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

- This causes a reduction in the \([\text{H}^+]\) 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?

\[(4.74)\]

<table>
<thead>
<tr>
<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>
</tr>
<tr>
<td>Change</td>
<td>−x M</td>
<td>+x M</td>
</tr>
<tr>
<td>Equilibrium</td>
<td>(0.30 − x) M</td>
<td>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.

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

<table>
<thead>
<tr>
<th></th>
<th>HF(_{aq})</th>
<th>H(^+)(_{aq})</th>
<th>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.

\([\text{HCOO}^-] = 9.0 \times 10^{-5} \text{ M}; \text{ pH } = 1.00\)
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⁻).
  \[ \text{HX}(aq) \rightleftharpoons \text{H}^+(aq) + \text{X}^-(aq) \]

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

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

- When a small amount of \( \text{H}^+ \) is added to the buffer, \( \text{X}^- \) is consumed to produce \( \text{HX} \).
  - 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:

$$\text{pH} = pK_a - \log \frac{[HX]}{[X^-]}$$

- An alternate form of this equation is:

$$\text{pH} = pK_a + \log \frac{[X^-]}{[HX]} = pK_a + \log \frac{\text{base}}{\text{acid}}$$

- The above equation is the **Henderson-Hasselbalch equation**.

  - Note that this equation uses the equilibrium concentrations of the acid and conjugate base.
  - However, if $K_a$ is sufficiently small (i.e., if the equilibrium concentration of the undissociated acid is close to the initial concentration), then we can use the initial values of the acid and base concentrations in order to get a good estimate of the pH.

**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)

<table>
<thead>
<tr>
<th></th>
<th>( \text{HC}_3\text{H}_5\text{O}_3(\text{aq}) )</th>
<th>( \text{H}^+(\text{aq}) )</th>
<th>( \text{C}_3\text{H}_5\text{O}_3^- (\text{aq}) )</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Initial</strong></td>
<td>0.12 M</td>
<td>0</td>
<td>0.10 M</td>
</tr>
<tr>
<td><strong>Change</strong></td>
<td>(-x) M</td>
<td>(+x) M</td>
<td>(+x) M</td>
</tr>
<tr>
<td><strong>Equilibrium</strong></td>
<td>((0.12 - x)) M</td>
<td>(x) M</td>
<td>((0.10 + x)) M</td>
</tr>
</tbody>
</table>

**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.
  - The addition of strong acid or base results in a neutralization reaction:
    
    \[
    \begin{align*}
    X^- + H_3O^+ &\rightarrow HX + H_2O \\
    HX + OH^- &\rightarrow X^- + H_2O 
    \end{align*}
    \]

- By knowing how much $H_3O^+$ or $OH^-$ was added we know how much $HX$ or $X^-$ is formed.

- An *equilibrium* calculation.

  - With the concentrations of $HX$ and $X^-$ (note the change in volume of solution) we can calculate the pH from the Henderson-Hasselbalch equation:
    \[
    pH = pK_a + \log \left(\frac{[X^-]}{[HX]}\right)
    \]
Sample Exercise 17.5 (p. 728)

A buffer is made by adding 0.300 mol of HC₂H₃O₂ and 0.300 mol NaC₂H₃O₂ 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 (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) (12.30)

<table>
<thead>
<tr>
<th></th>
<th>CH₃COOH(aq) + OH⁻(aq) → H₂O(l) + CH₃COO⁻(aq)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Buffer before addition</td>
<td>0.300 mol</td>
</tr>
<tr>
<td>Addition</td>
<td>0.020 mol</td>
</tr>
<tr>
<td>Buffer after addition</td>
<td>0.280 mol</td>
</tr>
</tbody>
</table>

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 (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. (1.70)
17.3 Acid-Base Titrations

- In an acid–base titration:
  - a solution of base of known concentration is added to an acid (or an acid of known concentration is added to a base).
  - acid–base indicators, or pH meters, are used to signal the equivalence point.
    - The *equivalence point* is the point at which stoichiometrically equivalent quantities of acid and base have been added.
  - 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
      - 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>Reaction</th>
<th>Before addition</th>
<th>Addition</th>
<th>After addition</th>
</tr>
</thead>
<tbody>
<tr>
<td>$H^+(aq)$</td>
<td>$5.00 \times 10^{-3}$ mol</td>
<td>$4.99 \times 10^{-3}$ mol</td>
<td>$0.10 \times 10^{-3}$ mol</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Species</th>
<th>Before</th>
<th>Addition</th>
<th>After</th>
</tr>
</thead>
<tbody>
<tr>
<td>$OH^-$</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>$H_2O$</td>
<td>—</td>
<td>—</td>
<td>—</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)
• How can we analyze the titration (i.e., how will we know when we are at the equivalence point?).
  • Consider adding a strong base (e.g., NaOH) to a solution of a strong acid (e.g., HCl).
  • We know the pH at the equivalence point is 7.00.
  • To detect the equivalence point, we use an indicator that changes color somewhere near pH 7.00.
  • Usually, we use phenolphthalein which changes color between pH 8.3 to 10.0.
    • In acid, phenolphthalein is colorless.
    • As NaOH is added, there is a slight pink color at the addition point.
    • When the flask is swirled and the reagents mixed, the pink color disappears.
    • At the end point, the solution is light pink.
    • If more base is added, the solution turns darker pink.
    • The equivalence point in a titration is the point at which the acid and base are present in stoichiometrically equivalent quantities.
    • The end point in a titration is the point where the indicator changes color.
      • The difference between the equivalence point and the end point is called the titration error.
  • The shape of a strong base-strong acid titration curve is very similar to a strong acid-strong base titration curve.
    • Initially, the strong base is in excess, so the pH > 7.
    • As acid is added, the pH decreases but is still greater than 7.
    • At the equivalence point, the pH is given by the salt solution (i.e., pH = 7).
    • After the equivalence point, the pH is given by the strong acid in excess, so pH is less than 7.
Weak Acid-Strong Base Titration

Consider the titration of acetic acid, $\text{HC}_2\text{H}_3\text{O}_2$ with $\text{NaOH}$.

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:
     \[
     \text{HC}_2\text{H}_3\text{O}_2 \text{ (aq)} + \text{OH}^- \text{ (aq)} \rightarrow \text{C}_2\text{H}_3\text{O}_2^- \text{ (aq)} + \text{H}_2\text{O} \text{ (l)}
     \]
   - 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.)
3. At the equivalence point, all the acetic acid has been consumed and all the NaOH has been consumed.
   - However, $\text{C}_2\text{H}_3\text{O}_2^-$ has been generated.
   - Therefore, the pH depends on the $\text{C}_2\text{H}_3\text{O}_2^-$ concentration.
   - The pH $> 7$ at the equivalence point.
   - More importantly, the pH of the equivalence point $\neq 7$ for a weak acid-strong base titration.

4. After the equivalence point:
   - The pH is given by the concentration of the excess strong base.
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 HC₂H₃O₂. \( (K_a = 1.8 \times 10^{-5}) \)

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

<table>
<thead>
<tr>
<th>Before addition</th>
<th>After addition</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₂COOH(aq)</td>
<td>CH₂COO⁻(aq)</td>
</tr>
<tr>
<td>OH⁻(aq)</td>
<td>CH₂COO⁺(aq)</td>
</tr>
<tr>
<td>5.00 \times 10^{-3} mol</td>
<td>4.50 \times 10^{-3} mol</td>
</tr>
<tr>
<td>0</td>
<td>0</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 (HC₇H₅O₂, \( K_a = 6.3 \times 10^{-5} \)). \( (4.20) \)

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 NH₃. \( (9.26) \)
Sample Exercise 17.8 (p. 735)

Calculate the pH at the equivalence point in the titration of 50.0 mL of 0.100 M HC₂H₃O₂ 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 (HC₇H₅O₂, Kₐ = 6.3 x 10⁻⁵) is titrated with 0.050 M NaOH

(8.21)

b) 40.0 mL of 0.100 M NH₃ is titrated with 0.100 HCl

(5.28)
The pH curve for a weak acid-strong base titration differs significantly from that of a strong acid-strong base titration.

- For a strong acid-strong base titration:
  - The pH begins at less than 7 and gradually increases as base is added.
  - Near the equivalence point, the pH increases dramatically.

- For a weak acid-strong base titration:
  - The initial pH rise is steeper than the strong acid-strong base case.
  - However, there is a leveling off due to buffer effects.
  - The middle section of the titration curve is not as steep for a weak acid-strong base titration.

The shape of the two curves after the equivalence point is the same because pH is determined by the strong base in excess.

The pH at the equivalence point differs also:
- The pH is 7.00 for the strong acid-strong base equivalence point.
- The pH is >7.00 for the weak acid-strong base equivalence point.

### 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>
Titration of a Weak Base with a Strong Acid

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

Diprotic acid.

Titration curve for the reaction of 50.0 mL of 0.10 M H$_3$PO$_3$ with 0.10 M NaOH.
17.4 Solubility Equilibria

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

$K_{sp} = \text{equilibrium constant for the equilibrium between an ionic solid solute and its saturated aqueous solution.}$

$= \text{solubility-product constant or the solubility product.}$

In general: the solubility product is equal to the product of the molar concentration of ions raised to powers corresponding to their stoichiometric coefficients. $K_{sp} = [\text{cation}]^m[\text{anion}]^n$ where $m, n = \text{stoichiometric coefficients}$

- Consider a saturated solution of BaSO$_4$ in contact with solid BaSO$_4$.

  $\text{BaSO}_4(s) \leftrightharpoons \text{Ba}^{2+}(aq) + \text{SO}_4^{2-}(aq)$

  - Because BaSO$_4(s)$ is a pure solid $\rightarrow$ the equilibrium expression depends only on the concentration of the ions.

  - $K_{sp}$ for BaSO$_4$ is: $K_{sp} = [\text{Ba}^{2+}][\text{SO}_4^{2-}].$ BaSO$_4$ falls out of $K$ because it is a solid.

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 $\rightarrow$ molar solubility (via molar mass).
    2. Convert molar solubility $\rightarrow$ 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.

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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 Mg$^{2+}$ or OH$^-$ ions in the solution, calculate $K_{sp}$ for this compound.

(1.6 x 10$^{-12}$)

Sample Exercise 17.11 (p. 740)

The $K_{sp}$ for CaF$_2$ is 3.9 x 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.

(1.6 x 10$^{-2}$ g CaF$_2$/L soln)
Practice Exercise 17.11

The $K_{sp}$ for LaF$_3$ is $2 \times 10^{-19}$. What is the solubility of LaF$_3$ 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**.

1. **Common-Ion Effect**

- Solubility is ↓ when a common ion is added (Le Châtelier’s principle):
  
  e.g. CaF₂:  CaF₂(s) ⇌ Ca²⁺(aq) + 2F⁻(aq)
  
  - Add more F⁻ (i.e., + NaF), the equilibrium shifts to offset the increase.
  
  - → CaF₂(s) is formed and precipitation occurs.
  
  - As NaF is added to the system, the solubility of CaF₂ ↓

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**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 10⁻² 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>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>−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, 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.

(4.0 x 10$^{-10}$ M)

2. Solubility and pH

• Apply Le Châtelier’s principle: $\text{Mg(OH)}_2(s) \rightleftharpoons \text{Mg}^{2+}(aq) + 2\text{OH}^-(aq)$

  • If OH$^-$ is removed, then the equilibrium $\rightarrow$ the right and Mg(OH)$_2$ dissolves.
  
  • OH$^-$ can be removed by adding a strong acid: $\text{OH}^-(aq) + \text{H}^+(aq) \rightleftharpoons \text{H}_2\text{O}(aq)$

  • As pH $\downarrow$, [H$^+$] $\uparrow$ and the solubility of Mg(OH)$_2$ $\uparrow$.

  e.g.: $\text{CaF}_2(s) \rightleftharpoons \text{Ca}^{2+}(aq) + 2\text{F}^-(aq)$

  • If F$^-$ is removed, $\rightarrow$ equilibrium shifts $\rightarrow$ the right $\rightarrow$CaF$_2$ dissolves.

  • F$^-$ can be removed by adding a strong acid: $\text{F}^-(aq) + \text{H}^+(aq) \rightleftharpoons \text{HF}(aq)$

  • As pH $\downarrow$, [H$^+$] $\uparrow$ and solubility of CaF$_2$ $\uparrow$. 
• The effect of pH on solubility can be dramatic, esp. if one or both ions involved are at least somewhat acidic or basic.

• In general:
  
  • The solubility of slightly soluble salts containing basic ions ↑ as pH ↓.
  
  • The more basic the anion → the greater the effect.

Dissolution of a precipitate in acid.

A white precipitate of Mg(OH)$_2(s)$ in contact with its saturated solution is in the test tube on the left.

The dropper poised above the solution surface contains hydrochloric acid.

(The anions accompanying the acid have been omitted to simplify the art.)
Sample Exercise 17.13 (p. 745)

Which of the following substances will be more soluble in acidic solution than in basic solution:

a) \( \text{Ni(OH)}_2(s) \)

b) \( \text{CaCO}_3(s) \)

c) \( \text{BaF}_2(s) \)

d) \( \text{AgCl}(s) \)

(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.

- e.g. AgCl has a very low solubility.
  - \( K_{sp} \) for AgCl = 1.8 x 10^{-10}
  - but the solubility is greatly ↑ if ammonia is added.
  - Why?

- Consider the formation of \( \text{Ag(NH}_3\text{)}_2^+ \):
  \[
  \text{Ag}^+(aq) + 2\text{NH}_3(aq) \rightleftharpoons \text{Ag(NH}_3\text{)}_2^+(aq)
  \]

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

- e.g. the addition of ammonia to AgCl (white salt):
  \[
  \text{AgCl(s)} \rightleftharpoons \text{Ag}^+(aq) + \text{Cl}^-(aq)
  \]
  \[
  \text{Ag}^+(aq) + 2\text{NH}_3(aq) \rightleftharpoons \text{Ag(NH}_3\text{)}_2^+(aq)
  \]

- overall reaction:
  \[
  \text{AgCl(s)} + 2\text{NH}_3(aq) \rightleftharpoons \text{Ag(NH}_3\text{)}_2^+(aq) + \text{Cl}^-(aq)
  \]

- → the \( \text{Ag}^+(aq) \) has been removed from solution.

- By Le Châtelier’s principle, the forward reaction (the dissolving of AgCl) is favored.

### TABLE 17.1 Formation Constants for Some Metal Complex Ions in Water at 25°C

<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^- )</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-} )</td>
</tr>
<tr>
<td>( \text{CdBr}_4^{2-} )</td>
<td>( 5 \times 10^{3} )</td>
<td>( \text{Cd}^{2+}(aq) + 4\text{Br}^-(aq) \rightleftharpoons \text{CdBr}_4^{2-}(aq) )</td>
</tr>
<tr>
<td>( \text{Cr(OH)}_4^- )</td>
<td>( 8 \times 10^{29} )</td>
<td>( \text{Cr}^{3+}(aq) + 4\text{OH}^- \rightleftharpoons \text{Cr(OH)}_4^- )</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-} )</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^{4-} )</td>
<td>( 1 \times 10^{35} )</td>
<td>( \text{Fe}^{2+}(aq) + 6\text{CN}^-(aq) \rightleftharpoons \text{Fe(CN)}_6^{4-}(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 …
Lewis bases can interact with metal ions, particularly with transition-metal ions, which can dramatically affect the solubility of a metal salt. AgCl, for example, will dissolve in the presence of aqueous ammonia because Ag⁺ interacts with the Lewis base NH₃.

\[
\begin{align*}
\text{AgCl(s)} & \quad \text{Ag(NH₃)₂⁺ (aq)} + \text{Cl⁻ (aq)} \\
\text{A saturated solution of AgCl in contact with solid AgCl} & \quad \text{When concentrated ammonia is added, Ag⁺ ions are consumed in the formation of the complex ion Ag(NH₃)₂⁺. The AgCl solid is being dissolved by the addition of NH₃.}
\end{align*}
\]

Using \( \text{NH}_3(aq) \) to dissolve \( \text{AgCl(s)} \).
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 $\text{NH}_3$ is added.

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

<table>
<thead>
<tr>
<th></th>
<th>$\text{Ag}^+ \text{(aq)}$</th>
<th>$\text{Ag}^+(\text{aq})$</th>
<th>+</th>
<th>$2 \text{NH}_3(\text{aq})$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial</td>
<td>0.010 $M$</td>
<td>0 $M$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Change</td>
<td>$-x$ $M$</td>
<td>$+x$ $M$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Equilibrium</td>
<td>0.010 $-x$ $M$</td>
<td>$x$ $M$</td>
<td>0.20 $M$</td>
<td></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 Al$^{3+}$, Cr$^{3+}$, Zn$^{2+}$, and 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:
    \[
    \begin{align*}
    \text{Al(H}_2\text{O)}_6^{3+}(aq) + \text{OH}^-(aq) & \rightleftharpoons \text{Al(H}_2\text{O)}_5\text{(OH)}_2^+(aq) + \text{H}_2\text{O}(l) \\
    \text{Al(H}_2\text{O)}_5\text{(OH)}_2^+(aq) + \text{OH}^-(aq) & \rightleftharpoons \text{Al(H}_2\text{O)}_4\text{(OH)}_2^+(aq) + \text{H}_2\text{O}(l) \\
    \text{Al(H}_2\text{O)}_4\text{(OH)}_2^+(aq) + \text{OH}^-(aq) & \rightleftharpoons \text{Al(H}_2\text{O)}_3\text{(OH)}_3(s) + \text{H}_2\text{O}(l) \\
    \text{Al(H}_2\text{O)}_3\text{(OH)}_3(s) + \text{OH}^-(aq) & \rightleftharpoons \text{Al(H}_2\text{O)}_2\text{(OH)}_4^-(aq) + \text{H}_2\text{O}(l)
    \end{align*}
    \]
  - Addition of an acid reverses these reactions
17.6 Precipitation and Separation of Ions

- Consider the following: \( \text{BaSO}_4(s) \rightleftharpoons \text{Ba}^{2+}(aq) + \text{SO}_4^{2-}(aq) \)

- At any instant in time, \( Q = [\text{Ba}^{2+}][\text{SO}_4^{2-}] \)
  
  - 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 \text{Pb(NO}_3)_2 is added to 0.40 L of 5.0 \times 10^{-3} M \text{Na}_2\text{SO}_4? (yes)

Practice Exercise 17.15

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

- Ions can be separated from each other based on the solubilities of their salts.
  - e.g. If HCl is added to a solution containing Ag⁺ and Cu²⁺, the silver precipitates ($K_{sp}$ for AgCl is $1.8 \times 10^{-10}$) while the Cu²⁺ remains in solution.
  - Removal of one metal ion from a solution is called *selective precipitation*.

- Sulfide ion is often used to separate metal ions.
  - e.g. mixture of Zn²⁺(aq) and Cu²⁺(aq).
    - CuS ($K_{sp}= 6 \times 10^{-37}$) is less soluble than ZnS ($K_{sp}= 2 \times 10^{-25}$).
    - → CuS will be removed from solution before ZnS.
    - As H₂S is bubbled through the acidified green solution, black CuS forms.
    - When the precipitate is removed, a colorless solution containing Zn²⁺(aq) remains.
    - When more H₂S is added to the solution, a second precipitate of white ZnS forms.

---

**Sample Exercise 17.16 (p. 751)**

A solution contains $1.0 \times 10^{-2}$ M Ag⁺ and $2.0 \times 10^{-2}$ M Pb²⁺. When Cl⁻ is added to the solution, both AgCl ($K_{sp} = 1.8 \times 10^{-10}$) and PbCl₂ ($K_{sp} = 1.7 \times 10^{-5}$) 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 PbCl₂; $> 1.8 \times 10^{-8}$ M for AgCl, precipitates first)
Practice Exercise 17.16

A solution consists of 0.050 M Mg²⁺ and 0.020 M Cu²⁺. 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.
**Ag^+**, **Pb^{2+}**, **Hg^{2+}

**Cu^{2+}, Bi^{3+}, Cd^{2+}, Pb^{2+}, Hg^{2+}, H_2AsO_3^-, AsO_4^{3-}, Sb^{3+}, Sn^{2+}, Sn^{4+}

**Al^{3+}, Fe^{2+}, Fe^{3+}, Co^{2+}, Ni^{2+}, Cr^{3+}, Zn^{2+}, Mn^{2+}

**Ba^{2+}, Ca^{2+}, Mg^{2+}

**Na^+, K^+, NH_4^+

---

Add 6 M HCl

**Precipitate**

**Group 1—Insoluble chlorides: AgCl, Hg_2Cl_2, PbCl_2**

**Remaining cations**

Add H_2S, 0.2 M HCl

**Precipitate**

**Group 2—Acid-insoluble sulfides: CuS, Bi_2S_3, CdS, PbS, HgS, As_2S_3, Sb_2S_3, SnS_2**

**Remaining cations**

Add (NH_4)_2S, pH 8

**Precipitate**

**Group 3—Base-insoluble sulfides and hydroxides: Al(OH)_3, Fe(OH)_3, Cr(OH)_3, ZnS, NiS, CoS, MnS**

**Remaining cations**

Add (NH_4)_2HPO_4, NH_3

**Precipitate**

**Group 4—in insoluble phosphates: Ba_3(PO_4)_2, Ca_3(PO_4)_2, MgNH_4PO_4**

**Group 5—Alkali metal ions and NH_4^+: Na^+, K^+, NH_4^+**
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)