Chapter 17. Additional Aspects of Aqueous Equilibria

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, from the addition of a strong electrolyte, (e.g., 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 the 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.
• 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.

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 \([\text{HX}]/[\text{X}^-]\) 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 \([\text{HX}]/[\text{X}^-]\) 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:

\[ K_a = \frac{[\text{H}^+][\text{X}^-]}{[\text{HX}]} \]

• Rearranging, we get:

\[ [\text{H}^+] = K_a \frac{[\text{HX}]}{[\text{X}^-]} \]

• If we take the negative natural logarithm of each side of the equation, we get:

\[ -\log[\text{H}^+] = -\log K_a - \log \frac{[\text{HX}]}{[\text{X}^-]} \]

• By definition:

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

• 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.

**Addition of Strong Acids or Bases to Buffers**

• Keep in mind that reactions between strong acids and weak bases proceed essentially to completion.
• The same is true for reactions between strong bases and weak acids.
  • If we do not exceed the buffering capacity of the buffer, then the added strong acid or base is completely consumed by reaction with the buffer.
• We can break the calculation into two parts.
  • A **stoichiometric** calculation.
    • The addition of a strong acid or base results in a neutralization reaction:
      \[
      X^- + H_3O^+ \rightarrow HX + H_2O \\
      HX + OH^- \rightarrow X^- + H_2O
      \]
    • By knowing how much \(H_3O^+\) or \(OH^-\) was added, we know how much \(HX\) or \(X^-\) was formed.
  • An **equilibrium** calculation.
    • With the concentrations of \(HX\) and \(X^-\) (taking into account the change in volume of the solution) we can calculate the pH from the Henderson-Hasselbalch equation:

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**.
• 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.

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 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:
       $$\text{HC}_2\text{H}_3\text{O}_2(aq) + \text{OH}^-(aq) \rightarrow \text{C}_2\text{H}_3\text{O}_2^- (aq) + \text{H}_2\text{O}(l)$$
     - 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).
  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 is NOT equal to 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.
     - 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 in the strong acid-strong base case.
       - However, then 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 due to the formation of a neutral salt.
       - The pH is > 7.00 for the weak acid-strong base equivalence point due to the formation of a basic salt.
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 \( \text{PO}_4^{3-} \).

Titrating with an Acid-Base Indicator
• How can we analyze the titration (i.e., how will we know when we are at the equivalence point)?
  • We often use a \( \text{pH} \) indicator.
    • The indicator chosen should begin and end its color change anywhere on the rapid-rise portion of the titration curve.
    • The \textit{end point} in a titration is the point where the indicator changes color.
      • It represents a close approximation of the equivalence point.
  • Consider adding a strong base (e.g., \( \text{NaOH} \)) to a solution of a strong acid (e.g., \( \text{HCl} \)).
    • We know the \text{pH} at the equivalence point is 7.00.
    • The \text{pH} changes rapidly only over the \text{pH} range from about \text{pH} 11 to 3.
    • To detect the equivalence point, we use an indicator that changes color somewhere close to the \text{pH} at the equivalence point.
      • Usually, we use phenolphthalein, which changes color between \text{pH} 8.3 and 10.0.
      • Methyl red is a poor choice as it changes color between \text{pH} 4.2 and 6.0, before the equivalence point is reached.
    • In acid, phenolphthalein is colorless.
    • As \( \text{NaOH} \) 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.
      • Consider adding a strong acid (e.g., \( \text{HCl} \)) to a solution of a weak base (e.g., \( \text{NH}_3 \)).
        • We know the \text{pH} at the equivalence point is 5.28.
        • Here methyl red is a good choice while phenolphthalein would be a poor choice for indicator.

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.
    \[
    \text{BaSO}_4(s) \rightleftharpoons \text{Ba}^{2+}(aq) + \text{SO}_4^{2-}(aq)
    \]
  • 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.
Solubility and $K_{sp}$

- **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.

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 of complexing agents.
  - *Amphoterism* is related to the effects of both pH and 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 CaF$_2$:
    \[ \text{CaF}_2(s) \leftrightharpoons \text{Ca}^{2+}(aq) + 2\text{F}^-(aq) \]
    - If more F$^-$ is added (i.e., by the addition of NaF), the equilibrium shifts to the left to offset the increase.
    - Therefore, CaF$_2$ is formed and precipitation occurs.
    - As NaF is added to the system, the solubility of CaF$_2$ decreases.
- In general, the solubility of a slightly soluble salt is decreased by the presence of a second salt that produces a common ion.

Solubility and pH

- Again, we apply Le Châtelier’s principle:
  \[ \text{Mg(OH)}_2(s) \leftrightharpoons \text{Mg}^{2+}(aq) + 2\text{OH}^-(aq) \]
  - If OH$^-$ is removed, then the equilibrium shifts toward 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 decreases, [H$^+$] increases and the solubility of Mg(OH)$_2$ increases.
  - Another example:
    \[ \text{PbF}_2(s) \leftrightharpoons \text{Pb}^{2+}(aq) + 2\text{F}^-(aq) \]
    - If the F$^-$ is removed, then the equilibrium shifts towards the right and PbF$_2$ dissolves.
    - F$^-$ can be removed by adding a strong acid:
      \[ \text{F}^-(aq) + \text{H}^+(aq) \rightleftharpoons \text{HF}(aq) \]
      - As pH decreases, [H$^+$] increases and solubility of PbF$_2$ 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.
Formation of Complex Ions

- Recall that metal ions may act as Lewis acids in aqueous solution (water may act as the Lewis base).
- Such an interaction may have a significant impact on metal salt solubility.
- For example, AgCl has a very low solubility.
  - $K_{sp}$ for AgCl = $1.8 \times 10^{-10}$
  - However, the solubility is greatly increased if ammonia is added.
- Why?
- Consider the formation of Ag(NH$_3$)$_2$\(^+\):
  \[
  \text{Ag}^+(aq) + 2\text{NH}_3(aq) \rightleftharpoons \text{Ag(NH}_3)_2^+(aq)
  \]
  The Ag(NH$_3$)$_2$\(^+\) is called a complex ion.
  NH$_3$ (the attached Lewis base) is called a ligand.
- The equilibrium constant for the reaction is called the formation constant, $K_f$:
  \[
  K_f = \frac{[\text{Ag(NH}_3)_2^+]}{[\text{Ag}^+][\text{NH}_3]^2} = 1.7 \times 10^7
  \]
  - Consider the addition of ammonia to AgCl (white salt):
    \[
    \text{AgCl}(s) \rightleftharpoons \text{Ag}^+(aq) + \text{Cl}^-(aq)
    \]
    \[
    \text{Ag}^+(aq) + 2\text{NH}_3(aq) \rightleftharpoons \text{Ag(NH}_3)_2^+(aq)
    \]
    - The overall reaction is:
      \[
      \text{AgCl}(s) + 2\text{NH}_3(aq) \rightleftharpoons \text{Ag(NH}_3)_2^+(aq) + \text{Cl}^-(aq)
      \]
    - Effectively, the Ag$^+$ has been removed from solution.
    - By Le Châtelier’s principle, the forward reaction (the dissolving of AgCl) is favored.

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 oxides and hydroxides will dissolve in either a strong acid or a strong base.
  - Examples are 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:
    \[
    \text{Al(H}_2\text{O})_6^{3+}(aq) + \text{OH}^-(aq) \rightleftharpoons \text{Al(H}_2\text{O})_5(\text{OH})^{2+}(aq) + \text{H}_2\text{O(l)}
    \]
    \[
    \text{Al(H}_2\text{O})_5(\text{OH})^{2+}(aq) + \text{OH}^-(aq) \rightleftharpoons \text{Al(H}_2\text{O})_4(\text{OH})^+(aq) + \text{H}_2\text{O(l)}
    \]
    \[
    \text{Al(H}_2\text{O})_4(\text{OH})^+(aq) + \text{OH}^-(aq) \rightleftharpoons \text{Al(H}_2\text{O})_3(\text{OH})^+(s) + \text{H}_2\text{O(l)}
    \]
    \[
    \text{Al(H}_2\text{O})_3(\text{OH})^+(s) + \text{OH}^-(aq) \rightleftharpoons \text{Al(H}_2\text{O})_2(\text{OH})^+(aq) + \text{H}_2\text{O(l)}
    \]
  - The 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 $Q = K_{sp}$.
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 Cu\(^{2+}\), the silver precipitates \((K_{sp} \text{ for AgCl is } 1.8 \times 10^{-10})\) while the Cu\(^{2+}\) 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 Zn\(^{2+}(aq)\) and Cu\(^{2+}(aq)\).
    • CuS \((K_{sp} = 6 \times 10^{-37})\) is less soluble than ZnS \((K_{sp} = 2 \times 10^{-25})\).
    • Thus, CuS will be removed from solution before ZnS.
    • As H\(_2\)S is bubbled through the acidified green solution, black CuS forms.
    • When the precipitate is removed, a colorless solution containing Zn\(^{2+}(aq)\) remains.
    • When more H\(_2\)S is added to the solution, a second precipitate of white ZnS forms.

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.

Selected Problems: 14, 15-17, 19, 22, 24, 27, 29, 30, 32, 35-37, 41, 43, 45, 46, 51, 54, 55, 59, 61, 67, 71, 72.