the pH When a Common Ion is Involved

Solution (Continued)

Because $K_a$ is small, we assume that $x$ is small compared to the original concentrations of CH$_3$COOH and CH$_3$COO$^-$ (0.30 M each). Thus, we can ignore the very small $x$ relative to 0.30 M, giving

The resulting value of $x$ is indeed small relative to 0.30, justifying the approximation made in simplifying the problem.

Finally, we calculate the pH from the equilibrium concentration of H$^+$(aq):

Comment: In Section 16.6 we calculated that a 0.30 M solution of CH$_3$COOH has a pH of 2.64, corresponding to $[H^+] = 2.3 \times 10^{-3}$ M. Thus, the addition of CH$_3$COONa has substantially decreased $[H^+]$ as we would expect from Le Châtelier’s principle.

Practice Exercise

Calculate the pH of a solution containing 0.085 M nitrous acid (HNO$_2$; $K_a = 4.5 \times 10^{-4}$) and 0.10 M potassium nitrite (KNO$_2$).

Answer: 3.42
Sample Exercise 17.2 Calculating Ion Concentrations When a Common is Involved

Calculate the fluoride ion concentration and pH of a solution that is 0.20 \( M \) in HF and 0.10 \( M \) in HCl.

Solution

Plan: We can again use the four steps outlined in Sample Exercise 17.1.

Solve: Because HF is a weak acid and HCl is a strong acid, the major species in solution are HF, H\( ^+ \), and Cl\( ^- \). The Cl\( ^- \), which is the conjugate base of a strong acid, is merely a spectator ion in any acid–base chemistry. The problem asks for [F\( ^- \)], which is formed by ionization of HF. Thus, the important equilibrium is

\[
\text{HF}(aq) \rightleftharpoons \text{H}^+(aq) + \text{F}^-(aq)
\]

The common ion in this problem is the hydrogen (or hydronium) ion. Now we can tabulate the initial and equilibrium concentrations of each species involved in this equilibrium:

<table>
<thead>
<tr>
<th></th>
<th>Initial</th>
<th>Change</th>
<th>Equilibrium</th>
</tr>
</thead>
<tbody>
<tr>
<td>[HF]</td>
<td>0.20 ( M )</td>
<td>- ( x ) ( M )</td>
<td>(0.20 - ( x )) ( M )</td>
</tr>
<tr>
<td>[H( ^+ )]</td>
<td>0.10 ( M )</td>
<td>+ ( x ) ( M )</td>
<td>(0.10 + ( x )) ( M )</td>
</tr>
<tr>
<td>[F( ^- )]</td>
<td>0</td>
<td>+ ( x ) ( M )</td>
<td>( x ) ( M )</td>
</tr>
</tbody>
</table>

The equilibrium constant for the ionization of HF, from Appendix D, is 6.8 \( \times \) 10\( ^{-4} \). Substituting the equilibrium-constant concentrations into the equilibrium expression gives

\[
K_a = 6.8 \times 10^{-4} = \frac{[\text{H}^+][\text{F}^-]}{[\text{HF}]} = \frac{(0.10 + x)(x)}{0.20 - x}
\]

\[
\frac{(0.10)(x)}{0.20} = 6.8 \times 10^{-4}
\]

\[
x = \frac{0.20}{0.10} (6.8 \times 10^{-4}) = 1.4 \times 10^{-3} \, \text{M} = [\text{F}^-]
\]
Sample Exercise 17.2 Calculating Ion Concentrations When a Common is Involved

Solution (Continued)

If we assume that $x$ is small relative to 0.10 or 0.20 $M$, this expression simplifies to

$$[H^+] = (0.10 + x) M \approx 0.10 M$$

Thus,

$$pH = 1.00$$

This $F^-$ concentration is substantially smaller than it would be in a 0.20 $M$ solution of HF with no added HCl. The common ion, $H^+$, suppresses the ionization of HF. The concentration of $H^+(aq)$ is

Comment: Notice that for all practical purposes, $[H^+]$ is due entirely to the HCl; the HF makes a negligible contribution by comparison.

Practice Exercise

Calculate the formate ion concentration and pH of a solution that is 0.050 $M$ in formic acid (HCOOH; $K_a = 1.8 \times 10^{-4}$) and 0.10 $M$ in HNO$_3$.

Answer: $[HCOO^-] = 9.0 \times 10^{-5}$; pH = 1.00
Sample Exercise 17.3 Calculating the pH of a Buffer

What is the pH of a buffer that is 0.12 M in lactic acid [CH₃CH(OH)COOH, or HC₃H₅O₃] and 0.10 M in sodium lactate [CH₃CH(OH)COONa or NaC₃H₅O₃]? For lactic acid, $K_a = 1.4 \times 10^{-4}$.

**Solution**

**Analyze:** We are asked to calculate the pH of a buffer containing lactic acid HC₃H₅O₃ and its conjugate base, the lactate ion (C₃H₅O₃⁻).

**Plan:** We will first determine the pH using the method described in Section 17.1. Because HC₃H₅O₃ is a weak electrolyte and NaC₃H₅O₃ is a strong electrolyte, the major species in solution are HC₃H₅O₃, Na⁺, and C₃H₅O₃⁻. The Na⁺ ion is a spectator ion. The HC₃H₅O₃–C₃H₅O₃⁻ conjugate acid–base pair determines [H⁺] and thus pH; [H⁺] can be determined using the acid dissociation equilibrium of lactic acid.

**Solve:** The initial and equilibrium concentrations of the species involved in this equilibrium are

<table>
<thead>
<tr>
<th></th>
<th>HC₃H₅O₃(aq)</th>
<th>H⁺(aq)</th>
<th>C₃H₅O₃⁻(aq)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial</td>
<td>0.12 M</td>
<td>0</td>
<td>0.10 M</td>
</tr>
<tr>
<td>Change</td>
<td>−x M</td>
<td>+x M</td>
<td>+x M</td>
</tr>
<tr>
<td>Equilibrium</td>
<td>(0.12 − x) M</td>
<td>x M</td>
<td>(0.10 + x) M</td>
</tr>
</tbody>
</table>

The equilibrium concentrations are governed by the equilibrium expression:

$$K_a = 1.4 \times 10^{-4} = \frac{[H^+][C_3H_5O_3^-]}{[HC_3H_5O_3]} = \frac{x(0.10 + x)}{(0.12 - x)}$$
Sample Exercise 17.3 Calculating the pH of a Buffer

Solution (Continued)

Because $K_a$ is small and a common ion is present, we expect $x$ to be small relative to either 0.12 or 0.10 M. Thus, our equation can be simplified to give

$$K_a = 1.4 \times 10^{-4} = \frac{x(0.10)}{0.12}$$

$$[H^+] = x = \left(\frac{0.12}{0.10}\right)(1.4 \times 10^{-4}) = 1.7 \times 10^{-4} \text{ M}$$

$$\text{pH} = -\log(1.7 \times 10^{-4}) = 3.77$$

Alternatively, we could have used the Henderson–Hasselbalch equation to calculate pH directly:

$$\text{pH} = pK_a + \log\left(\frac{[\text{base}]}{[\text{acid}]}\right) = 3.85 + \log\left(\frac{0.10}{0.12}\right)$$

$$= 3.85 + (-0.08) = 3.77$$

Practice Exercise

Calculate the pH of a buffer composed of 0.12 M benzoic acid and 0.20 M sodium benzoate. (Refer to Appendix D.)

Answer: 4.42
Sample Exercise 17.4 Preparing a Buffer

How many moles of NH₄Cl must be added to 2.0 L of 0.10 M NH₃ to form a buffer whose pH is 9.00? (Assume that the addition of NH₄Cl does not change the volume of the solution.)

Solution

**Analyze:** Here we are asked to determine the amount of NH₄⁺ ion required to prepare a buffer of a specific pH.

**Plan:** The major species in the solution will be NH₄⁺, Cl⁻, and NH₃. Of these, the ion is a spectator (it is the conjugate base of a strong acid). Thus, the NH₄⁺–NH₃ conjugate acid–base pair will determine the pH of the buffer solution. The equilibrium relationship between NH₄⁺ and NH₃ is given by the basedissociation constant for NH₃:

\[
\text{NH}_3(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{NH}_4^+(aq) + \text{OH}^-(aq) \quad K_b = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]} = 1.8 \times 10^{-5}
\]

The key to this exercise is to use this \(K_b\) expression to calculate \([\text{NH}_4^+]\).

**Solve:** We obtain \([\text{OH}^-]\) from the given pH:

\[
\text{pOH} = 14.00 - \text{pH} = 14.00 - 9.00 = 5.00
\]

\([\text{OH}^-] = 1.0 \times 10^{-5} \text{ M}\)

Because \(K_b\) is small and the common ion NH₄⁺ is present, the equilibrium concentration of NH₃ will essentially equal its initial concentration:

\[
[\text{NH}_3] = 0.10 \text{ M}
\]

\[
[\text{NH}_4^+] = K_b \frac{[\text{NH}_3]}{[\text{OH}^-]} = (1.8 \times 10^{-5}) \frac{(0.10 \text{ M})}{(1.0 \times 10^{-5} \text{ M})} = 0.18 \text{ M}
\]
Sample Exercise 17.4 Preparing a Buffer

Solution (Continued)

We now use the expression for $K_b$ to calculate $[\text{NH}_4^+]$:

Thus, for the solution to have $\text{pH} = 9.00$, $[\text{NH}_4^+]$ must equal 0.18 $M$. The number of moles of $\text{NH}_4\text{Cl}$ needed to produce this concentration is given by the product of the volume of the solution and its molarity:

(2.0 L)(0.18 mol $\text{NH}_4\text{Cl}$/L) = 0.36 mol $\text{NH}_4\text{Cl}$

Comment: Because $\text{NH}_4^+$ and $\text{NH}_3$ are a conjugate acid–base pair, we could use the Henderson–Hasselbalch equation (Equation 17.9) to solve this problem. To do so requires first using Equation 16.41 to calculate $pK_a$ for $\text{NH}_4^+$ from the value of $pK_b$ for $\text{NH}_3$. We suggest you try this approach to convince yourself that you can use the Henderson–Hasselbalch equation for buffers for which you are given $K_b$ for the conjugate base rather than $K_a$ for the conjugate acid.

Practice Exercise

Calculate the concentration of sodium benzoate that must be present in a 0.20 $M$ solution of benzoic acid ($C_6H_5\text{COOH}$) to produce a pH of 4.00.

*Answer:* 0.13 $M$
Sample Exercise 17.5  Calculating pH Changes in Buffers

A buffer is made by adding 0.300 mol CH₃COOH and 0.300 mol CH₃COONa to enough water to make 1.00 L of solution. The pH of the buffer is 4.74 (Sample Exercise 17.1). (a) Calculate the pH of this solution after 0.020 mol of NaOH is added. (b) For comparison, calculate the pH that would result if 0.020 mol of NaOH were added to 1.00 L of pure water (neglect any volume changes).

Solution

Analyze: We are asked to determine the pH of a buffer after addition of a small amount of strong base and to compare the pH change to the pH that would result if we were to add the same amount of strong base to pure water.

Plan: (a) Solving this problem involves the two steps outlined in Figure 17.3. Thus, we must first do a stoichiometry calculation to determine how the added OH⁻ reacts with the buffer and affects its composition. Then we can use the resultant composition of the buffer and either the Henderson–Hasselbalch equation or the equilibrium constant expression for the buffer to determine the pH.

Solve: Stoichiometry Calculation: The OH⁻ provided by NaOH reacts with CH₃COOH, the weak acid component of the buffer. Prior to this neutralization reaction, there are 0.300 mol each of CH₃COOH and CH₃COO⁻. Neutralizing the 0.020 mol OH⁻ requires 0.020 mol of CH₃COOH. Consequently, the amount of CH₃COOH decreases by 0.020 mol, and the amount of the product of the neutralization, CH₃COO⁻, increases by 0.020 mol. We can create a table to see how the composition of the buffer changes as a result of its reaction with OH⁻:

<table>
<thead>
<tr>
<th></th>
<th>CH₃COOH(aq)</th>
<th>OH⁻(aq)</th>
<th>→</th>
<th>H₂O(l)</th>
<th>CH₃COO⁻(aq)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Buffer before addition</td>
<td>0.300 mol</td>
<td>0</td>
<td></td>
<td>0</td>
<td>0.300 mol</td>
</tr>
<tr>
<td>Addition</td>
<td>—</td>
<td>0.020 mol</td>
<td></td>
<td>—</td>
<td></td>
</tr>
<tr>
<td>Buffer after addition</td>
<td>0.280 mol</td>
<td>0</td>
<td></td>
<td>—</td>
<td>0.320 mol</td>
</tr>
</tbody>
</table>
Sample Exercise 17.5 Calculating pH Changes in Buffers

Solution (Continued)

Equilibrium Calculation: We now turn our attention to the equilibrium that will determine the pH of the buffer, namely the ionization of acetic acid.

\[
\text{CH}_3\text{COOH}(aq) \rightleftharpoons \text{H}^+(aq) + \text{CH}_3\text{COO}^-(aq)
\]

Using the quantities of \(\text{CH}_3\text{COOH}\) and \(\text{CH}_3\text{COO}^-\) remaining in the buffer, we can determine the pH using the Henderson–Hasselbalch equation.

\[
pH = 4.74 + \log \frac{0.320 \text{ mol/1.00 L}}{0.280 \text{ mol/1.00 L}} = 4.80
\]

Comment Notice that we could have used mole amounts in place of concentrations in the Henderson–Hasselbalch equation and gotten the same result. The volumes of the acid and base are equal and cancel. If 0.020 mol of \(\text{H}^+\) was added to the buffer, we would proceed in a similar way to calculate the resulting pH of the buffer. In this case the pH decreases by 0.06 units, giving \(pH = 4.68\), as shown in the figure in the margin.

(b) To determine the pH of a solution made by adding 0.020 mol of \(\text{NaOH}\) to 1.00 L of pure water, we can first determine \(pOH\) using Equation 16.18 and subtracting from 14.

\[
pH = 14 - (-\log 0.020) = 12.30
\]

Note that although the small amount of \(\text{NaOH}\) changes the pH of water significantly, the pH of the buffer changes very little.

Practice Exercise

Determine (a) the pH of the original buffer described in Sample Exercise 17.5 after the addition of 0.020 mol \(\text{HCl}\) and (b) the pH of the solution that would result from the addition of 0.020 mol \(\text{HCl}\) to 1.00 L of pure water

Answers: (a) 4.68, (b) 1.70
Sample Exercise 17.6 Calculating pH for a Strong Acid-Strong Base Titration

Calculate the pH when the following quantities of 0.100 $M$ NaOH solution have been added to 50.0 mL of 0.100 $M$ HCl solution: (a) 49.0 mL, (b) 51.0 mL.

Solution

Analyze: We are asked to calculate the pH at two points in the titration of a strong acid with a strong base. The first point is just before the equivalence point, so we expect the pH to be determined by the small amount of strong acid that has not yet been neutralized. The second point is just after the equivalence point, so we expect this pH to be determined by the small amount of excess strong base.

Plan: (a) As the NaOH solution is added to the HCl solution, $H^+(aq)$ reacts with $OH^-(aq)$ to form $H_2O$. Both Na$^+$ and Cl$^-$ are spectator ions, having negligible effect on the pH. To determine the pH of the solution, we must first determine how many moles of $H^+$ were originally present and how many moles of $OH^-$ were added. We can then calculate how many moles of each ion remain after the neutralization reaction. To calculate [$H^+$], and hence pH, we must also remember that the volume of the solution increases as we add titrant, thus diluting the concentration of all solutes present.

Solve: The number of moles of $H^+$ in the original HCl solution is given by the product of the volume of the solution (50.0 mL = 0.0500 L) and its molarity (0.100 $M$):

$$\frac{(0.0500 \text{ L soln})(0.100 \text{ mol H}^+)\text{ 1 L soln}}{1 \text{ L soln}} = 5.00 \times 10^{-3} \text{ mol H}^+$$

Likewise, the number of moles of $OH^-$ in 49.0 mL of 0.100 $M$ NaOH is

$$\frac{(0.0490 \text{ L soln})(0.100 \text{ mol OH}^-)\text{ 1 L soln}}{1 \text{ L soln}} = 4.90 \times 10^{-3} \text{ mol OH}^-$$
Sample Exercise 17.6  Calculating pH for a Strong Acid-Strong Base Titration

Solution (Continued)

Because we have not yet reached the equivalence point, there are more moles of H\(^+\) present than OH\(^-\). Each mole of OH\(^-\) will react with one mole of H\(^+\). Using the convention introduced in Sample Exercise 17.5,

During the course of the titration, the volume of the reaction mixture increases as the NaOH solution is added to the HCl solution. Thus, at this point in the titration, the total volume of the solutions is

(We assume that the total volume is the sum of the volumes of the acid and base solutions.) Thus, the concentration of H\(^+(aq)\) is

The corresponding pH equals

\[
[H^+] = \frac{\text{moles } H^+(aq)}{\text{liters soln}} = \frac{0.10 \times 10^{-3} \text{ mol}}{0.09900 \text{ L}} = 1.0 \times 10^{-3} \text{ M}
\]

\[
-\log(1.0 \times 10^{-3}) = 3.00
\]

Plan: (b) We proceed in the same way as we did in part (a), except we are now past the equivalence point and have more OH\(^-\) in the solution than H\(^+\). As before, the initial number of moles of each reactant is determined from their volumes and concentrations. The reactant present in smaller stoichiometric amount (the limiting reactant) is consumed completely, leaving an excess of hydroxide ion.
Sample Exercise 17.6  Calculating pH for a Strong Acid-Strong Base Titration

Solution (Continued)

Solve:

<table>
<thead>
<tr>
<th></th>
<th>H(^+)(aq)</th>
<th>OH(^-)(aq)</th>
<th>→ H(_2)O(l)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Before addition</td>
<td>5.00 \times 10^{-3} mol</td>
<td>0</td>
<td>—</td>
</tr>
<tr>
<td>Addition</td>
<td></td>
<td>5.10 \times 10^{-3} mol</td>
<td></td>
</tr>
<tr>
<td>After addition</td>
<td>0</td>
<td>0.10 \times 10^{-3} mol</td>
<td>—</td>
</tr>
</tbody>
</table>

In this case the total volume of the solution is

Hence, the concentration of OH\(^-\)(aq) in the solution is

Thus, the pOH of the solution equals

and the pH equals

Practice Exercise

Calculate the pH when the following quantities of 0.100 \( M \) HNO\(_3\) have been added to 25.0 mL of 0.100 \( M \) KOH solution: (a) 24.9 mL, (b) 25.1 mL.

Answers: (a) 10.30, (b) 3.70
Sample Exercise 17.7 Calculating pH for a Weak Acid-Strong Base Titration

Calculate the pH of the solution formed when 45.0 mL of 0.100 M NaOH is added to 50.0 mL of 0.100 M CH₃COOH ($K_a = 1.8 \times 10^{-5}$).

Solution

Analyze: We are asked to calculate the pH before the equivalence point of the titration of a weak acid with a strong base.

Plan: We first must determine the number of moles of CH₃COOH and CH₃COO⁻ that are present after the neutralization reaction. We then calculate pH using $K_a$ together with [CH₃COOH] and [CH₃COO⁻].

Solve: Stoichiometry Calculation: The product of the volume and concentration of each solution gives the number of moles of each reactant present before the neutralization:

The 4.50 × 10⁻³ mol of NaOH consumes 4.50 × 10⁻³ mol of CH₃COOH:

<table>
<thead>
<tr>
<th></th>
<th>CH₃COOH(aq) +</th>
<th>OH⁻(aq) → CH₃COO⁻(aq) + H₂O(l)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Before addition</td>
<td>5.00 × 10⁻³ mol</td>
<td>0</td>
</tr>
<tr>
<td>Addition</td>
<td>4.50 × 10⁻³ mol</td>
<td>0</td>
</tr>
<tr>
<td>After addition</td>
<td>0.50 × 10⁻³ mol</td>
<td>4.50 × 10⁻³ mol</td>
</tr>
</tbody>
</table>

The total volume of the solution is

45.0 mL + 50.0 mL = 95.0 mL = 0.0950 L

The resulting molarities of CH₃COOH and CH₃COO⁻ after the reaction are therefore

$$[\text{CH}_3\text{COOH}] = \frac{0.50 \times 10^{-3} \text{ mol}}{0.0950 \text{ L}} = 0.0053 \text{ M}$$

$$[\text{CH}_3\text{COO}^-] = \frac{4.50 \times 10^{-3} \text{ mol}}{0.0950 \text{ L}} = 0.0474 \text{ M}$$
Sample Exercise 17.7 Calculating pH for a Weak Acid-Strong Base Titration

Solution (Continued)

Equilibrium Calculation: The equilibrium between CH₃COOH and CH₃COO⁻ must obey the equilibrium-constant expression for CH₃COOH

\[
K_a = \frac{[H^+][CH₃COO^-]}{[CH₃COOH]} = 1.8 \times 10^{-5}
\]

\[
[H^+] = K_a \times \frac{[CH₃COOH]}{[CH₃COO^-]} = (1.8 \times 10^{-5}) \times \left(\frac{0.0053}{0.0474}\right) = 2.0 \times 10^{-6} \text{ M}
\]

\[
\text{pH} = -\log(2.0 \times 10^{-6}) = 5.70
\]

Comment: We could have solved for pH equally well using the Henderson–Hasselbalch equation.

Practice Exercise

(a) Calculate the pH in the solution formed by adding 10.0 mL of 0.050 M NaOH to 40.0 mL of 0.0250 M benzoic acid (C₆H₅COOH, Ka = 6.3 × 10⁻⁵). (b) Calculate the pH in the solution formed by adding 10.0 mL of 0.100 M HCl to 20.0 mL of 0.100 M NH₃.

Answers: (a) 4.20, (b) 9.26
Sample Exercise 17.8 Calculating the pH at the Equivalence Point

Calculate the pH at the equivalence point in the titration of 50.0 mL of 0.100 M CH₃COOH with 0.100 M NaOH.

Solution

Analyze: We are asked to determine the pH at the equivalence point of the titration of a weak acid with a strong base. Because the neutralization of a weak acid produces its anion, which is a weak base, we expect the pH at the equivalence point to be greater than 7.

Plan: The initial number of moles of acetic acid will equal the number of moles of acetate ion at the equivalence point. We use the volume of the solution at the equivalence point to calculate the concentration of acetate ion. Because the acetate ion is a weak base, we can calculate the pH using $K_b$ and [CH₃COO⁻].

Solve: The number of moles of acetic acid in the initial solution is obtained from the volume and molarity of the solution:

$$\text{Moles} = M \times L = (0.100 \text{ mol}\cdot\text{L})(0.0500 \text{ L}) = 5.00 \times 10^{-3} \text{ mol CH₃COOH}$$

Hence $5.00 \times 10^{-3}$ mol of CH₃COO⁻ is formed. It will take 50.0 mL of NaOH to reach the equivalence point (Figure 17.9). The volume of this salt solution at the equivalence point is the sum of the volumes of the acid and base, 50.0 mL + 50.0 mL = 100.0 mL = 0.1000 L. Thus, the concentration of CH₃COO⁻ is

$$[\text{CH₃COO}^-] = \frac{5.00 \times 10^{-3} \text{ mol}}{0.1000 \text{ L}} = 0.0500 \text{ M}$$
Sample Exercise 17.8 Calculating the pH at the Equivalence Point

Solution (Continued)

The CH₃COO⁻ ion is a weak base.

\[
\text{CH}_3\text{COO}^- (aq) + \text{H}_2\text{O}(l) \leftrightarrow \text{CH}_3\text{COOH}(aq) + \text{OH}^- (aq)
\]

The \( K_b \) for CH₃COO⁻ can be calculated from the \( K_a \) value of its conjugate acid, \( K_b = K_w/K_a = (1.0 \times 10^{-14})/(1.8 \times 10^{-5}) = 5.6 \times 10^{-10} \). Using the \( K_b \) expression, we have

\[
K_b = \frac{[\text{CH}_3\text{COOH}][\text{OH}^-]}{[\text{CH}_3\text{COO}^-]} = \frac{(x)(x)}{0.0500 - x} = 5.6 \times 10^{-10}
\]

Making the approximation that \( 0.0500 - x \approx 0.0500 \), and then solving for \( x \), we have \( x = [\text{OH}^-] = 5.3 \times 10^{-6} \) M, which gives \( \text{pOH} = 5.28 \) \( \text{pH} = 8.72 \)

Check: The pH is above 7, as expected for the salt of a weak acid and strong base.

Practice Exercise

Calculate the pH at the equivalence point when (a) 40.0 mL of 0.025 M benzoic acid (C₆H₅COOH, \( K_a = 6.3 \times 10^{-5} \)) is titrated with 0.050 M NaOH; (b) 40.0 mL of 0.100 M NH₃ is titrated with 0.100 M HCl.

Answers: (a) 8.21, (b) 5.28
Sample Exercise 17.9 Writing Solubility-Product ($K_{sp}$) Expressions

Write the expression for the solubility-product constant for CaF$_2$, and look up the corresponding $K_{sp}$ value in Appendix D.

Solution

Analyze: We are asked to write an equilibrium-constant expression for the process by which CaF$_2$ dissolves in water.

Plan: We apply the same rules for writing any equilibrium-constant expression, excluding the solid reactant from the expression. We assume that the compound dissociates completely into its component ions.

Solve: Following the italicized rule stated previously, the expression for $K_{sp}$ is

$$CaF_2(s) \rightleftharpoons Ca^{2+}(aq) + 2 F^-(aq)$$

In Appendix D we see that this $K_{sp}$ has a value of $3.9 \times 10^{-11}$.

Practice Exercise

Give the solubility-product-constant expressions and the values of the solubility-product constants (from Appendix D) for the following compounds: (a) barium carbonate, (b) silver sulfate.

Answers: (a) $K_{sp} = [Ba^{2+}][CO_3^{2-}] = 5.0 \times 10^{-9}$; (b) $K_{sp} = [Ag^+]^2[SO_4^{2-}] = 1.5 \times 10^{-5}$
Sample Exercise 17.10  Calculating $K_{sp}$ from Solubility

Solid silver chromate is added to pure water at 25 °C. Some of the solid remains undissolved at the bottom of the flask. The mixture is stirred for several days to ensure that equilibrium is achieved between the undissolved Ag$_2$CrO$_4$(s) and the solution. Analysis of the equilibrated solution shows that its silver ion concentration is $1.3 \times 10^{-4}$ M. Assuming that Ag$_2$CrO$_4$ dissociates completely in water and that there are no other important equilibria involving the Ag$^+$ or CrO$_4^{2-}$ ions in the solution, calculate $K_{sp}$ for this compound.

Solution

Analyze: We are given the equilibrium concentration of Ag$^+$ in a saturated solution of Ag$_2$CrO$_4$. From this information, we are asked to determine the value of the solubility product constant, $K_{sp}$, for Ag$_2$CrO$_4$.

Plan: The equilibrium equation and the expression for $K_{sp}$ are

$$\text{Ag}_2\text{CrO}_4(s) \rightleftharpoons 2 \text{Ag}^+(aq) + \text{CrO}_4^{2-}(aq) \quad K_{sp} = [\text{Ag}^+]^2[\text{CrO}_4^{2-}]$$

To calculate $K_{sp}$, we need the equilibrium concentrations of Ag$^+$ and CrO$_4^{2-}$. We know that at equilibrium $[\text{Ag}^+] = 1.3 \times 10^{-4}$ M. All the Ag$^+$ and CrO$_4^{2-}$ ions in the solution come from the Ag$_2$CrO$_4$ that dissolves. Thus, we can use $[\text{Ag}^+]$ to calculate $[\text{CrO}_4^{2-}]$.

Solve: From the chemical formula of silver chromate, we know that there must be 2 Ag$^+$ ions in solution for each CrO$_4^{2-}$ ion in solution. Consequently, the concentration of CrO$_4^{2-}$ is half the concentration of Ag$^+$:

$$[\text{CrO}_4^{2-}] = \left(\frac{1.3 \times 10^{-4} \text{ mol Ag}^+}{L}\right)\left(\frac{1 \text{ mol CrO}_4^{2-}}{2 \text{ mol Ag}^+}\right) = 6.5 \times 10^{-5} \text{ M}$$

We can now calculate the value of $K_{sp}$.

$$K_{sp} = [\text{Ag}^+]^2[\text{CrO}_4^{2-}] = (1.3 \times 10^{-4})^2(6.5 \times 10^{-5}) = 1.1 \times 10^{-12}$$
Sample Exercise 17.10  Calculating $K_{sp}$ from Solubility

Solution (Continued)

Check: We obtain a small value, as expected for a slightly soluble salt. Furthermore, the calculated value agrees well with the one given in Appendix D, $1.2 \times 10^{-12}$.

Practice Exercise

A saturated solution of Mg(OH)$_2$ in contact with undissolved solid is prepared at 25 ºC. The pH of the solution is found to be 10.17. Assuming that Mg(OH)$_2$ dissociates completely in water and that there are no other simultaneous equilibria involving the Mg$^{2+}$ or OH$^-$ ions in the solution, calculate $K_{sp}$ for this compound.

Answer: $1.6 \times 10^{-12}$
Sample Exercise 17.11  Calculating Solubility from $K_{sp}$

The $K_{sp}$ for CaF$_2$ is $3.9 \times 10^{-11}$ at 25 °C. Assuming that CaF$_2$ dissociates completely upon dissolving and that there are no other important equilibria affecting its solubility, calculate the solubility of CaF$_2$ in grams per liter.

**Solution**

**Analyze:** We are given $K_{sp}$ for CaF$_2$ and are asked to determine solubility. Recall that the *solubility* of a substance is the quantity that can dissolve in solvent, whereas the *solubility-product constant*, $K_{sp}$, is an equilibrium constant.

**Plan:** We can approach this problem by using our standard techniques for solving equilibrium problems. We write the chemical equation for the dissolution process and set up a table of the initial and equilibrium concentrations. We then use the equilibrium constant expression. In this case we know $K_{sp}$, and so we solve for the concentrations of the ions in solution.

**Solve:** Assume initially that none of the salt has dissolved, and then allow $x$ moles/liter of CaF$_2$ to dissociate completely when equilibrium is achieved.

The stoichiometry of the equilibrium dictates that 2$x$ moles/liter of F$^-$ are produced for each $x$ moles/liter of CaF$_2$ that dissolve. We now use the expression for $K_{sp}$ and substitute the equilibrium concentrations to solve for the value of $x$:

\[
K_{sp} = [Ca^{2+}][F^-]^2 = (x)(2x)^2 = 4x^3 = 3.9 \times 10^{-11}
\]

\[
x = \sqrt[3]{\frac{3.9 \times 10^{-11}}{4}} = 2.1 \times 10^{-4} \text{ M}
\]
Sample Exercise 17.11 Calculating Solubility from $K_{sp}$

Solution

(Remember that $\sqrt[y]{x} = x^{1/y}$ to calculate the cube root of a number, you can use the $y^x$ function on your calculator, with $x = \frac{1}{3}$.) Thus, the molar solubility of CaF$_2$ is $2.1 \times 10^{-4}$ mol/L. The mass of CaF$_2$ that dissolves in water to form a liter of solution is

$$\left(\frac{2.1 \times 10^{-4} \text{ mol CaF}_2}{1 \text{ L soln}}\right) \left(\frac{78.1 \text{ g CaF}_2}{1 \text{ mol CaF}_2}\right) = 1.6 \times 10^{-2} \text{ g CaF}_2/\text{L soln}$$

Check: We expect a small number for the solubility of a slightly soluble salt. If we reverse the calculation, we should be able to recalculate the solubility product: $K_{sp} = (2.1 \times 10^{-4})(4.2 \times 10^{-4})^2 = 3.7 \times 10^{-11}$, close to the starting value for $K_{sp}$, $3.9 \times 10^{-11}$.

Comment: Because F$^-$ is the anion of a weak acid, you might expect that the hydrolysis of the ion would affect the solubility of CaF$_2$. The basicity of F$^-$ is so small ($K_b = 1.5 \times 10^{-11}$), however, that the hydrolysis occurs to only a slight extent and does not significantly influence the solubility. The reported solubility is 0.017 g/L at 25 °C, in good agreement with our calculation.

Practice Exercise

The $K_{sp}$ for LaF$_3$ is $2 \times 10^{-19}$. What is the solubility of LaF$_3$ in water in moles per liter?

Answer: $9 \times 10^{-6}$ mol/L
Sample Exercise 17.12 Calculating the Effect of a Common Ion on Solubility

Calculate the molar solubility of CaF₂ at 25 °C in a solution that is (a) 0.010 M in Ca(NO₃)₂, (b) 0.010 M in NaF.

Solution

Analyze: We are asked to determine the solubility of CaF₂ in the presence of two strong electrolytes, each of which contains an ion common to CaF₂. In (a) the common ion is Ca²⁺, and NO₃⁻ is a spectator ion. In (b) the common ion is F⁻, and Na⁺ is a spectator ion.

Plan: Because the slightly soluble compound is CaF₂, we need to use the K_{sp} for this compound, which is available in Appendix D:

\[ K_{sp} = [Ca^{2+}][F^-]^2 = 3.9 \times 10^{-11} \]

The value of \( K_{sp} \) is unchanged by the presence of additional solutes. Because of the common-ion effect, however, the solubility of the salt will decrease in the presence of common ions. We can again use our standard equilibrium techniques of starting with the equation for CaF₂ dissolution, setting up a table of initial and equilibrium concentrations, and using the \( K_{sp} \) expression to determine the concentration of the ion that comes only from CaF₂.

Solve: (a) In this instance the initial concentration of Ca²⁺ is 0.010 M because of the dissolved Ca(NO₃)₂:

<table>
<thead>
<tr>
<th></th>
<th>CaF₂(s)</th>
<th>Ca²⁺(aq)</th>
<th>2 F⁻(aq)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial</td>
<td>—</td>
<td>0.010 M</td>
<td>0</td>
</tr>
<tr>
<td>Change</td>
<td>—</td>
<td>+x M</td>
<td>+2x M</td>
</tr>
<tr>
<td>Equilibrium</td>
<td>—</td>
<td>(0.010 + x) M</td>
<td>2x M</td>
</tr>
</tbody>
</table>

Substituting into the solubility-product expression gives

\[ K_{sp} = 3.9 \times 10^{-11} = [Ca^{2+}][F^-]^2 = (0.010 + x)(2x)^2 \]
Sample Exercise 17.12 Calculating the Effect of a Common Ion on Solubility

Solution (Continued)

This would be a messy problem to solve exactly, but fortunately it is possible to simplify matters greatly. Even without the common-ion effect, the solubility of CaF₂ is very small ($2.1 \times 10^{-4} \text{ M}$). Thus, we assume that the $0.010 \text{ M}$ concentration of Ca²⁺ from Ca(NO₃)₂ is very much greater than the small additional concentration resulting from the solubility of CaF₂; that is, $x$ is small compared to $0.010 \text{ M}$, and $0.010 + x \approx 0.010$.

We then have

The very small value for $x$ validates the simplifying assumption we have made. Our calculation indicates that $3.1 \times 10^{-5} \text{ mol}$ of solid CaF₂ dissolves per liter of the $0.010 \text{ M}$ Ca(NO₃)₂ solution. 

(b) In this case the common ion is F⁻, and at equilibrium we have

Assuming that $2x$ is small compared to $0.010 \text{ M}$ (that is, $0.010 + 2x \approx 0.010$), we have

Thus, $3.9 \times 10^{-7} \text{ mol}$ of solid CaF₂ should dissolve per liter of $0.010 \text{ M}$ NaF solution.
Sample Exercise 17.12  Calculating the Effect of a Common Ion on Solubility

Solution (Continued)

Comment: The molar solubility of CaF$_2$ in pure water is $2.1 \times 10^{-4}$ M (Sample Exercise 17.11). By comparison, our calculations above show that the solubility of CaF$_2$ in the presence of 0.010 M Ca$^{2+}$ is $3.1 \times 10^{-5}$ M, and in the presence of 0.010 M F$^-$ ion it is $3.9 \times 10^{-7}$ M. Thus, the addition of either Ca$^{2+}$ or F$^-$ to a solution of CaF$_2$ decreases the solubility. However, the effect of F$^-$ on the solubility is more pronounced than that of Ca$^{2+}$ because [F$^-$] appears to the second power in the $K_{sp}$ expression for CaF$_2$, whereas Ca$^{2+}$ appears to the first power.

Practice Exercise

The value for $K_{sp}$ for manganese(II) hydroxide, Mn(OH)$_2$, is $1.6 \times 10^{-13}$. Calculate the molar solubility of Mn(OH)$_2$ in a solution that contains 0.020 M NaOH.

Answer: $4.0 \times 10^{-10}$ M
Sample Exercise 17.13  Predicting the Effect of Acid on Solubility

Which of the following substances will be more soluble in acidic solution than in basic solution: (a) Ni(OH)$_2$(s), (b) CaCO$_3$(s), (c) BaF$_2$(s), (d) AgCl(s)?

Solution

**Analyze:** The problem lists four sparingly soluble salts, and we are asked to determine which will be more soluble at low pH than at high pH.

**Plan:** Ionic compounds that dissociate to produce a basic anion will be more soluble in acid solution. (a) Ni(OH)$_2$(s) will be more soluble in acidic solution because of the basicity of OH$^-$. The H$^+$ ion reacts with the OH$^-$ ion, forming water.

\[
\text{Ni(OH)$_2$(s) } \rightleftharpoons \text{ Ni}^{2+}(aq) + 2 \text{OH}^-(aq)
\]
\[
2 \text{OH}^-(aq) + 2 \text{H}^+(aq) \rightarrow 2 \text{H}_2\text{O(l)}
\]

Overall: \( \text{Ni(OH)$_2$(s) } + 2 \text{H}^+(aq) \rightleftharpoons \text{Ni}^{2+}(aq) + 2 \text{H}_2\text{O(l)} \)

(b) Similarly, CaCO$_3$(s) dissolves in acid solutions because CO$_3^{2-}$ is a basic anion.

\[
\text{CaCO}_3(s) \rightleftharpoons \text{Ca}^{2+}(aq) + \text{CO}_3^{2-}(aq)
\]
\[
\text{CO}_3^{2-}(aq) + 2 \text{H}^+(aq) \rightarrow \text{H}_2\text{CO}_3(aq)
\]
\[
\text{H}_2\text{CO}_3(aq) \rightarrow \text{CO}_2(g) + \text{H}_2\text{O(l)}
\]

Overall: \( \text{CaCO}_3(s) + 2 \text{H}^+(aq) \rightleftharpoons \text{Ca}^{2+}(aq) + \text{CO}_2(g) + \text{H}_2\text{O(l)} \)

The reaction between CO$_3^{2-}$ and H$^+$ occurs in a stepwise fashion, first forming HCO$_3^-$. H$_2$CO$_3$ forms in appreciable amounts only when the concentration of H$^+$ is sufficiently high.

(c) The solubility of BaF$_2$ is also enhanced by lowering the pH, because F$^-$ is a basic anion.

\[
\text{BaF}_2(s) \rightleftharpoons \text{Ba}^{2+}(aq) + 2 \text{F}^-(aq)
\]
\[
2 \text{F}^-(aq) + 2 \text{H}^+(aq) \rightarrow 2 \text{HF}(aq)
\]

Overall: \( \text{BaF}_2(s) + 2 \text{H}^+(aq) \rightleftharpoons \text{Ba}^{2+}(aq) + 2 \text{HF}(aq) \)
Sample Exercise 17.13  Predicting the Effect of Acid on Solubility

Solution

(d) The solubility of AgCl is unaffected by changes in pH because Cl\(^{-}\) is the anion of a strong acid and therefore has negligible basicity.

Practice Exercise

Write the net ionic equation for the reaction of the following copper(II) compounds with acid:

(a) CuS,  (b) Cu(N_3)_2.

*Answers:* (a) CuS(s) + H^+(aq) \rightleftharpoons Cu^{2+}(aq) + HS^-(aq)
(b) Cu(N_3)_2(s) + 2 H^+(aq) \rightleftharpoons Cu^{2+}(aq) + 2 HN_3(aq)
Sample Exercise 17.14  Evaluating an Equilibrium Involving a Complex Ion

Calculate the concentration of Ag\(^{+}\) present in solution at equilibrium when concentrated ammonia is added to a 0.010 \( M \) solution of AgNO\(_3\) to give an equilibrium concentration of \([\text{NH}_3]\) = 0.20 \( M \). Neglect the small volume change that occurs when NH\(_3\) is added.

Solution

**Analyze:** When NH\(_3(aq)\) is added to Ag\(^{+}(aq)\), a reaction occurs forming Ag(NH\(_3\))\(_2^{+}\) as shown in Equation 17.22. We are asked to determine what concentration of Ag\(^{+}(aq)\) will remain uncombined when the NH\(_3\) concentration is brought to 0.20 \( M \) in a solution originally 0.010 \( M \) in AgNO\(_3\).

**Plan:** We first assume that the AgNO\(_3\) is completely dissociated, giving 0.10 \( M \) Ag\(^{+}\). Because \( K_f \) for the formation of Ag(NH\(_3\))\(_2^{+}\) is quite large, we assume that essentially all the Ag\(^{+}\) is then converted to Ag(NH\(_3\))\(_2^{+}\) and approach the problem as though we are concerned with the *dissociation* of Ag(NH\(_3\))\(_2^{+}\) rather than its *formation*. To facilitate this approach, we will need to reverse the equation to represent the formation of Ag\(^{+}\) and NH\(_3\) from Ag(NH\(_3\))\(_2^{+}\) and also make the corresponding change to the equilibrium constant.

\[
\frac{1}{K_f} = \frac{1}{1.7 \times 10^7} = 5.9 \times 10^{-8}
\]

**Solve:** If [Ag\(^{+}\)] is 0.010 \( M \) initially, then [Ag(NH\(_3\))\(_2^{+}\)] will be 0.010 \( M \) following addition of the NH\(_3\). We now construct a table to solve this equilibrium problem. Note that the NH\(_3\) concentration given in the problem is an *equilibrium* concentration rather than an initial concentration.

<table>
<thead>
<tr>
<th>( \text{Ag(NH}_3\text{)}_2^{+}(aq) )</th>
<th>( \text{Ag}^{+}(aq) )</th>
<th>+</th>
<th>2 ( \text{NH}_3(aq) )</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Initial</strong></td>
<td>0.010 ( M )</td>
<td>0 ( M )</td>
<td></td>
</tr>
<tr>
<td><strong>Change</strong></td>
<td>(-x ) ( M )</td>
<td>(+x ) ( M )</td>
<td></td>
</tr>
<tr>
<td><strong>Equilibrium</strong></td>
<td>0.010 (-x) ( M )</td>
<td>(x) ( M )</td>
<td>0.20 ( M )</td>
</tr>
</tbody>
</table>
Sample Exercise 17.14  Evaluating an Equilibrium Involving a Complex Ion

Solution (Continued)

Because the concentration of Ag⁺ is very small, we can ignore $x$ in comparison with 0.010. Thus, $0.010 - x \approx 0.010 \ M$. Substituting these values into the equilibrium constant expression for the dissociation of Ag(NH₃)₂⁺, we obtain

$$\frac{[Ag^+][NH_3]^2}{[Ag(NH_3)_2^+]} = \frac{(x)(0.20)^2}{0.010} = 5.9 \times 10^{-8}$$

Solving for $x$, we obtain $x = 1.5 \times 10^{-8} \ M = [Ag^+]$. Thus, formation of the Ag(NH₃)₂⁺ complex drastically reduces the concentration of free Ag⁺ ion in solution.

Practice Exercise

Calculate [Cr³⁺] in equilibrium with Cr(OH)₄⁻ when 0.010 mol of Cr(NO₃)₃ is dissolved in a liter of solution buffered at pH 10.0.

*Answer:* $1 \times 10^{-16} \ M$
Sample Exercise 17.15  Predicting Whether a Precipitate Will Form

Will a precipitate form when 0.10 L of $8.0 \times 10^{-3} \ M \ Pb(NO_3)_2$ is added to 0.40 L of $5.0 \times 10^{-3} \ M \ Na_2SO_4$?

Solution

Analyze: The problem asks us to determine whether a precipitate will form when two salt solutions are combined. Plan: We should determine the concentrations of all ions immediately upon mixing of the solutions and compare the value of the reaction quotient, $Q$, to the solubility-product constant, $K_{sp}$, for any potentially insoluble product. The possible metathesis products are PbSO$_4$ and NaNO$_3$. Sodium salts are quite soluble; PbSO$_4$ has a $K_{sp}$ of $6.3 \times 10^{-7}$ (Appendix D), however, and will precipitate if the Pb$^{2+}$ and SO$_4^{2-}$ concentrations are high enough for $Q$ to exceed $K_{sp}$ for the salt.

Solve: When the two solutions are mixed, the total volume becomes $0.10 \ L + 0.40 \ L = 0.50 \ L$. The number of moles of Pb$^{2+}$ in 0.10 L of $8.0 \times 10^{-3} \ M \ Pb(NO_3)_2$ is

\[
(0.10 \ L)(8.0 \times 10^{-3} \ \text{mol/L}) = 8.0 \times 10^{-4} \ \text{mol}
\]

The concentration of Pb$^{2+}$ in the 0.50-L mixture is therefore

\[
[Pb^{2+}] = \frac{8.0 \times 10^{-4} \ \text{mol}}{0.50 \ \text{L}} = 1.6 \times 10^{-3} \ \text{M}
\]

The number of moles of SO$_4^{2-}$ in 0.40 L of $5.0 \times 10^{-3} \ M \ Na_2SO_4$ is

\[
(0.40 \ L)(5.0 \times 10^{-3} \ \text{mol/L}) = 2.0 \times 10^{-3} \ \text{mol}
\]

Therefore, $[SO_4^{2-}]$ in the 0.50-L mixture is

\[
[SO_4^{2-}] = \frac{2.0 \times 10^{-3} \ \text{mol}}{0.50 \ \text{L}} = 4.0 \times 10^{-3} \ \text{M}
\]

We then have

\[
Q = [Pb^{2+}][SO_4^{2-}] = (1.6 \times 10^{-3})(4.0 \times 10^{-3}) = 6.4 \times 10^{-6}
\]

Because $Q > K_{sp}$, PbSO$_4$ will precipitate.
Sample Exercise 17.15  Predicting Whether a Precipitate Will Form

Practice Exercise

Will a precipitate form when 0.050 L of $2.0 \times 10^{-2} M$ NaF is mixed with 0.010 L of $1.0 \times 10^{-2} M$ Ca(NO$_3$)$_2$?

*Answer:* Yes, CaF$_2$ precipitates because $Q = 4.6 \times 10^{-8}$ is larger than $K_{sp} = 3.9 \times 10^{-11}$
Sample Exercise 17.16 Calculating Ion Concentrations for Precipitation

A solution contains $1.0 \times 10^{-2} M$ Ag$^+$ and $2.0 \times 10^{-2} M$ Pb$^{2+}$. When Cl$^-$ is added to the solution, both AgCl ($K_{sp} = 1.8 \times 10^{-10}$) and PbCl$_2$ ($K_{sp} = 1.7 \times 10^{-5}$) precipitate from the solution. What concentration of Cl$^-$ is necessary to begin the precipitation of each salt? Which salt precipitates first?

**Solution**

**Analyze:** We are asked to determine the concentration of Cl$^-$ necessary to begin the precipitation from a solution containing Ag$^+$ and Pb$^{2+}$, and to predict which metal chloride will begin to precipitate first.

**Plan:** We are given $K_{sp}$ values for the two possible precipitates. Using these and the metal ion concentrations, we can calculate what concentration of Cl$^-$ ion would be necessary to begin precipitation of each. The salt requiring the lower Cl$^-$ ion concentration will precipitate first.

**Solve:** For AgCl we have

\[
K_{sp} = [\text{Ag}^+][\text{Cl}^-] = 1.8 \times 10^{-10}
\]

Because $[\text{Ag}^+] = 1.0 \times 10^{-2} M$, the greatest concentration of Cl$^-$ that can be present without causing precipitation of AgCl can be calculated from the $K_{sp}$ expression

\[
[\text{Cl}^-] = \frac{1.8 \times 10^{-10}}{1.0 \times 10^{-2}} = 1.8 \times 10^{-8} M
\]

Any Cl$^-$ in excess of this very small concentration will cause AgCl to precipitate from solution. Proceeding similarly for PbCl$_2$, we have

\[
K_{sp} = [\text{Pb}^{2+}][\text{Cl}^-]^2 = 1.7 \times 10^{-5}
\]

\[
[2.0 \times 10^{-2}][\text{Cl}^-]^2 = 1.7 \times 10^{-5}
\]

\[
[\text{Cl}^-]^2 = \frac{1.7 \times 10^{-5}}{2.0 \times 10^{-2}} = 8.5 \times 10^{-4}
\]

\[
[\text{Cl}^-] = \sqrt{8.5 \times 10^{-4}} = 2.9 \times 10^{-2} M
\]
Sample Exercise 17.16  Calculating Ion Concentrations for Precipitation

Solution (Continued)

Thus, a concentration of Cl\(^{-}\) in excess of \(2.9 \times 10^{-2}\) \(M\) will cause PbCl\(_2\) to precipitate.

Comparing the concentrations of Cl\(^{-}\) required to precipitate each salt, we see that as Cl\(^{-}\) is added to the solution, AgCl will precipitate first because it requires a much smaller concentration of Cl\(^{-}\). Thus, Ag\(^{+}\) can be separated from by slowly adding Cl\(^{-}\) so \([\text{Cl}^{-}]\) is between \(1.8 \times 10^{-8}\) \(M\) and \(2.9 \times 10^{-2}\) \(M\).

Practice Exercise

A solution consists of \(0.050\) \(M\) Mg\(^{2+}\) and \(0.020\) \(M\) Cu\(^{2+}\). Which ion will precipitate first as OH\(^{-}\) is added to the solution? What concentration of OH\(^{-}\) is necessary to begin the precipitation of each cation? [\(K_{sp} = 1.8 \times 10^{-11}\) for Mg(OH)\(_2\), and \(K_{sp} = 4.8 \times 10^{-20}\) for Cu(OH)\(_2\).]

Answer: Cu(OH)\(_2\) precipitates first. Cu(OH)\(_2\) begins to precipitate when \([\text{OH}^{-}]\) exceeds \(1.5 \times 10^{-9}\) \(M\); Mg(OH)\(_2\) begins to precipitate when \([\text{OH}^{-}]\) exceeds \(1.9 \times 10^{-5}\) \(M\).
Sample Integrative Exercise  Putting Concepts Together

A sample of 1.25 L of HCl gas at 21 ºC and 0.950 atm is bubbled through 0.500 L of 0.150 M NH₃ solution. Calculate the pH of the resulting solution assuming that all the HCl dissolves and that the volume of the solution remains 0.500 L.

Solution

The number of moles of HCl gas is calculated from the ideal-gas law.

\[ n = \frac{PV}{RT} = \frac{(0.950 \text{ atm})(1.25 \text{ L})}{(0.0821 \text{ L-atm/mol-K})(294 \text{ K})} = 0.0492 \text{ mol HCl} \]

The number of moles of NH₃ in the solution is given by the product of the volume of the solution and its concentration.

Moles NH₃ = (0.500 L)(0.150 mol NH₃/L) = 0.0750 mol NH₃

The acid HCl and base NH₃ react, transferring a proton from HCl to NH₃, producing NH₄⁺ and Cl⁻ ions.

\[ \text{HCl}(g) + \text{NH}_3(aq) \rightarrow \text{NH}_4^+(aq) + \text{Cl}^-(aq) \]

To determine the pH of the solution, we first calculate the amount of each reactant and each product present at the completion of the reaction.

<table>
<thead>
<tr>
<th></th>
<th>HCl(g)</th>
<th>NH₃(aq)</th>
<th>NH₄⁺(aq)</th>
<th>Cl⁻(aq)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Before addition</td>
<td>0.0492 mol</td>
<td>0 mol</td>
<td>0 mol</td>
<td>0 mol</td>
</tr>
<tr>
<td>Addition</td>
<td></td>
<td>0.0750 mol</td>
<td></td>
<td></td>
</tr>
<tr>
<td>After addition</td>
<td>0 mol</td>
<td>0.0258 mol</td>
<td>0.0492 mol</td>
<td>0.0492 mol</td>
</tr>
</tbody>
</table>
Sample Integrative Exercise  Putting Concepts Together

Solution (Continued)

Thus, the reaction produces a solution containing a mixture of NH₃, NH₄⁺, and Cl⁻. The NH₃ is a weak base (K_b = 1.8 × 10⁻⁵), NH₄⁺ is its conjugate acid, and Cl⁻ is neither acidic nor basic. Consequently, the pH depends on [NH₃] and [NH₄⁺].

\[
\begin{align*}
[NH_3] &= \frac{0.0258 \text{ mol NH}_3}{0.500 \text{ L soln}} = 0.0516 \text{ M} \\
[NH_4^+] &= \frac{0.0492 \text{ mol NH}_4^+}{0.500 \text{ L soln}} = 0.0984 \text{ M}
\end{align*}
\]

We can calculate the pH using either \(K_b\) for NH₃ or \(K_a\) for NH₄⁺. Using the \(K_b\) expression, we have

\[
K_b = \frac{[NH_4^+][OH^-]}{[NH_3]} = \frac{(0.0984 + x)(x)}{(0.0516 - x)} \approx \frac{(0.0984)x}{0.0516} = 1.8 \times 10^{-5}
\]

\[
x = [OH^-] = \frac{(0.0516)(1.8 \times 10^{-5})}{0.0984} = 9.4 \times 10^{-6} \text{ M}
\]

Hence, pOH = –log(9.4 × 10⁻⁶) = 5.03 and pH = 14.00 – pOH = 14.00 – 5.03 = 8.97.

Hence, pOH = –log(9.4 × 10⁻⁶) = 5.03 and pH = 14.00 – pOH = 14.00 – 5.03 = 8.97.