Chapter 17. Additional Aspects of Equilibrium

17.1 The Common Ion Effect

- The dissociation of a weak electrolyte is decreased by the addition of a strong electrolyte that has an ion in common with the weak electrolyte.

- For example, consider the ionization of a weak acid, acetic acid.

\[ \text{HC}_2\text{H}_3\text{O}_2(aq) \rightleftharpoons \text{H}^+(aq) + \text{C}_2\text{H}_3\text{O}_2^-(aq) \]

- If we add additional C\(_2\)H\(_3\)O\(_2^-\) ions by the addition of a strong electrolyte, (e.g., NaC\(_2\)H\(_3\)O\(_2\)) the equilibrium is shifted to the left.

- This causes a reduction in the [H\(^+\)] and a decrease in the percent ionization of the acetic acid.

- By adding sodium acetate, we have disturbed the acetic acid equilibrium.

- In effect, we have added a product of this equilibrium (i.e., the acetate ion).
  - This phenomenon is called the common-ion effect.
  - The extent of ionization of a weak electrolyte is decreased by adding to the solution a strong electrolyte that has an ion in common with the weak electrolyte.

- Common ion equilibrium problems are solved following the same pattern as other equilibrium problems.

- **However, the initial concentration of the common ion (from the salt) must be considered.**
Sample Exercise 17.1 (p. 720)

What is the pH of a solution made by adding 0.30 mol of acetic acid (HC₂H₃O₂) and 0.30 mol of sodium acetate (NaC₂H₃O₂) to enough water to make 1.0 L of solution?

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

<table>
<thead>
<tr>
<th>Initial</th>
<th>0.30 M</th>
<th>0</th>
<th>0.30 M</th>
</tr>
</thead>
<tbody>
<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>

Practice Exercise 17.1

Calculate the pH of a solution containing 0.085 M nitrous acid (HNO₂, $K_a = 4.5 \times 10^{-4}$) and 0.10 M potassium nitrite (KNO₂).

(3.42)
Sample Exercise 17.2 (p. 722)

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

\[ [\text{F}^-] = 1.4 \times 10^{-3} \text{ M}; \quad \text{pH} = 1.00 \]

<table>
<thead>
<tr>
<th></th>
<th>( \text{HF}(aq) )</th>
<th>( \text{H}^+(aq) )</th>
<th>( \text{F}^-(aq) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial</td>
<td>0.20 M</td>
<td>0.10 M</td>
<td>0</td>
</tr>
<tr>
<td>Change</td>
<td>(-x) M</td>
<td>(+x) M</td>
<td>(+x) M</td>
</tr>
<tr>
<td>Equilibrium</td>
<td>((0.20 - x)) M</td>
<td>((0.10 + x)) M</td>
<td>(x) M</td>
</tr>
</tbody>
</table>

Practice Exercise 17.2

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 HNO₃.

\[ [\text{HCOO}^-] = 9.0 \times 10^{-5} \text{ M}; \quad \text{pH} = 1.00 \]
17.2 Buffered Solutions

A buffered solution or buffer is a solution that resists a drastic change in pH upon addition of small amounts of strong acid or strong base.

Composition and Action of Buffered Solutions

- A buffer consists of a mixture of a weak acid (HX) and its conjugate base (X^-):
  \[ HX(aq) \rightleftharpoons H^+(aq) + X^-(aq) \]

- Thus a buffer contains both:
  - An acidic species (to neutralize OH^-)
  - A basic species (to neutralize H^+).

- When a small amount of OH^- is added to the buffer, the OH^- reacts with HX to produce X^- and water.
  - But the [HX]/[X^-] ratio remains more or less constant, so the pH is not significantly changed.

- When a small amount of H^+ is added to the buffer, X^- is consumed to produce HX.
  - Once again, the [HX]/[X^-] ratio is more or less constant, so the pH does not change significantly.

Calculating the pH of a Buffer

- The pH of the buffer is related to \( K_a \) and to the relative concentrations of the acid and base.
- We can derive an equation that shows the relationship between conjugate acid–base concentrations, pH and \( K_a \).
- By definition:
  \[ K_a = \frac{[H^+][X^-]}{[HX]} \]

- Rearranging, we get:
  \[ [H^+] = K_a \frac{[HX]}{[X^-]} \]

- If we take the negative natural logarithm of each side of the equation we get:
  \[ -\log[H^+] = -\log K_a - \log \frac{[HX]}{[X^-]} \]

- By definition:
  \[ pH = pK_a - \log \frac{[HX]}{[X^-]} \]

- An alternate form of this equation is:
  \[ pH = pK_a + \log \frac{[X^-]}{[HX]} = pK_a + \log \frac{\text{base}}{\text{acid}} \]

- The above equation is the **Henderson-Hasselbalch equation**.
  - Note that this equation uses the equilibrium concentrations of the acid and conjugate base.
Buffer Capacity and pH Range

- **Buffer capacity** is the amount of acid or base that can be neutralized by the buffer before there is a significant change in pH.

- Buffer capacity depends on the concentrations of the components of the buffer.
  - The greater the concentrations of the conjugate acid–base pair, the greater the buffer capacity.

- The **pH range** of a buffer is the pH range over which it is an effective buffer.
  - The pH range of a buffer is generally within one pH unit of the $pK_a$ of the buffering agent.

**Sample Exercise 17.3 (p. 725)**

What is the pH of a buffer that is 0.12 M in lactic acid (HC₃H₅O₃) and 0.10 M in sodium lactate (Na C₃H₅O₃)? For lactic acid, $K_a = 1.4 \times 10^{-4}$.

\[(3.77)\]

\[
\begin{array}{c|c|c|c}
\text{HC}_3\text{H}_5\text{O}_3(aq) & \rightleftharpoons & \text{H}^+(aq) & + \\
\text{C}_3\text{H}_5\text{O}_3^-(aq) \\
\hline
\text{Initial} & 0.12 \text{ M} & 0 & 0.10 \text{ M} \\
\text{Change} & -x \text{ M} & +x \text{ M} & +x \text{ M} \\
\text{Equilibrium} & (0.12 - x) \text{ M} & x \text{ M} & (0.10 + x) \text{ M} \\
\end{array}
\]

**Practice Exercise 17.3**

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

\[(4.42)\]
Sample Exercise 17.4 (p. 726)

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.)

(0.36 mol)

Practice Exercise 17.4

Calculate the concentration of sodium benzoate that must be present in a 0.20 M solution of benzoic acid (HC₇H₅O₂) to produce a pH of 4.00.

(0.13 M)
Addition of Strong Acids or Bases to Buffers

- We break the calculation into two parts.
  - A *stoichiometric* calculation.
  - An *equilibrium* calculation.

Sample Exercise 17.5 (p. 728)

A buffer is made by adding 0.300 mol of HC$_2$H$_3$O$_2$ and 0.300 mol NaC$_2$H$_3$O$_2$ 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. 

\[ \text{pH} = 4.80 \]

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).

\[ \text{pH} = 12.30 \]

Practice Exercise 17.5

Determine

a) the pH of the original buffer described in Sample Exercise 17.5 after the addition of 0.020 mol HCl, and

\[ \text{pH} = 4.68 \]

b) the pH of the solution that would result from the addition of 0.020 mol HCl to 1.00 L of pure water.

\[ \text{pH} = 1.70 \]
17.3 Acid-Base Titrations

- The plot of pH versus volume during a titration is called a **pH titration curve**.

**Strong Acid-Strong Base Titrations**

- Consider adding a strong base (e.g., NaOH) to a solution of a strong acid (e.g., HCl).

- We can divide the titration curve into four regions.

  1. **Initial pH (before any base is added).**
     - The pH is given by the strong acid solution.
     - Therefore, pH < 7.

  2. **Between the initial pH and the equivalence point.**
     - When base is added before the equivalence point the pH is given by the amount of strong acid in excess.
     - Therefore, pH < 7.

  3. **At the equivalence point.**
     - The amount of base added is stoichiometrically equivalent to the amount of acid originally present.
     - The cation of a strong base and the anion of a strong acid do not undergo hydrolysis.
     - Therefore, pH = 7.00.

  4. **After the equivalence point.**
     - The pH is determined by the excess base in the solution.
     - Therefore, pH > 7.

**Seven Steps to solving titration problems:**

**Analyze the problem, then:**

1. **Determine # moles of each reactant.**
2. **Determine # moles of all species after reaction.**
3. **Calculate new volume after reaction.**
4. **Determine molarities of all species (combine Steps 2 & 3).**
5. **Equilibrium calculation – RICE table.** *
6. **Equilibrium calculation, substituting results from Step 5 into $K_a$.** *
7. **$[H^+] \rightarrow pH$. May mean $[OH^-] \rightarrow pOH \rightarrow 14.00 - pOH = pH$.** *

*not required for strong acid-strong base titrations
Sample Exercise 17.6 (p. 731)

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 (3.00)
b) 51.0 mL (11.00)

<table>
<thead>
<tr>
<th>H⁺(aq)</th>
<th>OH⁻(aq)</th>
<th>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>4.90 × 10⁻³ mol</td>
<td>—</td>
</tr>
<tr>
<td>After addition</td>
<td>0.10 × 10⁻³ mol</td>
<td>0</td>
</tr>
</tbody>
</table>

Practice Exercise 17.6

Calculate the pH when the following quantities of 0.10 M HNO₃ have been added to 25.0 mL of 0.10 M KOH solution:

a) 24.9 mL (10.30)
b) 25.1 mL (3.70)
Weak Acid-Strong Base Titration

Again, we divide the titration into four general regions:

1. Before any base is added:
   - The solution contains only weak acid.
   - Therefore, pH is given by the equilibrium calculation.

2. Between the initial pH and the equivalence point.
   - As strong base is added it consumes a stoichiometric quantity of weak acid:
     \[ \text{HC}_2\text{H}_3\text{O}_2(aq) + \text{OH}^-(aq) \rightarrow \text{C}_2\text{H}_3\text{O}_2^-(aq) + \text{H}_2\text{O}(l) \]
   - However, there is an excess of acetic acid.
   - Therefore, we have a mixture of weak acid and its conjugate base.
     - Thus the composition of the mixture is that of a buffer.
     - The pH is given by the buffer calculation.
     - First the amount of \( \text{C}_2\text{H}_3\text{O}_2^- \) generated is calculated, as well as the amount of \( \text{HC}_2\text{H}_3\text{O}_2 \) consumed. (Stoichiometry.)
     - Then the pH is calculated using equilibrium conditions. (Henderson-Hasselbalch equation.)
Sample Exercise 17.7 (p. 735)

Calculate the pH of the solution formed when 45.0 mL of 0.100 M NaOH solution is added to 50.0 mL of 0.100 M \( \text{HC}_2\text{H}_3\text{O}_2 \). \( (K_a = 1.8 \times 10^{-5}) \)

\( (2.0 \times 10^{-6} \text{ M}) \)

<table>
<thead>
<tr>
<th></th>
<th>CH(_3)COOH(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>0</td>
</tr>
<tr>
<td>Addition</td>
<td></td>
<td>4.50 \times 10^{-3} mol</td>
<td></td>
</tr>
<tr>
<td>After addition</td>
<td>0.50 \times 10^{-3} mol</td>
<td>0</td>
<td>4.50 \times 10^{-3} mol</td>
</tr>
</tbody>
</table>

Practice Exercise 17.7

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 \( (\text{HC}_7\text{H}_5\text{O}_2, K_a = 6.3 \times 10^{-5}) \). \( (4.20) \)

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 \( \text{NH}_3 \). \( (9.26) \)
Sample Exercise 17.8 (p. 735)
Calculate the pH at the equivalence point in the titration of 50.0 mL of 0.100 M \( \text{HC}_2\text{H}_3\text{O}_2 \) with 0.100 M NaOH.

(8.72)

Practice Exercise 17.8
Calculate the pH at the equivalence point when
a) 40.0 mL of 0.025 M benzoic acid (\( \text{HC}_7\text{H}_5\text{O}_2 \), \( K_a = 6.3 \times 10^{-5} \)) is titrated with 0.050 M NaOH
(8.21)

b) 40.0 mL of 0.100 M \( \text{NH}_3 \) is titrated with 0.100 HCl
(5.28)
## Strong acid/Weak acid Titrations

<table>
<thead>
<tr>
<th>Strong Acid</th>
<th>Weak Acid</th>
</tr>
</thead>
<tbody>
<tr>
<td>• pH begins at 7, gradual ↑ as base is added</td>
<td>• Initial pH ↑ is steeper than for strong acid</td>
</tr>
<tr>
<td>• pH ↑ dramatically near equivalence point</td>
<td>• pH levels off (buffer effect)</td>
</tr>
<tr>
<td>• pH equivalence point = 7.00</td>
<td>• pH at equivalence point &gt; 7.00</td>
</tr>
<tr>
<td>• Shape of curve after equivalence point is due to [base]</td>
<td>• Shape of curve after equivalence point is due to [base]</td>
</tr>
</tbody>
</table>

## Titrations of Polyprotic Acids

- In polyprotic acids, the ionizable protons dissociate in a series of steps.
  - Therefore, in a titration there are \( n \) equivalence points corresponding to each ionizable proton.

- In the titration of \( \text{H}_3\text{PO}_4 \) with \( \text{NaOH} \) there are three equivalence points:
  - one for the formation of \( \text{H}_2\text{PO}_4^- \),
  - one for the formation of \( \text{HPO}_4^{2-} \), and
  - one for the formation of \( \text{PO}_4^{3-} \).

![Diprotic acid.](image)

Titrination curve for the reaction of 50.0 mL of 0.10 M \( \text{H}_3\text{PO}_3 \) with 0.10 M \( \text{NaOH} \).
17.4 Solubility Equilibria

The Solubility-Product Constant, $K_{sp}$

$K_{sp}$ is the equilibrium constant for the equilibrium between an ionic solid solute and its saturated aqueous solution = solubility-product constant or the solubility product.

Sample Exercise 17.9 (p. 738)

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

Practice Exercise 17.9

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
**Solubility and** $K_{sp}$

- **Solubility** = the maximum amount of solute that can be dissolved in a standard volume of solvent.
  - often expressed as grams of solid that will dissolve per liter of solution (g/L).

- **Molar solubility** = the number of moles of solute that dissolve to form a liter of saturated solution.

- We can use the **solubility** to find $K_{sp}$ and vice versa.

  - **To convert solubility to** $K_{sp}$:
    1. Convert **solubility** → **molar solubility** (via molar mass).
    2. Convert **molar solubility** → **molar concentration of ions at equilibrium** (equilibrium calculation).
    3. Use the equilibrium [ions] in the $K_{sp}$ expression.

  - **To convert** $K_{sp}$ **to solubility**:
    1. Write the $K_{sp}$ expression.
    2. Let $x$ = the **molar solubility** of the salt.
    3. Use the **stoichiometry** of the reaction to express the concentration of each species in terms of $x$.
    4. Substitute these concentrations into the equilibrium expression and solve for $x$.
    5. This calculation works best for salts whose ions have low charges.

**Sample Exercise 17.10 (p. 739)**

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.

$(1.1 \times 10^{-12})$
Practice Exercise 17.10

A saturated solution of Mg(OH)₂ in contact with undissolved solid is prepared at 25°C. 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 Mg²⁺ or OH⁻ ions in the solution, calculate $K_{sp}$ for this compound.

$(1.6 \times 10^{-12})$

Sample Exercise 17.11 (p. 740)

The $K_{sp}$ for CaF₂ is $3.9 \times 10^{-11}$ at 25°C. Assuming that CaF₂ dissociates completely upon dissolving and that there are no other important equilibria affecting its solubility, calculate the solubility of CaF₂ in grams per liter.

$(1.6 \times 10^{-2}$ g CaF₂/L soln)
Practice Exercise 17.11

The $K_{sp}$ for LaF₃ is $2 \times 10^{-19}$. What is the solubility of LaF₃ in water in moles per liter?

$(9 \times 10^{-6} \text{ mol/L})$
17.5 Factors That Affect Solubility

- Three factors that have a significant impact on solubility are:
  1. The presence of a common ion.
  2. The pH of the solution.
  3. The presence or absence of complexing agents.

Sample Exercise 17.12 (p. 742)

Calculate the molar solubility of CaF₂ at 25°C in a solution that is
a) 0.010 M Ca(NO₃)₂  (3.1 x 10⁻⁵ mol CaF₂/L 0.010 M Ca(NO₃)₂)
b) 0.010 M in NaF       (3.9 x 10⁻⁷ mol CaF₂/L 0.010 M NaF)

<table>
<thead>
<tr>
<th></th>
<th>CaF₂(s)</th>
<th>Ca²⁺(aq)</th>
<th>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>−x M</td>
<td>+x M</td>
<td>+2x M</td>
</tr>
<tr>
<td>Equilibrium</td>
<td>(0.010 + x) M</td>
<td>2x M</td>
<td></td>
</tr>
</tbody>
</table>
Practice Exercise 17.12

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

$(4.0 \times 10^{-10} \text{ M})$
Sample Exercise 17.13 (p. 745)

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)

(a-c)
### Practice Exercise 17.13

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

- a) CuS
- b) Cu(N₃)₂
3. Formation of Complex Ions

- Metal ions may act as Lewis acids in aqueous solution (water may act as the Lewis base). → may have a significant impact on metal salt solubility.

- Consider the formation of Ag(NH₃)₂⁺: \( \text{Ag}^+(aq) + 2\text{NH}_3(aq) \rightleftharpoons \text{Ag(NH}_3\text{)}_2^+(aq) \)
  - \( \text{Ag(NH}_3\text{)}_2^+ \) is called a complex ion.
  - \text{NH}_3 (the attached Lewis base) = a ligand.
  - equilibrium constant = the formation constant, \( K_f \):
    \[
    K_f = \frac{[\text{Ag(NH}_3\text{)}_2^+]}{[\text{Ag}^+][\text{NH}_3]^2} = 1.7 \times 10^7
    \]

<table>
<thead>
<tr>
<th>Complex Ion</th>
<th>( K_f )</th>
<th>Equilibrium Equation</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{Ag(NH}_3\text{)}_2^+ )</td>
<td>( 1.7 \times 10^7 )</td>
<td>( \text{Ag}^+(aq) + 2\text{NH}_3(aq) \rightleftharpoons \text{Ag(NH}_3\text{)}_2^+(aq) )</td>
</tr>
<tr>
<td>( \text{Ag(CN)}_2^- )</td>
<td>( 1 \times 10^{21} )</td>
<td>( \text{Ag}^+(aq) + 2\text{CN}^-(aq) \rightleftharpoons \text{Ag(CN)}_2^-(aq) )</td>
</tr>
<tr>
<td>( \text{Ag(S}_2\text{O}_3\text{)}_2^{3-} )</td>
<td>( 2.9 \times 10^{13} )</td>
<td>( \text{Ag}^+(aq) + 2\text{S}_2\text{O}_3^{2-}(aq) \rightleftharpoons \text{Ag(S}_2\text{O}_3\text{)}_2^{3-}(aq) )</td>
</tr>
<tr>
<td>( \text{CdBr}_2^- )</td>
<td>( 5 \times 10^3 )</td>
<td>( \text{Cd}^{2+}(aq) + 4\text{Br}^-(aq) \rightleftharpoons \text{CdBr}_2^-\text{(aq)} )</td>
</tr>
<tr>
<td>( \text{Cr(OH)}_4^- )</td>
<td>( 8 \times 10^{20} )</td>
<td>( \text{Cr}^{3+}(aq) + 4\text{OH}^-(aq) \rightleftharpoons \text{Cr(OH)}_4^-\text{(aq)} )</td>
</tr>
<tr>
<td>( \text{Co(SCN)}_4^{2-} )</td>
<td>( 1 \times 10^3 )</td>
<td>( \text{Co}^{2+}(aq) + 4\text{SCN}^-(aq) \rightleftharpoons \text{Co(SCN)}_4^{2-}(aq) )</td>
</tr>
<tr>
<td>( \text{Cu(NH}_3\text{)}_4^{2+} )</td>
<td>( 5 \times 10^{12} )</td>
<td>( \text{Cu}^{2+}(aq) + 4\text{NH}_3(aq) \rightleftharpoons \text{Cu(NH}_3\text{)}_4^{2+}(aq) )</td>
</tr>
<tr>
<td>( \text{Cu(CN)}_4^{2-} )</td>
<td>( 1 \times 10^{25} )</td>
<td>( \text{Cu}^{2+}(aq) + 4\text{CN}^-(aq) \rightleftharpoons \text{Cu(CN)}_4^{2-}(aq) )</td>
</tr>
<tr>
<td>( \text{Ni(NH}_3\text{)}_6^{2+} )</td>
<td>( 1.2 \times 10^9 )</td>
<td>( \text{Ni}^{2+}(aq) + 6\text{NH}_3(aq) \rightleftharpoons \text{Ni(NH}_3\text{)}_6^{2+}(aq) )</td>
</tr>
<tr>
<td>( \text{Fe(CN)}_6^{3-} )</td>
<td>( 1 \times 10^{35} )</td>
<td>( \text{Fe}^{2+}(aq) + 6\text{CN}^-(aq) \rightleftharpoons \text{Fe(CN)}_6^{3-}(aq) )</td>
</tr>
<tr>
<td>( \text{Fe(CN)}_6^{3-} )</td>
<td>( 1 \times 10^{42} )</td>
<td>( \text{Fe}^{3+}(aq) + 6\text{CN}^-(aq) \rightleftharpoons \text{Fe(CN)}_6^{3-}(aq) )</td>
</tr>
</tbody>
</table>

Common ions that form complexes: \( \text{NH}_3, \text{CN}^-, \text{OH}^-, \text{SCN}^-, \) halogens

Clue in Reactions Question = an excess of concentrated … is added to …

Chapters 5 and 13 The Ultimate Equations Handbook
Sample Exercise 17.14 (p. 748)

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

($[\text{Ag}^+] = 1.5 \times 10^{-8} \text{ M}$)

<table>
<thead>
<tr>
<th></th>
<th>$\text{Ag(NH}_3)_2^{2+}$ (aq)</th>
<th>$\text{Ag}^+$ (aq)</th>
<th>$+2 \text{NH}_3(aq)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial</td>
<td>$0.010 \text{ M}$</td>
<td>$0 \text{ M}$</td>
<td></td>
</tr>
<tr>
<td>Change</td>
<td>$-x \text{ M}$</td>
<td>$+x \text{ M}$</td>
<td></td>
</tr>
<tr>
<td>Equilibrium</td>
<td>$0.010 - x \text{ M}$</td>
<td>$x \text{ M}$</td>
<td>$0.20 \text{ M}$</td>
</tr>
</tbody>
</table>

Practice Exercise 17.14

Calculate $[\text{Cr}^{3+}]$ in equilibrium with $\text{Cr(OH)}_4^-$ when 0.010 mol of $\text{Cr(NO}_3)_3$ is dissolved in a liter of solution buffered at pH 10.0.

($[\text{Cr}^{3+}] = 1 \times 10^{-16} \text{ M}$)
**Amphotericism**
- Substances that are capable of acting either as an acid or a base are **amphoteric**.
  - The term is similar to one discussed earlier: *amphiprotic*, which relates more generally to any species that can either gain or lose a proton.
- Amphoteric metal hydroxides and oxides will dissolve in either a strong acid or a strong base.
  - e.g.: hydroxides and oxides of $\text{Al}^{3+}$, $\text{Cr}^{3+}$, $\text{Zn}^{2+}$, and $\text{Sn}^{2+}$.
  - The hydroxides generally form complex ions with several hydroxide ligands attached to the metal:
    \[
    \text{Al(OH)}_3(s) + \text{OH}^-(aq) \rightleftharpoons \text{Al(OH)}_4(aq)
    \]
- Hydrated metal ions act as weak acids.
  - As strong base is added, protons are removed:
    \[
    \text{Al(H}_2\text{O)}_6^{3+}(aq) + \text{OH}^-(aq) \rightleftharpoons \text{Al(H}_2\text{O)}_5\text{(OH)}^{2+}(aq) + \text{H}_2\text{O}(l)
    \]
    \[
    \text{Al(H}_2\text{O)}_5\text{(OH)}^{2+}(aq) + \text{OH}^-(aq) \rightleftharpoons \text{Al(H}_2\text{O)}_4\text{(OH)}^+(aq) + \text{H}_2\text{O}(l)
    \]
    \[
    \text{Al(H}_2\text{O)}_4\text{(OH)}^+(aq) + \text{OH}^-(aq) \rightleftharpoons \text{Al(H}_2\text{O)}_3\text{(OH)}(s) + \text{H}_2\text{O}(l)
    \]
    \[
    \text{Al(H}_2\text{O)}_3\text{(OH)}(s) + \text{OH}^-(aq) \rightleftharpoons \text{Al(H}_2\text{O)}_2\text{(OH)}_3(aq) + \text{H}_2\text{O}(l)
    \]
- Addition of an acid reverses these reactions

**17.6 Precipitation and Separation of Ions**
- If $Q > K_{sp}$, precipitation occurs until $Q = K_{sp}$.
- If $Q = K_{sp}$ equilibrium exists (saturated solution).
- If $Q < K_{sp}$, solid dissolves until $Q = K_{sp}$.
Sample Exercise 17.15 (p.751)

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$_2$SO$_4$? (yes)

Practice Exercise 17.15

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$_3$)$_2$? (yes)

Selective Precipitation of Ions

- Ions can be separated from each other based on the solubilities of their salts.
Sample Exercise 17.16 (p. 751)

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?

($> 2.9 \times 10^{-2}$ M for PbCl$_2$; $> 1.8 \times 10^{-8}$ M for AgCl, precipitates first)

Practice Exercise 17.16

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)$_2$)

(Cu(OH)$_2$ precipitates first, when [OH$^-] > 1.5 \times 10^{-9}$ M; Mg(OH)$_2$ precipitates when [OH$^-] > 1.9 \times 10^{-5}$ M)
17.7 Qualitative Analysis for Metallic Elements

- **Quantitative analysis** is designed to determine how much metal ion is present.
- **Qualitative analysis** is designed to detect the presence of metal ions.
  - Typical qualitative analysis of a metal ion mixture involves:
    1. Separation of ions into five major groups on the basis of their differential solubilities.
      - Insoluble chlorides.
      - Acid-insoluble sulfides.
      - Base-insoluble sulfides and hydroxides.
      - Insoluble phosphates.
      - Alkali metals and ammonium ion.
    2. Individual ions within each group are separated by selectively dissolving members of the group.
    3. Specific tests are used to determine whether a particular ion is present or absent.
Sample Integrative Exercise 17 (p. 755)

A sample of 1.25 L of HCl gas at 21°C 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 of the HCl dissolves and that the volume of the solution remains 0.500 L.

(pH = 8.97)