Chapter 17

Major Concepts:

✓ Common existing ions in solution can have a significant effect on the solubility (Ksp) of substances. This is called the common-ion effect.

✓ Buffered solutions are comprised of a weak acid and its conjugate base. They are unique because they are able to resist pH changes upon the addition of small amounts of strong acids or strong bases.

✓ Titrations can be analyzed by plotting pH versus volume of the amount of titrant added to solution. The graph of these titrations can identify the Ka or Kb value of the unknown solution.

✓ Ions can be selectively precipitated out of solution based on solubility principles.

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.

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

- 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.

**Practice Questions**

1. 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 a 1.0 L solution? \[ K_a = 1.8 \times 10^{-5} \]

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

   *Adding the acetate ion will cause the equilibrium to shift left, this will cause the pH to become more basic (rise)*

   \[
   I \quad 0.30 \text{ M} \\
   C \quad -x \quad 0 \quad +x \\
   E \quad 0.30-x \quad +x \quad 0.30+x
   \]

   \[ x = 1.8 \times 10^{-5} = \frac{x}{0.30} \rightarrow x = 1.8 \times 10^{-5} \]

   \[ \text{pH} = -\log[1.8 \times 10^{-5}] = 4.74 \quad \text{(8.7 molar solution)} \]

2. 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).

   \[
   \text{HNO}_2(aq) \rightleftharpoons \text{H}^+(aq) + \text{NO}_2^-(aq)
   \]

   \[
   I \quad 0.085 \text{ M} \\
   C \quad -x \quad 0 \quad +x \\
   E \quad 0.085-x \quad +x \quad 0.10+x
   \]

   *A common ion will counteract the dissociation, so we may be able to skip the ionization formula*

   \[ K_a = 4.5 \times 10^{-4} = \frac{(x)(x)}{0.085} \rightarrow x = 3.8 \times 10^{-4} \quad \text{pH} = -\log[3.8 \times 10^{-4}] = 3.42 \]
(3) Calculate the fluoride ion concentration and pH of a solution that is 0.20 M HF and 0.10 M HCl.

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

\[ I \]
\[ C \] \quad 0.20 \text{ M} \quad 0.10 \text{ M} \quad 0 \text{ M} \\
\[ E \] \quad -x \quad +x \quad +x \\
\[ 0.20 - x \quad 0.10 + x \quad x \]

\[ K_a = \frac{[\text{H}^+][\text{F}^-]}{[\text{HF}]} = 6.8 \times 10^{-4} = \frac{(0.10+x)(x)}{(0.20-x)} \text{ (IS CHANGE NEGligible)} = 0.00136 \text{ M} \]

\[ \text{pH} = -\log [0.10 + 0.00136] = 0.99 \]

(4) Calculate the formate ion concentration and pH of a solution that is 0.050 M in formic acid (HCHO₂; \( K_a = 1.8 \times 10^{-4} \)) and 0.10 M in HNO₃.

$$\text{HCHO}_2(aq) \rightleftharpoons \text{H}^+(aq) + \text{CHO}_2^- (aq)$$

\[ I \]
\[ C \] \quad 0.050 \text{ M} \quad 0.10 \text{ M} \quad 0 \text{ M} \\
\[ E \] \quad -x \quad +x \quad +x \\
\[ 0.050 - x \quad 0.10 + x \quad x \]

\[ K_a = \frac{[\text{CHO}_2^-][\text{H}^+]}{[\text{HCHO}_2^-]} \quad \alpha = \frac{(0.10x)}{(0.050)} = 9 \times 10^{-5} \text{ M} \]

\[ \text{pH} = -\log [0.10 + (9 \times 10^{-5})] \]

\[ \text{pH} = 1.0 \]
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 (HA) and its conjugate base (A⁻).

\[ \text{HA}(aq) \rightarrow \text{H}^+(aq) + \text{A}^-(aq) \]

Thus, a buffer contains both:

- an acidic species (to neutralize OH⁻) and
- a basic species (to neutralize H⁺).

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

\[ \text{HA} + \text{OH}^- \leftrightarrow \text{HOH} + \text{A}^- \]

\[ \text{pH} \uparrow \text{ (more conjugate base)} \]

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

\[ \text{H}_3\text{O}^+ + \text{A}^- \leftrightarrow \text{HOH} + \text{HA} \]

\[ \text{pH} \downarrow \text{ (more conjugate acid)} \]
Practice Questions

(1) What is the pH of a buffer that is 0.12 M in lactic acid (HC₃H₅O₃) and 0.10 M in sodium lactate? For lactic acid, Ka = 1.4 x 10⁻⁴.

\[
\text{HC}_3\text{H}_5\text{O}_3(aq) \rightleftharpoons H^+(aq) + \text{C}_3\text{H}_5\text{O}_3^-(aq)
\]

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*Common ion neg!*

\[
K_a = 1.4 \times 10^{-4} = \frac{(0.10x)}{(0.12)} = 1.7 \times 10^{-4} M \quad (\text{pH} = 3.77)
\]

(2) Calculate the pH of a buffer composed of 0.12 M benzoic acid and 0.20 M sodium benzoate. (Ka = 6.3 x 10⁻⁵)

\[
\text{HC}_7\text{H}_5\text{O}_2(aq) \rightleftharpoons H^+(aq) + \text{C}_7\text{H}_5\text{O}_2^-(aq)
\]

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*Common ion neg!*

\[
K_a = (6.3 \times 10^{-5}) = \frac{(0.20x)}{(0.12)} = 3.78 \times 10^{-5} \quad (\text{pH} = 4.42)
\]
(3) 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.)

(Kb = 1.8 x 10⁻⁵)

\[ \text{NH}_3(a_q) + \text{H}_2\text{O} \rightleftharpoons \text{NH}_4^+(a_q) + \text{OH}^-(a_q) \]

\[ \text{I} \quad -10 \text{ M} \]
\[ \text{C} \quad -1 \times 10^{-5} \]
\[ \text{E} \quad (10) - (1 \times 10^{-5}) \quad \frac{0 + 1 \times 10^{-5}}{1 \times 10^{-5} \text{ M}} \]

\[ \text{K}_b = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]} = \frac{(1 \times 10^{-5})(1 \times 10^{-5})}{10} \]

\[ 1.8 \times 10^{-5} = \frac{(1 \times 10^{-5})(1 \times 10^{-5})}{10} \]

\[ \text{pH} = 9 \quad \text{P} \text{OH} = 5 \]

\[ Y = 0.18 \text{ M} = \frac{X \text{ mol}}{2.0 \text{ L}} \quad \rightarrow \quad X = 0.36 \text{ mol} \]

(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. (Ka = 6.3 x 10⁻⁵)

\[ \text{HC}_7\text{H}_5\text{O}_2(a_q) + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{C}_7\text{H}_5\text{O}_2^- (a_q) \]

\[ \text{I} \quad 0.20 \text{ M} \]
\[ \text{C} \quad -1 \times 10^{-4} \]
\[ \text{E} \quad (0.20) - (1 \times 10^{-4}) \quad \frac{1 \times 10^{-4} \text{ M}}{1 \times 10^{-4}} \]

\[ Y = 0.12 \text{ M} \]

\[ 0.3 \times 10^{-5} = \frac{(1 \times 10^{-4})(1 \times 10^{-4})}{0.20} \]
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.

Calculating the pH of a Buffer with the Addition of Strong Acids or Bases

We break the calculation into two parts.

- This is a stoichiometry calculation.
  - The addition of a strong acid or base results in a neutralization reaction:
    \[
    \text{A}^- + \text{H}_3\text{O}^+ \rightleftharpoons \text{HA} + \text{H}_2\text{O} \\
    \text{HA} + \text{OH}^- \rightleftharpoons \text{A}^- + \text{H}_2\text{O}
    \]
  - By knowing how much $\text{H}_3\text{O}^+$ or how much $\text{OH}^-$ was added, we know how much HA or $\text{A}^-$ was formed.

- With the concentrations of $\text{HX}$ and $\text{X}^-$ (taking into account the change in volume of the solution) we can calculate the pH from the Henderson-Hasselbalch equation:

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

  # Mostly used to identify changes in the pH of a buffer

  # Reversed for bases

  - This is the equilibrium calculation.

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 undisassociated 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.
Calculating the pH of a buffer after the addition of acid or base

First consider how the neutralization reaction between the added strong acid or base and the buffer affects the composition of the buffer (stoichiometry calculation). Then calculate the pH of the remaining buffer (equilibrium calculation). As long as the amount of added acid or base does not exceed the buffer capacity, the Henderson-Hasselbalch equation can be used for the equilibrium calculation.
Practice Questions

(1) A buffer is made by adding 0.300 mol HC\(_2\)H\(_2\)O\(_2\) (\(K_a = 1.8 \times 10^{-5}\)) and 0.300 mol NaC\(_2\)H\(_2\)O\(_2\) to enough water to make 1.00 L of solution. The pH of the buffer is 4.74.

a. Calculate the pH of the solution after 0.020 mol of NaOH is added

b. For comparison, calculate the pH that would result if 0.020 mol of NaOH was added to 1.00 L of pure water (neglect any volume changes)

\[
\begin{array}{c}
\text{Step 1: React} \\
\text{H}_2\text{C}_2\text{H}_2\text{O}_2(aq) + \text{OH}^-(aq) \rightarrow \text{HO}^- + \text{C}_2\text{H}_2\text{O}_2\text{^-}(aq)
\end{array}
\]

\[
\begin{array}{c|c|c|c}
\text{C} & \text{E} & \text{F} \\
\text{H}_2\text{C}_2\text{H}_2\text{O}_2 & 0.300 & -0.020 & -0.280 \\
\text{OH}^- & -0.020 & +0.020 & \\
\text{HO}^- & 0 & \\
\text{C}_2\text{H}_2\text{O}_2\text{^-} & 0.320 \\
\text{H}_2\text{O} & 1.00L \\
\end{array}
\]

\[
\begin{array}{c}
\text{Step 2: How much x?} \\
\text{C} & \text{I} & \text{E} \\
\text{H}_2\text{C}_2\text{H}_2\text{O}_2 & 0.300 & -0.020 & -0.280 \\
\text{OH}^- & -0.020 & +0.020 & \\
\text{HO}^- & 0 & \\
\text{C}_2\text{H}_2\text{O}_2\text{^-} & 0.320 \\
\text{H}_2\text{O} & 1.00L \\
\end{array}
\]

\[
\text{pH} = \text{p}K_a + \log \left( \frac{\text{[A]}}{\text{[HA]}} \right) = 4.74 + \log \left( \frac{0.280}{0.320} \right) = 4.80
\]

\[
\text{pH} = -\log \left( \text{[OH}^-] \right) = -\log \left( \text{[0.02 mol]} \right) = 1.70
\]

(2) Determine:

a. The pH of the original buffer described in the previous question after the addition of 0.020 mol HCl, and

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

\[
\begin{array}{c}
\text{Step 3: New pH} \\
\text{[H}_3\text{O}^+ \text{ increases, no base]} \\
\text{pH} = \text{p}K_a + \log \left( \frac{\text{[A]}}{\text{[HA]}} \right) = 4.74 + \log \left( \frac{0.280}{0.320} \right) = 4.80
\end{array}
\]

\[
\text{pH} = -\log \left( \text{[H}^+] \right) -\log \left( \text{[0.02 mol]} \right) = 1.70
\]
Lesson #1 Homework

1) (a) Consider the equilibrium \( B (aq) + H_2O (l) \rightleftharpoons HB^+ (aq) + OH^- (aq) \).
   Using Le Chatelier’s principle, explain the effect of the presence of a salt of \( HB^+ \) on the
   ionization of \( B \).
   (b) Give an example of a salt that can decrease the ionization of \( NH_3 \) in solution.

2) Does the pH increase, decrease, or remain the same when each of the following is added:
   (a) \( NaNO_2 \) to a solution of \( HNO_2 \)
   (b) \( (CH_3NH_3)Cl \) to a solution of \( CH_3NH_2 \)
   (c) sodium formate to a solution of formic acid
   (d) potassium bromide to a solution of hydrobromic acid
   (e) HCl to a solution of \( NaC_2H_3O_2 \)

3) Use information from Appendix D to calculate the pH of:
   (a) a solution that is 0.160 M in sodium formate (\( NaCHO_2 \)) and 0.260 M in formic acid
       (\( HCHO_2 \))
   (b) a solution that is 0.210 M in pyridine (\( C_5H_5N \)) and 0.350 M in pyridinium chloride
       (\( C_5H_5NCl \))
   (c) a solution that is made by combining 125 mL of 0.050 M hydrofluoric acid with
       50.0 mL of 0.10 M sodium fluoride.

4) (a) Calculate the percent ionization of 0.0075 M butanoic acid (\( Ka = 1.5 \times 10^{-5} \))
   (b) Calculate the percent ionization of 0.0075 M butanoic acid in a solution containing
       0.085 M sodium butanoate.

5) (a) Calculate the pH of a buffer that is 0.12 M in lactic acid and 0.11 M in sodium lactate
   (b) Calculate the pH of a buffer formed by mixing 85 mL of 0.13 M lactic acid with
       95 mL of 0.15 M sodium lactate.
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 excess base in the solution.
   - Therefore, pH > 7.
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 and 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.
Practice Questions

(1) 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

* Strong base added to a strong acid. Both are monoprotic

(a) Acid will be in excess:

\[
\frac{0.0058\text{ mol } \text{H}^+}{0.049\text{ mol } \text{OH}^-} = 0.001 \text{ mol } \text{H}^+ \times 5.11 \text{ mL} = 0.001 \text{ N } \text{H}^+ \\
(-\log(0.001)) = \text{pH} = 3
\]

(b) Base will be in excess:

\[
\frac{51.0\text{ mL } \text{OH}^-}{50.0\text{ mL } \text{H}^+} = \frac{0.001 \text{ mol } \text{OH}^-}{0.101 \text{ L}} = 9.9 \times 10^{-4} \text{ M } \text{OH}^- \\
\text{pH} = -\log(9.9 \times 10^{-4}) = 4.01
\]
(2) Calculate the pH when the following quantities of 0.100 M HNO₃ have been added to 25.0 mL of 0.100 M KOH solution: (a) 24.9 mL, (b) 25.1 mL.

(a) Base in excess:

\[
\begin{align*}
\text{.00250 mol OH}^- & - \text{.00249 mol H}^+ \\
\text{.00001 mol H}^+ & \times 5 \text{ OH}^- \\
\text{.00001 mol OH}^- & \div \text{.04997 L} = \frac{2.0 \times 10^{-4} \text{ M OH}^-}{1} \\
\text{pOH} & = -\log (2.0 \times 10^{-4}) \\
\text{pH} & = 10.3
\end{align*}
\]

(b) Acid in excess:

\[
\begin{align*}
\text{.00001 mol H}^+ & \div \text{.0501 L} = \frac{1.99 \times 10^{-4} \text{ M H}^+}{1} \\
\text{pH} & = -\log [H^+] \\
\text{pH} & = 3.7
\end{align*}
\]
Weak Acid – Strong Base Titrations

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:
     $$\text{HC}_2\text{H}_3\text{O}_2(aq) + \text{OH}^-(aq) \leftrightarrow \text{C}_2\text{H}_5\text{O}_2^-(aq) + \text{H}_2\text{O}(l)$$
   - 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 $\text{C}_2\text{H}_5\text{O}_2^-$ 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, $\text{C}_2\text{H}_5\text{O}_2^-$ has been generated.
   - Therefore, the pH depends on the $\text{C}_2\text{H}_5\text{O}_2^-$ concentration.
   - The pH $> 7$ at the equivalence point.

4. **After the equivalence point:**
   - the pH is given by the concentration of the excess strong base.
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, then there is a leveling off due to buffer effects.
  - The inflection point 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.

**Procedure for calculating the pH when a weak acid is partially neutralized by a strong base**

\[
\text{Solution containing weak acid and strong base} \xrightarrow{\text{Neutralization}} HX + OH^- \rightarrow X^- + H_2O \xrightarrow{\text{Calculate [HX] and [X\text{\textsuperscript{\textminus}]} after reaction}} \xrightarrow{\text{Use } K_a \text{ [HX], and [X\text{\textsuperscript{\textminus}]} to calculate [H\textsuperscript{\text{\textplus}}]}} \xrightarrow{\text{pH}} \]

Stoichiometric calculation \xrightarrow{\text{Equilibrium calculation}}
**Effect of $K_a$ on titration curves**

This set of curves shows the influence of acid strength ($K_a$) on the curve for titration with NaOH. Each curve represents titration of 50.0 mL of 0.10 M acid with 0.10 M NaOH. The weaker the acid, the higher the initial pH and the smaller the pH change at the equivalence point.

THE INFLECTION POINTS DIMINISHES AS BASES BECOME WEAKER.
Practice Questions

(1) 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 HC₂H₃O₂ (Ka = 1.8 x 10⁻⁵)

\[ \text{H}_2\text{C}_2\text{H}_3\text{O}_2 (aq) + \text{OH}^- (aq) \rightarrow \text{H}_2\text{O}(l) + \text{C}_2\text{H}_3\text{O}_2^- (aq) \]

\[ \begin{array}{ccc}
\text{I} & 0.005 \text{ mol} & 0.0045 \text{ mol} \\
\text{C} & - & - \\
\text{E} & 0.0005 \text{ mol} & 0 \text{ mol} \\
\end{array} \]

\[ \text{Buffer pH} = pK_a + \log \frac{[\text{C}_2\text{H}_3\text{O}_2^-]}{[\text{H}_2\text{C}_2\text{H}_3\text{O}_2]} \quad \text{* Requires molarity} \]

\[ \text{M H}_2\text{C}_2\text{H}_3\text{O}_2 = \frac{0.005 \text{ mol}}{0.095 \text{ L}} = 0.053 \text{ M} \]

\[ \text{M C}_2\text{H}_3\text{O}_2^- = \frac{0.0045 \text{ mol}}{0.095 \text{ L}} = 0.0474 \text{ M} \]

\[ \text{pH} = [-\log(1.8 \times 10^{-5})] + \log \frac{[0.0474]}{0.053} \]

\[ \text{pH} = 4.74 + 0.95 \]

\[ \text{pH} = 5.69 \]
(2) 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 \((HC_7H_5O_2, Ka = 6.3 \times 10^{-5})\)

\[
\text{Strong Base to Weak Acid} \quad \text{Buffer}
\]

\[
HC_7H_5O_2(aq) + OH^-(aq) \rightarrow H_2O(l) + C_7H_5O_2^-(aq)
\]

\[
\begin{align*}
I & \quad 0.001 \text{ mol} & \quad 0.0005 \text{ mol} & \quad 0.0005 \text{ mol} \\
C & \quad -0.0005 & \quad -0.0005 & \quad +0.0005 \\
E & \quad 0.0005 \text{ mol} & \quad 0 & \quad 0.0005 \text{ mol}
\end{align*}
\]

* since mol are equal, so will be the molalities *

\[
pH = pK_a + \log \frac{[A^-]}{[HA]} \Rightarrow -\log (6.3 \times 10^{-5}) = 4.78
\]

(3) 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.

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

* Strong Acid Added to a Weak Base

\[
NH_3(aq) + H_3O^+(aq) \rightarrow NH_4^+(aq) + H_2O(l)
\]

\[
\begin{align*}
I & \quad 0.002 \text{ mol} & \quad 0.001 \text{ mol} & \quad 0 \text{ mol} \\
C & \quad -0.001 & \quad -0.001 & \quad +0.001 \\
E & \quad 0.001 \text{ mol} & \quad 0 & \quad 0.001 \text{ mol}
\end{align*}
\]

\[
pOH = pK_b + \log \frac{[NH_4^+]}{[NH_3]}
\]

* again, equal mol's cancel each other out *

\[
pOH = pK_b = -\log (1.8 \times 10^{-5})
\]

\[
pOH = 4.74
\]

\[
\text{pH} = 9.26
\]
(4) Calculate the pH at the equivalence point in the titration of 50.0 mL of 0.100 M HC$_2$H$_3$O$_2$ with 0.100 M NaOH.

**Step 1 - Neutralization & Production of CB**

\[ HC_2H_3O_2(aq) + OH^-(aq) \rightarrow H_2O(l) + C_2H_3O_2^- (aq) \]

\[ I = 0.005 \text{ mol} \quad - \quad 0.005 \text{ mol} \]
\[ C = -0.005 \quad - \quad -0.005 \]
\[ E = 0 \quad - \quad +0.005 \]

**Concentration of CB:**

\[ \frac{0.005 \text{ mol}}{100 \text{ L}} = 0.005 \text{ N} C_2H_3O_2^- \]

**Step 2 - The equilibrium of the CB**

\[ C_2H_3O_2^- (aq) + H_2O(l) \rightleftharpoons H_2C_2H_3O_2 (aq) + OH^- (aq) \]

\[ I = 0.05 \text{ N} \quad - \quad 0 \quad +x \]
\[ C = -x \quad +x \quad +x \quad +x \]
\[ E = 0.05 - x \quad - \quad x \quad - \quad x \]

* Acting as a base, so:

\[ K_w = (K_a)(K_b) \rightarrow K_b = \frac{(6 \times 10^{-4})}{(1.79 \times 10^{-5})} \rightarrow K_b = 3.4 \times 10^{-10} \]

\[ K_b = \frac{[H_2C_2H_3O_2][OH^-]}{[C_2H_3O_2^-]} = 5.6 \times 10^{-10} = \frac{x^2}{0.05-x} \quad (\text{Negligible}) \]

\[ x = 5.3 \times 10^{-6} \text{ N} [OH^-] \]
\[ pOH = -\log [5.3 \times 10^{-6}] \]
\[ pOH = 5.3 \]
\[ pH = 8.7 \]
(5) Calculate the pH at the equivalence point when:
   a. 40.0 mL of 0.025 M benzoic acid (HC₇H₅O₂, $K_a = 6.3 \times 10^{-5}$) is titrated with 0.050 M NaOH
   b. 40.0 mL of 0.100 M NH₃ is titrated with 0.100 M HCl

   a) Strong base added to a weak acid

   $\text{HC}_7\text{H}_5\text{O}_2^- + \text{OH}^- \rightarrow \text{H}_2\text{O} + \text{C}_7\text{H}_5\text{O}_2^{2-}$

   $\text{I} = 0.01 \text{ mol}$   $\text{C} = 0.01 \text{ mol}$

   $\text{E} = \frac{0.01 \text{ mol}}{0.05 \text{ mol}} \rightarrow \frac{0.01 \text{ mol}}{0.06 \text{ mol}} = 0.167 \text{ M}$

   The CB equilibrium

   $\text{C}_7\text{H}_5\text{O}_2^- + \text{H}_2\text{O} \rightarrow \text{HC}_7\text{H}_5\text{O}_2^- + \text{OH}^-$

   $\text{I} = 0.167 \text{ M}$

   $\text{C} = -x$

   $\text{E} = 0.167 - x$

   $K_w = (K_a) (K_b) = \frac{1 \times 10^{-14}}{6.3 \times 10^{-5}} = K_b = 1.6 \times 10^{-10}$

   $K_b = \frac{[\text{HC}_7\text{H}_5\text{O}_2^-] [\text{OH}^-]}{[\text{C}_7\text{H}_5\text{O}_2^-]} = 1.6 \times 10^{-10} \times \frac{x^2}{0.167 \text{ M}}$

   $x = 1.6 \times 10^{-6} \text{ M} [\text{OH}]$

   $pOH = -\log [1.6 \times 10^{-6}]$

   $pOH = 5.8$

   $\text{pH} = 8.2$
(b) Strong Acid to a Weak Base

\[ \text{NH}_3 (aq) + \text{H}_3\text{O}^+ (aq) \rightleftharpoons \text{NH}_4^+ (aq) + \text{H}_2\text{O}(l) \]

\[ \begin{array}{c}
\text{I} \\
\text{C} \\
\text{E}
\end{array} \quad \begin{array}{c}
-0.040 \text{ mol} \\
\cdot 0.040 \text{ mol} \\
\cdot 0.040 \text{ mol}
\end{array} \]

\[ \cdot 0.040 \text{ mol} \times 0.8 \equiv 0.032 \text{ mol} \]

\[ = 0.32 \text{ mol NH}_4^+ \]

Equilibrium of the Conjugate Acid

\[ \text{NH}_4^+ (aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{NH}_3 (aq) + \text{H}_3\text{O}^+ (aq) \]

\[ \begin{array}{c}
\text{I} \\
\text{C} \\
\text{E}
\end{array} \quad \begin{array}{c}
-0.050 \text{ M} \\
\cdot x \\
\cdot 0.050 - x
\end{array} \]

\[ \begin{array}{c}
\text{K}_w = (\text{K}_a)(\text{K}_b) = \frac{1 \times 10^{-14}}{1.8 \times 10^{-10}} = \text{K}_b 5.56 \times 10^{-5} \]

\[ \text{K}_b = \frac{[\text{NH}_3][\text{H}_3\text{O}^+]}{[\text{NH}_4^+]} = 5.56 \times 10^{-5} = \frac{x^2}{0.050} \]

\[ x = \sqrt{2.78} = 0.0517 \equiv \text{pH} = -\log \left( \frac{0.0517}{5.56 \times 10^{-5}} \right) = 2.8 \]
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 \( \text{PO}_4^{3-} \).

*Figure: Diprotic acid
Titration curve for the reaction of 50.0 mL of 0.10 M \( \text{H}_3\text{PO}_4 \) with 0.10 M \( \text{NaOH} \)*
Lesson #2 Homework

1) A buffer is prepared by adding 5.0 g of ammonia (NH₃) and 20.0 g of ammonium chloride (NH₄Cl) to enough water to form 2.50 L of solution.
   (a) What is the pH of this buffer?
   (b) Write the complete ionic equation for the reaction that occurs when a few drops of nitric acid are added to the buffer.
   (c) Write the complete ionic equation for the reaction that occurs when a few drops of potassium hydroxide are added to the buffer.

2) How many moles of sodium hypobromite (NaBrO) should be added to 1.00 L of 0.050 M hypobromous acid (HBrO) to form a buffer solution of 9.15? Assume that no volume change occurs when the NaBrO is added.

3) A buffer solution contains 0.10 mol of acetic acid and 0.13 mol of sodium acetate in 1.00 L.
   (a) What is the pH of this buffer?
   (b) What is the pH of the buffer after the addition on 0.02 mol of KOH?
   (c) What is the pH of the buffer after the addition on 0.02 mol of nitric acid?

4) How many milliliters of 0.105 M HCl are needed to titrate each of the following solutions to the equivalence point:
   (a) 55.0 mL of 0.0950 M NaOH
   (b) 22.5 mL of 0.118 M NH₃
   (c) 125.0 mL of a solution that contains 1.35 g of NaOH per liter
17.4 Solubility Equilibria

The Solubility – Product Constant $K_{sp}$

Consider a saturated solution of $\text{BaSO}_4$ in contact with solid $\text{BaSO}_4$.

- We can write an equilibrium expression for the dissolving of the slightly soluble solid.
  \[ \text{BaSO}_4(s) \leftrightharpoons \text{Ba}^{2+}(aq) + \text{SO}_4^{2-}(aq) \]

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

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

  - $K_{sp}$ is called the **solubility-product constant**, or the **solubility product**.

  - $K_{sp}$ for $\text{BaSO}_4$ is:
  \[ K_{sp} = [\text{Ba}^{2+}][\text{SO}_4^{2-}] \]

In general the solubility product is equal to the product of the molar concentration of ions raised to powers corresponding to their stoichiometric coefficients.

Practice Questions

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

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

2. 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.

   (a) $\text{BaCO}_3$
   \[ K_{sp} = [\text{Ba}^{2+}][\text{CO}_3^{2-}] = 5.0 \times 10^{-9} \]

   (b) $\text{Ag}_2\text{SO}_4$
   \[ K_{sp} = [\text{Ag}^+][\text{SO}_4^{2-}] = 1.5 \times 10^{-5} \]
Solubility and Ksp

*Solubility* is the amount of substance that dissolves to form a saturated solution.

- This is often expressed as grams of solute that will dissolve per liter of solution.

*Molar solubility* is 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 $K_{sp}$:
  - Convert solubility into molar solubility (via molar mass).
  - Convert molar solubility into the molar concentration of ions at equilibrium (equilibrium calculation).
  - Use the equilibrium concentration of ions in the $K_{sp}$ expression.

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

*Relationships between solubility and $K_{sp}$*
Practice Questions

(1) 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 the equilibrium is achieved between the undissolved Ag₃CrO₄ (s) and the solution. Analysis of that equilibrated solution shows that its silver ion concentration is \(1.3 \times 10^{-4}\) M. Assuming that the Ag₃CrO₄ dissociates completely in water and that there are no other important equilibria involving the Ag⁺ or CrO₄²⁻ ions in the solution, calculate the Ksp for this compound.

\[
\begin{align*}
Ag₃CrO₄(s) & \rightleftharpoons 2 \text{Ag}^+(aq) + \text{CrO}_4^{2-}(aq) \\
K_{sp} &= \left[\text{Ag}^+\right]^2\left[\text{CrO}_4^{2-}\right] \\
&= \frac{1.3 \times 10^{-4}}{2 \text{ mol}} = \frac{X}{1 \text{ mol}} \\
X &= 6.5 \times 10^{-5} \text{ M} \text{CrO}_4^{2-}(aq)
\end{align*}
\]

\[
K_{sp} = \left[1.3 \times 10^{-4}\right]^2 \left[6.5 \times 10^{-5}\right] \\
= 1.6 \times 10^{-12}
\]

(2) 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 the Ksp for this compound.

\[
\begin{align*}
\text{Mg(OH)}_2(s) & \rightleftharpoons \text{Mg}^{2+}(aq) + 2 \text{OH}^-(aq) \\
K_{sp} &= \left[\text{Mg}^{2+}\right]\left[\text{OH}^-ight]^2 \\
&= \frac{2 \text{ mol}}{1.48 \times 10^{-4} \text{ M} \text{OH}^-} \\
&= 1.6 \times 10^{-12}
\end{align*}
\]

\[
\begin{align*}
\text{pH} &= 10.17 \\
\text{pOH} &= 3.83 \\
\text{pOH} - \text{pOH} &= 1.48 \times 10^{-4} \text{ M OH}^- \\
\frac{2 \text{ mol}}{1.48 \times 10^{-4}} &= \frac{x}{1 \text{ mol}} \\
x &= 74 \times 10^{-5} \text{ M Mg}^{2+}
\end{align*}
\]
(3) The Ksp 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.

\[ \text{CaF}_2 (s) \rightleftharpoons \text{Ca}^{2+} (aq) + 2 \text{F}^- (aq) \]

\[ K_{sp} = [\text{Ca}^{2+}][\text{F}^-]^2 \]

\[ 3.9 \times 10^{-11} = [x][2x]^2 \]

\[ 4x^3 = 3.9 \times 10^{-11} \]

(\text{Divide by 4; then } x = \frac{3}{2} \sqrt[3]{\frac{3.9 \times 10^{-11}}{4}} \approx 2.14 \times 10^{-4} \text{ M} \]

\[ x = 2.14 \times 10^{-4} \text{ M} \]

\[ = \frac{2.14 \times 10^{-4} \text{ mol}}{L} \times \frac{78.19 \text{ g}}{1 \text{ mol CaF}_2} = 0.1164 \text{ g/L} \]

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

\[ \text{LaF}_3 (s) \rightleftharpoons \text{La}^{3+} (aq) + 3 \text{F}^- (aq) \]

\[ K_{sp} = [\text{La}^{3+}][\text{F}^-]^3 \]

\[ 2 \times 10^{-19} = [x][3x]^3 \]

\[ 27x^4 = 2 \times 10^{-19} \]

(\text{Solve for } x \approx 9.27 \times 10^{-6} \text{ M} \text{ or } 9.27 \times 10^{-6} \text{ mol/L})
17.5 Factors that Affect Solubility

Three factors that have a significant impact on solubility are:

- the presence of a common ion,
- the pH of the solution, and
- the presence or absence of complexing agents.

**Common-Ion Effect**

The solubility of a slightly soluble salt is decreased when a common ion is added.

- This is an application of Le Châtelier's principle.

Consider the solubility of CaF₂:

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

- If more F⁻ is added (i.e., by the addition of NaF), the equilibrium shifts to offset the increase.
- Therefore, CaF₂(s) is formed and precipitation occurs.
  - As NaF is added to the system, the solubility of CaF₂ decreases.

In general, the solubility of a slightly soluble salt is decreased by the presence of a second salt that produces a common ion.
Practice Questions

(1) 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.

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

*In each case, adding a common ion will decrease solubility*

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

I

\[ \begin{array}{c}
\text{I} \\
\text{C} \\
\text{E}
\end{array} \]

\[ \begin{array}{c}
? \\
-x \\
-x
\end{array} \]

\[ \begin{array}{c}
0.010 M \\
+x \\
\quad x
\end{array} \]

\[ \begin{array}{c}
0 \\
+2x \\
2x
\end{array} \]

*Δ is negligible due to \( K_{sp} \) being so small*

\[ K_{sp} = 3.9 \times 10^{-11} = [0.010 M]^1 [2x]^2 \]

\[ 0.040x^2 = 3.9 \times 10^{-11} \]

\[ x = 3.1 \times 10^{-5} \text{ mol dissociated} \]
(2) The value for Ksp 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.

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

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

\[
\begin{align*}
\text{NaOH} & : 0 \text{ M} & \text{NaOH} & : 0.020 \text{ M} \\
\text{Mn}^{2+} & : x & \text{OH}^- & : 2x + 0.020 \text{ M} \\
\text{E} & : 2 - x & \text{C} & : -x \\
\end{align*}
\]

$$1.6 \times 10^{-13} = [x][0.020]^2$$

\[
\begin{align*}
x = 4 \times 10^{-10} \text{ M} \quad \text{dissociated}
\end{align*}
\]
Lesson #3 Homework

1) Consider the titration of 30.0 mL of 0.030 M NH₃ with 0.025 M HCl. Calculate the pH after the following volumes of titrant has been added:
   (a) 0 mL
   (b) 10.0 mL
   (c) 20.0 mL
   (d) 35.0 mL
   (e) 36.0 mL
   (f) 37.0 mL

2) Calculate the pH at the equivalence point in titrating 0.100 M solutions of each of the following with 0.080 M NaOH:
   (a) Hydrobromic acid
   (b) Lactic acid (HC₃H₂O₃)
   (c) Sodium hydrogen chromate (NaHCrO₄)

3) Furoic acid (HC₄H₂O₃) has a Ka value of 6.76 x 10⁻⁴ at 25°C. Calculate the pH at 25°C of:
   (a) A solution formed by adding 35.0 g of furoic acid and 30.0 g of sodium furoate (NaC₄H₅) to enough water to form 0.250 L of solution
   (b) A solution formed by mixing 30.0 mL of 0.250 M HC₄H₂O₃ and 20.0 mL of 0.22 M NaC₄H₅O₂ and diluting the total value to 125 mL
   (c) A solution prepared by adding 50.0 mL of 1.65 M NaOH solution to 0.500 L of 0.0850 M HC₄H₂O₃
Solubility and pH

Again we apply Le Châtelier's principle:

\[ \text{Mg(OH)}_2(s) \rightleftharpoons \text{Mg}^{2+}(aq) + 2\text{OH}^- (aq) \]

- If \( \text{OH}^- \) is removed, then the equilibrium shifts toward the right and \( \text{Mg(OH)}_2 \) dissolves.
- \( \text{OH}^- \) can be removed by adding a strong acid:
  \[ \text{OH}^- (aq) + \text{H}^+ (aq) \rightleftharpoons \text{H}_2\text{O}(aq) \]
- As pH decreases, \([\text{H}^+]\) increases and the solubility of \( \text{Mg(OH)}_2 \) increases.

Another example:

\[ \text{CaF}_2(s) \rightleftharpoons \text{Ca}^{2+}(aq) + 2\text{F}^- (aq) \]

- If the \( \text{F}^- \) is removed, then the equilibrium shifts towards the right and \( \text{CaF}_2 \) dissolves.
- \( \text{F}^- \) can be removed by adding a strong acid:
  \[ \text{F}^- (aq) + \text{H}^+ (aq) \rightleftharpoons \text{HF}(aq) \]
- As pH decreases, \([\text{H}^+]\) increases and solubility of \( \text{CaF}_2 \) increases.

The effect of pH on solubility can be dramatic.
The effect is most significant if one or both ions involved are at least somewhat acidic or basic.

- In general:
  - the solubility of slightly soluble salts containing basic ions increases as pH decreases.
  - the more basic the anion is, the greater the effect.
Practice Questions

(1) Which of the following substances will be more soluble in acidic solution than in basic solution:
(a) Ni(OH)₂ (s), (b) CaCO₃ (s), (c) BaF₂ (s), (d) AgCl (s)?

(a) Ni(OH)₂ (s) → Ni²⁺(aq) + 2OH⁻(aq)
- Adding base forces ← shift, decreasing solubility. *yes

(b) CaCO₃ (s) ⇌ Ca²⁺(aq) + CO₃²⁻(aq)
  [CO₃²⁻] is the CB of H₂CO₃ (A WA),
  thus solubility ↑ as pH ↓ *yes

(c) BaF₂ (s) ⇌ Ba²⁺(aq) + 2F⁻(aq)
  [F⁻] is a CB of a weak A to,
  solubility ↑ as pH ↓ *yes

(d) AgCl (s) ⇌ Ag⁺(aq) + Cl⁻(aq)
  [Cl⁻] is a CB of a SA *no
Lesson #4 Homework

1) (a) If the molar solubility of CaF$_2$ at 35°C is $1.24 \times 10^{-3}$ mol/L, what is the Ksp at this temperature?
(b) It is found that $1.1 \times 10^{-2}$ g of SrF$_2$ dissolves per 100 mL of aqueous solution at 25°C. Calculate the solubility product for SrF$_2$.
(c) The Ksp of Ba(IO$_3$)$_2$ at 25°C is $6.0 \times 10^{-10}$. What is the molar solubility?

2) A 1.00 L solution saturated at 25°C with calcium oxalate (CaC$_2$O$_4$) contains 0.0061 g of CaC$_2$O$_4$. Calculate the Ksp for this salt.

3) Calculate the solubility of LaF$_3$ in grams per liter in:
(a) Pure water
(b) 0.010 M KF solution
(c) 0.050 M LaCl$_3$ solution

4) Which of the following salts will be substantially more soluble in acidic solution than in pure water?
(a) ZnCO$_3$
(b) ZnS
(c) BiI$_3$
(d) AgCN
(e) Ba$_3$(PO$_4$)$_2$
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 \( Q = K_{sp} \).

*Recall that a high \( K \) drives the reaction forward (soluble).*

*Recall that a high \( Q \) drives the reaction reverse (precipitate formation).*

Practice Questions

(1) 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\(_4\)?

\[ \text{Pb(NO}_3\text{)}_2(aq) + \text{Na}_2\text{SO}_4(aq) \rightleftharpoons \text{PbSO}_4(s) + 2 \text{NaNO}_3(aq) \]

*From Reference:

\[ \text{PbSO}_4(s) \rightleftharpoons \text{Pb}^{2+}(aq) + \text{SO}_4^{2-}(aq) \]

\[ K_{sp} = [\text{Pb}^{2+}][\text{SO}_4^{2-}] = 6.3 \times 10^{-7} \]

*In reaction when mixed:

\[ \text{Pb}^{2+}(aq) + \text{SO}_4^{2-}(aq) \rightleftharpoons \text{PbSO}_4(s) \]

\[ \frac{8.0 \times 10^{-4} \text{ mol}}{0.15 \text{ L}} = 0.0533 \text{ M} \]

\[ \frac{0.002 \text{ mol}}{0.15 \text{ L}} = 0.0133 \text{ M} \]

\[ Q = [0.0016 \text{ M}] [0.004 \text{ M}] = 6.4 \times 10^{-4} \]

\[ Q > K \]

ppt Forms
(2) Will a precipitate form when 0.050 L of 2.0 x 10^{-2} M NaF is mixed with 0.010 L of 1.0 x 10^{-2} M Ca(NO_3)_2?

\[ 2 \text{ NaF}^{(aq)} + \text{Ca(NO}_3)_2^{(aq)} \rightarrow 2 \text{ NaNO}_3^{(aq)} + \text{CaF}_2^{(s)} \]

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

\[ \text{CaF}_2^{(s)} \rightarrow \text{Ca}^{2+}^{(aq)} + 2\text{F}^-^{(aq)} \]

\[ K_{sp} \text{ IN Rxn, WHEN MIXED} \]

\[ [\text{Ca}^{2+}] = \frac{1 \times 10^{-4} \text{ mol}}{0.060 \text{ L}} = 0.0167 \text{ M} \]

\[ [\text{F}^-] = \frac{0.001 \text{ mol}}{0.060 \text{ L}} = 0.0167 \text{ M} \]

\[ Q = [0.0167][0.0167]^2 = 4.66 \times 10^{-7} \]

\[ Q > K \text{ : precipitate forms} \]
Selective Precipitation of Ions

Ions can be separated from each other based on the solubilities of their salts.

- Example: 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.

The sulfide ion is often used to separate metal ions.

- Example: Consider a mixture of Zn²⁺(aq) and Cu²⁺(aq).
  - CuS ($K_{sp}$ = $6 \times 10^{-37}$) is less soluble than ZnS ($K_{sp}$ = $2 \times 10^{-28}$).
  - Thus, 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.

Practice Questions

(1) A solution contains $1.0 \times 10^{-3}$ 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?

\[
Ag^+(aq) + Pb^{2+}(aq) + Cl^-(aq) \rightleftharpoons AgCl(s) + PbCl_2(s)
\]

\begin{align*}
\text{(1) } & \text{AgCl(s): } K_{sp} = [Ag^+] [Cl^-] = 1.8 \times 10^{-10} \\
& = [1.0 \times 10^{-3} M] [x] = 1.8 \times 10^{-8} M [Cl^-] \text{ needed to ppt.}
\end{align*}

\begin{align*}
\text{(2) } & \text{PbCl}_2(s): \quad K_{sp} = [Pb^{2+}] [Cl^-]^2 = 1.7 \times 10^{-5} \\
& = [2.0 \times 10^{-2} M] [x]^2 \quad x = 0.29 M [Cl^-] \text{ needed to ppt.}
\end{align*}

AgCl will ppt first.
(2) 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? [Ksp = 1.8 x 10$^{-11}$ for Mg(OH)$_2$, and Ksp = 2.2 x 10$^{-30}$ for Cu(OH)$_2$.]

\[
\text{Mg}^{2+} + \text{Cu}^{2+} + \text{OH}^- \rightleftharpoons \text{Mg(OH)}_2 + \text{Cu(OH)}_2
\]

\[
\text{Ksp } [\text{Mg(OH)}_2] = 1.8 \times 10^{-11} = \frac{[\text{Mg}][\text{OH}^-]^2}{1.9 \times 10^{-5} \text{ M} \text{ [OH}^-]} \text{ needed}
\]

\[
\text{Ksp } [\text{Cu(OH)}_2] = 2.2 \times 10^{-20} = \frac{[\text{Cu}][\text{OH}^-]^2}{1.1 \times 10^{-9} \text{ M} \text{ [OH}^-]} \text{ needed}
\]

Cu(OH)$_2$ precipitates first.

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. separation of individual ions within each group by selectively dissolving members of the group.
  3. specific tests to determine whether a particular ion is present or absent.