Acid-Base Equilibria

Contents and Concepts

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2. Polyprotic Acids
3. Base-Ionization Equilibria
4. Acid–Base Properties of Salt Solutions

Solutions of a Weak Acid or Base with Another Solute
5. Common-Ion Effect
6. Buffers
7. Acid–Base Titration Curves

Learning Objectives

Solutions of a Weak Acid or Base
• Acid-Ionization Equilibria
  – a. Write the chemical equation for a weak acid undergoing acid ionization in aqueous solution.
  – b. Define acid-ionization constant and degree of ionization.
  – c. Determine $K_a$ from the solution pH.
  – d. Calculate concentrations of species in a weak acid solution using $K_a$ (approximation method).

1. Acid-Ionization Equilibria (cont)
   a. State the assumption that allows for using approximations when solving problems.
   b. Calculate concentrations of species in a weak acid solution using $K_a$ (quadratic formula).

2. Polyprotic Acids
   a. State the general trend in the ionization constants of a polyprotic acid.
   b. Calculate concentrations of species in a solution of a diprotic acid.

3. Base-Ionization Equilibria
   – a. Write the chemical equation for a weak base undergoing ionization in aqueous solution.
   – b. Define base-ionization constant.
   – c. Calculate concentrations of species in a weak base solution using $K_b$.

4. Acid–Base Properties of Salt Solutions
   – a. Write the hydrolysis reaction of an ion to form an acidic solution.
   – b. Write the hydrolysis reaction of an ion to form a basic solution.
   – c. Predict whether a salt solution is acidic, basic, or neutral.
   – d. Obtain $K_a$ from $K_b$ or $K_b$ from $K_a$.
   – e. Calculating concentrations of species in a salt solution.
Solutions of a Weak Acid or Base with Another Solute

5. Common-Ion Effect
   - a. Explain the common-ion effect.
   - b. Calculate the common-ion effect on acid ionization (effect of a strong acid).
   - c. Calculate the common-ion effect on acid ionization (effect of a conjugate base).

6. Buffers
   - a. Define buffer and buffer capacity.
   - b. Describe the pH change of a buffer solution with the addition of acid or base.
   - c. Calculate the pH of a buffer from given volumes of solution.
   - d. Calculate the pH of a buffer when a strong acid or a strong base is added.
   - e. Learn the Henderson–Hasselbalch equation.
   - f. State when the Henderson–Hasselbalch equation can be applied.

7. Acid–Base Titration Curves (cont)
   - f. Describe the curve for the titration of a weak base by a strong acid.
   - g. Calculate the pH of a solution at several points of a titration of a weak base by a strong acid.

Solutions of a Weak Acid or Base

• The simplest acid-base equilibria are those in which a single acid or base solute reacts with water.
  - In this chapter, we will first look at solutions of weak acids and bases.
  - We must also consider solutions of salts, which can have acidic or basic properties as a result of the reactions of their ions with water.

7. Acid–Base Titration Curves
   - a. Define equivalence point.
   - b. Describe the curve for the titration of a strong acid by a strong base.
   - c. Calculate the pH of a solution of a strong acid and a strong base.
   - d. Describe the curve for the titration of a weak acid by a strong base.
   - e. Calculate the pH at the equivalence point in the titration of a weak acid by a strong base.

The simplest acid–base equilibria are those in which a weak acid or a weak base reacts with water.

• We can write an acid equilibrium reaction for the generic acid, HA.

• \( \text{HA}(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{H}_3\text{O}^+(aq) + \text{A}^-(aq) \)
Acetic acid is a weak acid. It reacts with water as follows:

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

Here \( A = \text{C}_2\text{H}_3\text{O}_2^-(aq) \)

The equilibrium constant for the reaction of a weak acid with water is called the \textit{acid-ionization constant} (or acid-dissociation constant), \( K_a \).

\[ K_a = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}]} \]

Liquid water is not included in the equilibrium constant expression.

Acid-Ionization Equilibria

\textbf{Acid ionization} (or acid dissociation) is the reaction of an acid with water to produce hydronium ion (hydrogen ion) and the conjugate base anion.

- When acetic acid is added to water it reacts as follows.

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

- Because acetic acid is a weak electrolyte, it ionizes to a small extent in water.

\textbf{Acid-Ionization Equilibria}

- For a weak acid, the equilibrium concentrations of ions in solution are determined by the \textit{acid-ionization constant} (also called the acid-dissociation constant).

  - Consider the generic monoprotic acid, \( \text{HA} \).

\[ \text{HA}(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{H}_3\text{O}^+(aq) + \text{A}^-(aq) \]

  - The corresponding equilibrium expression is:

\[ K_c = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}][\text{H}_2\text{O}]} \]

- Since the concentration of water remains relatively constant, we rearrange the equation to get:

\[ K_a = [\text{H}_2\text{O}]K_c = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}]} \]

  - Thus, \( K_a \), the acid-ionization constant, equals the constant \( [\text{H}_2\text{O}]K_c \).

\[ K_a = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}]} \]

- Table 17.1 lists acid-ionization constants for various weak acids.

\begin{table}[h]
\centering
\caption{Acid-Ionization Constants at 25°C*}
\begin{tabular}{|c|c|c|}
\hline
\textbf{Substance} & \textbf{Formula} & \textbf{\( K_a \)} \\
\hline
Acetic acid & \text{HC}_2\text{H}_3\text{O}_2 & 1.7 \times 10^{-5} \\
Benzoic acid & \text{HC}_{6}\text{H}_5\text{O}_2 & 6.3 \times 10^{-5} \\
Boric acid & \text{H}_3\text{BO}_3 & 5.9 \times 10^{-10} \\
Carbonic acid & \text{H}_2\text{CO}_3 & 4.3 \times 10^{-7} \\
Cyanic acid & \text{HOCN} & 4.8 \times 10^{-11} \\
Formic acid & \text{HCO}_2 & 1.7 \times 10^{-4} \\
Hydrocyanic acid & \text{HCN} & 4.9 \times 10^{-10} \\
Hydrofluoric acid & \text{HF} & 6.8 \times 10^{-4} \\
Hydrogen sulfate ion & \text{HSO}_4^- & 1.1 \times 10^{-2} \\
Hydrogen sulfide & \text{H}_2\text{S} & 3.9 \times 10^{-8} \\
Iodic acid & \text{HIO} & 1.2 \times 10^{-37} \\
Hypochlorous acid & \text{HClO} & 3.5 \times 10^{-8} \\
Nitric acid & \text{HNO}_3 & 4.5 \times 10^{-6} \\
Oxalic acid & \text{H}_2\text{C}_2\text{O}_4 & 5.6 \times 10^{-2} \\
Sulfuric acid & \text{H}_2\text{SO}_4 & 5.1 \times 10^{-2} \\
\hline
\end{tabular}
\end{table}
**TABLE 16.1 Acid-Ionization Constants at 25°C**

<table>
<thead>
<tr>
<th>Substance</th>
<th>Formula</th>
<th>$K_a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetic acid</td>
<td>HCO$_2$H</td>
<td>$1.7 \times 10^{-5}$</td>
</tr>
<tr>
<td>Benzoic acid</td>
<td>HCO$_2$H</td>
<td>$6.3 \times 10^{-5}$</td>
</tr>
<tr>
<td>Boric acid</td>
<td>H$_2$B$_3$O$_5$</td>
<td>$5.9 \times 10^{-10}$</td>
</tr>
<tr>
<td>Carbonic acid</td>
<td>H$_2$CO$_3$</td>
<td>$4.3 \times 10^{-7}$</td>
</tr>
<tr>
<td>Cyanic acid</td>
<td>HOCN</td>
<td>$3.5 \times 10^{-4}$</td>
</tr>
<tr>
<td>Formic acid</td>
<td>HCO$_2$N</td>
<td>$1.7 \times 10^{-4}$</td>
</tr>
<tr>
<td>Hydrocyanic acid</td>
<td>HCN</td>
<td>$4.9 \times 10^{-10}$</td>
</tr>
<tr>
<td>Hydrofluoric acid</td>
<td>HF</td>
<td>$6.8 \times 10^{-4}$</td>
</tr>
<tr>
<td>Hydrogen sulfate</td>
<td>H$_2$SO$_4$</td>
<td>$1.1 \times 10^{-2}$</td>
</tr>
<tr>
<td>Hydrogencarbonate</td>
<td>HS</td>
<td>$8.9 \times 10^{-8}$</td>
</tr>
<tr>
<td>Hypochlorous acid</td>
<td>HClO</td>
<td>$3.5 \times 10^{-9}$</td>
</tr>
<tr>
<td>Nitric acid</td>
<td>HNO$_3$</td>
<td>$4.5 \times 10^{-4}$</td>
</tr>
<tr>
<td>Oxalic acid</td>
<td>H$_2$C$_2$O$_4$</td>
<td>$5.6 \times 10^{-2}$</td>
</tr>
<tr>
<td>HCN</td>
<td>$4.9 \times 10^{-10}$</td>
<td></td>
</tr>
</tbody>
</table>

**Calculations with $K_a$**

- Given the value of $K_a$ and the initial concentration of HA, you can calculate the equilibrium concentration of all species.
- Given the value of $K_a$ and the initial concentration of HA, you can calculate the degree of ionization and the percent ionization.
- Given the pH of the final solution and the initial concentration of HA, you can find the value of $K_a$ and the percent ionization.

**Experimental Determination of $K_a$**

- The degree of ionization of a weak electrolyte is the fraction of molecules that react with water to give ions.
  - Electrical conductivity or some other colligative property can be measured to determine the degree of ionization.
  - With weak acids, the pH can be used to determine the equilibrium composition of ions in the solution.

**Calculations with $K_a$**

- Given the value of $K_a$ and the initial concentration of HA, you can calculate the equilibrium concentration of all species.
- Given the value of $K_a$ and the initial concentration of HA, you can calculate the degree of ionization and the percent ionization.
- Given the pH of the final solution and the initial concentration of HA, you can find the value of $K_a$ and the percent ionization.

**A Problem To Consider**

- Nicotinic acid is a weak monoprotic acid with the formula HC$_6$H$_4$NO$_2$. A 0.012 M solution of nicotinic acid has a pH of 3.39 at 25°C. Calculate the acid-ionization constant for this acid at 25°C and the percent ionization
  - It is important to realize that the solution was made 0.012 M in nicotinic acid, however, some molecules ionize making the equilibrium concentration of nicotinic acid less than 0.012 M.
  - We will abbreviate the formula for nicotinic acid as HNic.
Let $x$ be the moles per liter of product formed.

\[
\text{HNic}(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{H}_3\text{O}^+(aq) + \text{Nic}^-(aq)
\]

<table>
<thead>
<tr>
<th>Starting</th>
<th>0.012</th>
</tr>
</thead>
<tbody>
<tr>
<td>Change</td>
<td>-x</td>
</tr>
<tr>
<td>Equilibrium</td>
<td>0.012 - x</td>
</tr>
</tbody>
</table>

The equilibrium-constant expression is:

\[
K_a = \frac{[\text{H}_3\text{O}^+][\text{Nic}^-]}{[\text{HNic}]}
\]

Substituting the expressions for the equilibrium concentrations, we get

\[
K_a = \frac{x^2}{(0.012 - x)}
\]

We can obtain the value of $x$ from the given pH.

\[
x = [\text{H}_3\text{O}^+] = \text{anti log}(-\text{pH})
\]

\[
x = \text{anti log}(3.39)
\]

\[
x = 4.1 \times 10^{-4} = 0.00041
\]

Substitute this value of $x$ in our equilibrium expression.

Note first, however, that

\[
(0.012 - x) = (0.012 - 0.00041) = 0.01159 \approx 0.012
\]

The concentration of unionized acid remains virtually unchanged.

Another Problem

• Sore-throat medications sometimes contain the weak acid phenol, $\text{HC}_6\text{H}_5\text{O}$. A 0.10 M solution of phenol has a pH of 5.43 at 25°C.

  a. What is the acid-ionization constant, $K_a$, for phenol at 25°C?

  b. What is the degree of ionization?

<table>
<thead>
<tr>
<th>$\text{HC}_6\text{H}_5\text{O}(aq)$</th>
<th>$\text{H}_2\text{O}(l)$</th>
<th>$\text{H}_3\text{O}^+(aq)$</th>
<th>$\text{C}_6\text{H}_5\text{O}^-(aq)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial</td>
<td>0.10</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Change</td>
<td>$-x$</td>
<td>$+x$</td>
<td>$+x$</td>
</tr>
<tr>
<td>Equilibrium</td>
<td>$0.10 - x$</td>
<td>$x$</td>
<td>$x$</td>
</tr>
</tbody>
</table>

We were told that pH = 5.43. That allows us to find $[\text{H}_3\text{O}^+] = 3.7 \times 10^{-6}$ M = $x = [\text{C}_6\text{H}_5\text{O}^-]$.

Now we find $[\text{HC}_6\text{H}_5\text{O}] = 0.10 - x = 0.10$ M.

Substitute this value of $x$ in our equilibrium expression.

\[
K_a = \frac{x^2}{(0.012 - x)} \approx \frac{(0.00041)^2}{(0.012)} = 1.4 \times 10^{-5}
\]

To obtain the degree of dissociation:

\[
\text{Degree of dissociation} = \frac{0.00041}{0.012} = 0.034
\]

The percent ionization is obtained by multiplying by 100, which gives 3.4%.

Do Exercise 17.1 Look at Problems 17.29 and 17.30

Finally, we write the expression for $K_a$ and substitute the concentrations we now know.

\[
\text{HC}_6\text{H}_5\text{O} + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{C}_6\text{H}_5\text{O}^-
\]

\[
[\text{H}_3\text{O}^+] = [\text{C}_6\text{H}_5\text{O}^-] = 3.7 \times 10^{-6} M
\]

\[
[\text{HC}_6\text{H}_5\text{O}] = 0.10 M
\]

\[
K_a = \frac{[\text{H}_3\text{O}^+][\text{C}_6\text{H}_5\text{O}^-]}{[\text{HC}_6\text{H}_5\text{O}]}
\]

\[
K_a = \frac{(3.7 \times 10^{-6})^2}{0.10}
\]

\[
K_a = 1.4 \times 10^{-10}
\]
• The degree of ionization is the ratio of ionized concentration to original concentration:

\[
\text{Degree of ionization} = \frac{x}{0.100} = 3.7 \times 10^{-6}
\]

Degree of ionization = \(3.7 \times 10^{-6}\)

• Percent ionization is the degree of ionization \(\times 100\%\):

\[
\text{Percent ionization} = 3.7 \times 10^{-3}\% \text{ or } 0.0037\%
\]

• Percent ionization = \(3.7 \times 10^{-3}\%\) or \(0.0037\%\)

---

**Simplifying Assumption for Acid and Base Ionizations**

- The equilibrium concentration of the acid is most often \([\text{HA}]_0 - x\).

- If \(x\) is much, much less than \([\text{HA}]_0\), we can assume that subtracting \(x\) makes no difference to \([\text{HA}]\):

  \([\text{HA}]_0 - x \approx [\text{HA}]_0\)

- This is a valid assumption when the ratio of \([\text{HA}]_0\) to \(K_a\) is > 10^3. If it is not valid, you must use the quadratic equation to solve the problem.

---

| \(\text{HA}(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{H}_3\text{O}^+(aq) + \text{A}^-(aq)\) |
|-----------------|-----------------|-----------------|-----------------|
| **Initial**     | 0.200           | 0               | 0               |
| **Change**      | \(-x\)          | \(+x\)          | \(+x\)          |
| **Equilibrium** | 0.200 - \(x\)   | \(x\)           | \(x\)           |

\[K_a = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}]}\]

\[2.6 \times 10^{-5} = \frac{x^2}{0.200 - x}\]

\[0.200 - x \approx 0.200\]

\[5.2 \times 10^{-6} = x^2\]

\[x = 2.3 \times 10^{-3}\ M = [\text{H}_3\text{O}^+]\]

\[\text{pH} = -\log[\text{H}_3\text{O}^+] = -\text{pH}(2.3 \times 10^{-3})\]

\[\text{pH} = 2.64\]

---

• Para-hydroxybenzoic acid is used to make certain dyes. What are the concentrations of this acid, of hydronium ion, and of para-hydroxybenzoate ion in a 0.200 M aqueous solution at 25°C? What is the pH of the solution and the degree of ionization of the acid? The \(K_a\) of this acid is \(2.6 \times 10^{-3}\).

We will use the generic formula \(\text{HA}\) for para-hydroxybenzoic acid and the following equilibrium:

\[
\text{HA} + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{A}^-
\]

---

**Calculations With \(K_a\)**

• Once you know the value of \(K_a\), you can calculate the equilibrium concentrations of species \(\text{HA}, \text{A}^-,\) and \(\text{H}_3\text{O}^+\) for solutions of different molarities.

  - The general method for doing this was discussed in Chapter 15.
Calculations With $K_a$

- Note that in our previous example, the degree of dissociation was so small that "x" was negligible compared to the concentration of nicotinic acid.

- It is the small value of the degree of ionization that allowed us to ignore the subtracted x in the denominator of our equilibrium expression.

- The degree of ionization of a weak acid depends on both the $K_a$ and the concentration of the acid solution (see Figure 16.3).

- If the simplifying assumption is not valid, you can solve the equilibrium equation exactly by using the quadratic equation.

- The next example illustrates this with a solution of aspirin (acetylsalicylic acid), $HC_9H_7O_4$, a common headache remedy.

- The molar mass of $HC_9H_7O_4$ is 180.2 g.

  From this we find that the sample contained 0.00180 mol of the acid.

  Hence, the concentration of the acetylsalicylic acid is $0.00180 \text{ mol}/0.500 \text{ L} = 0.0036 \text{ M}$ (Retain two significant figures, the same number of significant figures in $K_a$).

- How do you know when you can use this simplifying assumption?

  - It can be shown that if the acid concentration, $C_a$, divided by the $K_a$ exceeds 100, that is,

  $\frac{C_a}{K_a} > 100$

  - then this simplifying assumption of ignoring the subtracted x gives an acceptable error of less than 5%.

  - If we substitute the equilibrium concentrations and the $K_a$ into the equilibrium constant expression, we get

  \[
  \frac{[H_2O^+]\text{[Acs}^-]}{[HAc]} = K_a
  \]

- These data are summarized below.

<table>
<thead>
<tr>
<th>Starting</th>
<th>Change</th>
<th>Equilibrium</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0036</td>
<td>-x</td>
<td>0.0036-x</td>
</tr>
<tr>
<td></td>
<td>+x</td>
<td>+x</td>
</tr>
<tr>
<td></td>
<td>x</td>
<td>x</td>
</tr>
</tbody>
</table>

Abbreviate the formula for acetylsalicylic acid as $HAc$ and let x be the amount of $H_3O^+$ formed per liter.

- The amount of acetylsalicylate ion is also x mol; the amount of nonionized acetylsalicylic acid is $(0.0036-x)$ mol.

- Note that

$\frac{C_a}{K_a} = \frac{0.0036}{3.3 \times 10^{-4}} = 11$

which is less than 100, so we must solve the equilibrium equation exactly.

Figure 16.3: Variation of Percent Ionization of a Weak Acid with Concentration

- Concentration of nicotinic acid (M)
  - 0
  - 0.02
  - 0.04
  - 0.06
  - 0.08
  - 0.10
  - Percent ionization
  - 0
  - 1
  - 2
  - 3
  - 4
  - 5

- Abbreviate the formula for acetylsalicylic acid as $HAc$ and let x be the amount of $H_3O^+$ formed per liter.

- The amount of acetylsalicylate ion is also x mol; the amount of nonionized acetylsalicylic acid is $(0.0036-x)$ mol.

- These data are summarized below.

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<thead>
<tr>
<th>Starting</th>
<th>Change</th>
<th>Equilibrium</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0036</td>
<td>-x</td>
<td>0.0036-x</td>
</tr>
<tr>
<td></td>
<td>+x</td>
<td>+x</td>
</tr>
<tr>
<td></td>
<td>x</td>
<td>x</td>
</tr>
</tbody>
</table>

Abbreviate the formula for acetylsalicylic acid as $HAc$ and let x be the amount of $H_3O^+$ formed per liter.

- The amount of acetylsalicylate ion is also x mol; the amount of nonionized acetylsalicylic acid is $(0.0036-x)$ mol.
\[
\frac{[H_3O^+][Ac^{-}]}{[HAc]} = K_a
\]
\[
x^2 = 3.3 \times 10^{-4}
\]
You can solve this equation exactly by using the quadratic formula.
Rearranging the preceding equation to put it in the form \(ax^2 + bx + c = 0\), we get
\[
x^2 + (3.3 \times 10^{-4})x - (1.2 \times 10^{-6}) = 0
\]
Now substitute into the quadratic formula.
\[
x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}
\]
Now substitute into the quadratic formula.
\[
x = \frac{-3.3 \times 10^{-4} \pm \sqrt{(3.3 \times 10^{-4})^2 - 4(1.2 \times 10^{-6})}}{2}
\]
The lower sign in \(\pm\) gives a negative root which we can ignore.
Taking the upper sign, we get
\[
x = [H_3O^+] = 9.4 \times 10^{-4}
\]
Now we can calculate the pH.
\[
pH = -\log(9.4 \times 10^{-4}) = 3.03
\]
Check your answer by substituting the hydrogen ion concentration into the equilibrium expression and calculate \(K_a\).

• Polyprotic Acids
• A polyprotic acid has more than one acidic proton—for example, \(H_2SO_4\), \(H_2SO_3\), \(H_2CO_3\), \(H_3PO_4\).

• These acids have successive ionization reactions with \(K_{a1}\), \(K_{a2}\), \ldots

• The next example illustrates how to do calculations for a polyprotic acid.

Polyprotic Acids
• Some acids have two or more protons (hydrogen ions) to donate in aqueous solution. These are referred to as polyprotic acids.
  • Sulfuric acid, for example, can lose two protons in aqueous solution.
  \[
  H_2SO_4(aq) + H_2O(l) \rightarrow H_3O^+(aq) + HSO_4^-(aq)
  \]
  \[
  HSO_4^-(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + SO_4^{2-}(aq)
  \]
  • The first proton is lost completely followed by a weak ionization of the hydrogen sulfate ion, \(HSO_4^-\).

• For a weak diprotic acid like carbonic acid, \(H_2CO_3\), two simultaneous equilibria must be considered.
  \[
  H_2CO_3(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + HCO_3^-(aq)
  \]
  \[
  HCO_3^-(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + CO_3^{2-}(aq)
  \]
  • Each equilibrium has an associated acid-ionization constant.
  • For the loss of the first proton
  \[
  K_{a1} = \frac{[H_3O^+][HCO_3^-]}{[H_2CO_3]} = 4.3 \times 10^{-7}
  \]

Do Exercise 16.3
See problems 16.43-44
Each equilibrium has an associated acid-ionization constant.

- For the loss of the second proton

\[ K_{a2} = \frac{[H_2O^+] [CO_3^{2-}]}{[HCO_3^-]} = 4.8 \times 10^{-11} \]

- In general, the second ionization constant, \( K_{a2} \), for a polyprotic acid is smaller than the first ionization constant, \( K_{a1} \).

- In the case of a triprotic acid, such as \( H_3PO_4 \), the third ionization constant, \( K_{a3} \), is smaller than the second one, \( K_{a2} \).

When several equilibria occur at once, it might appear complicated to calculate equilibrium compositions.

However, reasonable assumptions can be made that simplify these calculations as we show in the next example.

A Problem To Consider

- Ascorbic acid (vitamin C) is a diprotic acid, \( H_2C_6H_6O_6 \). What is the pH of a 0.10 M solution?
- What is the concentration of the ascorbate ion, \( C_6H_6O_6^{2-} \)?

The acid ionization constants are \( K_{a1} = 7.9 \times 10^{-5} \) and \( K_{a2} = 1.6 \times 10^{-12} \).

- For diprotic acids, \( K_{a2} \) is so much smaller than \( K_{a1} \) that the smaller amount of hydronium ion produced in the second reaction can be neglected.

- The pH can be determined by simply solving the equilibrium problem posed by the first ionization.

If we abbreviate the formula for ascorbic acid as \( H_2Asc \), then the first ionization is:

\[ H_2Asc(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + HAsc^-(aq) \]

\[ H_2Asc(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + HAsc^- (aq) \]

The equilibrium constant expression is

\[ \frac{[H_2O^+] [HAsc^-]}{[H_2Asc]} = K_{a1} \]

Substituting into the equilibrium expression

\[ \frac{x^2}{(0.10 - x)} = 7.9 \times 10^{-5} \]

Assuming that \( x \) is much smaller than 0.10, you get

\[ x \approx (7.9 \times 10^{-5}) \times (0.10) \]

\[ x \approx 2.8 \times 10^{-3} = 0.0028 \]

The hydronium ion concentration is 0.0028 M, so

\[ pH = -\log(0.0028) = 2.55 \]

- The ascorbate ion, \( Asc^{2-} \), which we will call \( y \), is produced only in the second ionization of \( H_2Asc \).

\[ HAsc^- (aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + Asc^{2-} (aq) \]

- Assume the starting concentrations for \( HAsc^- \) and \( H_3O^+ \) to be those from the first equilibrium.

\[ HAsc^- (aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + Asc^{2-} (aq) \]

\[ HAsc^- (aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + Asc^{2-} (aq) \]

\[ \begin{array}{c|c|c|c|c|c|c} \hline \text{Starting} & 0.0028 & 0.0028 & 0 \hline \text{Change} & -y & +y & +y \hline \text{Equilibrium} & 0.0028-x & 0.0028+y & y \hline \end{array} \]
The equilibrium constant expression is

$$\frac{[H_3O^+][Asc^{2-}]}{[HAsc^+]} = K_{a2}$$

Substituting into the equilibrium expression

$$\frac{(0.0028 + y)(y)}{(0.0028 - y)} = 1.6 \times 10^{-12}$$

Assuming $y$ is much smaller than 0.0028, the equation simplifies to

$$\frac{(0.0028)(y)}{(0.0028)} = 1.6 \times 10^{-12}$$

Hence,

$$y \approx [Asc^{2-}] = 1.6 \times 10^{-12}$$

The concentration of the ascorbate ion equals $K_{a2}$.

\[
\begin{align*}
\text{H}_2\text{A}(aq) &\rightleftharpoons \text{H}_3\text{O}^+(aq) + \text{HA}^- \\
\text{Initial} &\quad + 0.10 \quad 0 \quad \text{(aq)} \\
\text{Change} &\quad -x \quad +x \quad +x \\
\text{Equilibrium} &\quad 0.10 - x \quad x \quad x \\
\end{align*}
\]

$$K_{a1} = \frac{[\text{H}_2\text{O}^-][\text{HA}^-]}{[\text{H}_2\text{A}]} \quad 9.2 \times 10^{-4} = \frac{x^2}{0.10 - x}$$

$$\frac{0.10}{9.2 \times 10^{-4}} < 1000$$

We cannot use the simplifying assumption.

Hence,

$$y \approx [Asc^{2-}] = 1.6 \times 10^{-12}$$

The concentration of the ascorbate ion equals $K_{a2}$.

Tartaric acid, $\text{H}_2\text{C}_4\text{H}_4\text{O}_6$, is a diprotic acid used in food products. What is the pH of a 0.10 M solution? What is the concentration of the $\text{C}_4\text{H}_4\text{O}_6^{2-}$ ion in the same solution?

- $K_{a1} = 9.2 \times 10^{-4}$; $K_{a2} = 4.3 \times 10^{-5}$.

First, we will use the first acid-ionization equilibrium to find $[\text{H}^+]$ and $[\text{HC}_4\text{H}_4\text{O}_6^-]$. In these calculations, we will use the generic formula $\text{H}_2\text{A}$ for the acid.

Next, we will use the second acid-ionization equilibrium to find $[\text{C}_4\text{H}_4\text{O}_6^{2-}]$.

\[
\begin{align*}
9.2 \times 10^{-4}(0.10 - x) &= x^2 \\
9.2 \times 10^{-5} - 9.2 \times 10^{-4}x &= x^2 \\
x^3 + 9.2 \times 10^{-4}x - 9.2 \times 10^{-5} &= 0 \\
a &= 1 \quad b = 9.2 \times 10^{-4} \quad c = -9.2 \times 10^{-5} \\
x &= \frac{-b \pm \sqrt{b^2 - 4ac}}{2a} \\
x &= \frac{-9.2 \times 10^{-4} \pm \sqrt{(9.2 \times 10^{-4})^2 - 4(1)(-9.2 \times 10^{-5})}}{2(1)} \\
x &= \frac{-9.2 \times 10^{-4} \pm (1.92 \times 10^{-2})}{2} = -4.6 \times 10^{-4} \pm 9.6 \times 10^{-3}
\end{align*}
\]

$\boxed{x = 9.1 \times 10^{-3}}$ and $\boxed{x = -1.0 \times 10^{-2}}$

We eliminate the negative value because it is physically impossible to have a negative concentration. At the end of the first acid-ionization equilibrium, the concentrations are

$[\text{H}_3\text{O}^+] = 9.1 \times 10^{-3}$ M  \\
$[\text{HA}^-] = 9.0 \times 10^{-4}$ M  \\
$[\text{HA}] = 9.1 \times 10^{-3}$ M

Now we use these for the second acid-ionization equilibrium.
Base-Ionization Equilibria

- The concentration of water is nearly constant.

\[ K_b = [H_2O]K_c = \frac{[NH_4^+][OH^-]}{[NH_3]} \]

- In general, a weak base B with the base ionization

\[ B(aq) + H_2O(l) \rightleftharpoons HB^+(aq) + OH^-(aq) \]

has a base ionization constant equal to

\[ K_b = \frac{[HB^+][OH^-]}{[B]} \]

Table 17.2 lists ionization constants for some weak bases.

### Table 16.2  Base-Ionization Constants at 25°C

<table>
<thead>
<tr>
<th>Substance</th>
<th>Formula</th>
<th>( K_b )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ammonia</td>
<td>NH_3</td>
<td>( 1.8 \times 10^{-3} )</td>
</tr>
<tr>
<td>Aniline</td>
<td>C_6H_{5}NH_2</td>
<td>( 4.2 \times 10^{-10} )</td>
</tr>
<tr>
<td>Dimethylamine</td>
<td>(CH_3)_2NH</td>
<td>( 5.1 \times 10^{-4} )</td>
</tr>
<tr>
<td>Ethylamine</td>
<td>C_2H_5NH_2</td>
<td>( 4.7 \times 10^{-4} )</td>
</tr>
<tr>
<td>Hydrazine</td>
<td>N_2H_4</td>
<td>( 1.7 \times 10^{-6} )</td>
</tr>
<tr>
<td>Hydroxylamine</td>
<td>NH_2OH</td>
<td>( 1.1 \times 10^{-9} )</td>
</tr>
<tr>
<td>Methylamine</td>
<td>CH_3NH_2</td>
<td>( 4.4 \times 10^{-9} )</td>
</tr>
<tr>
<td>Pyridine</td>
<td>C_5H_5N</td>
<td>( 1.4 \times 10^{-9} )</td>
</tr>
<tr>
<td>Urac</td>
<td>NH_2CHN_2H_2</td>
<td>( 1.5 \times 10^{-14} )</td>
</tr>
</tbody>
</table>

- Writing \( K_b \) Reactions
  
  - The bases in Table 16.2 are nitrogen bases; that is, the proton they accept adds to a nitrogen atom. Next we'll practice writing the \( K_b \) reactions.
  
  - Ammonium becomes ammonium ion:

\[ \text{NH}_3 + H_2O \rightarrow \text{NH}_4^+ + OH^- \]

- Ethylamine becomes ethyl ammonium ion:

\[ C_2H_5NH_2 + H_2O \rightarrow C_2H_5NH_3^+ + OH^- \]

- Writing \( K_a \) Reactions

<table>
<thead>
<tr>
<th>Substance</th>
<th>Formula</th>
<th>( K_a )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetic Acid</td>
<td>CH_3COOH</td>
<td>( 1.8 \times 10^{-5} )</td>
</tr>
<tr>
<td>Benzoic Acid</td>
<td>C_6H_5COOH</td>
<td>( 6.3 \times 10^{-5} )</td>
</tr>
<tr>
<td>Citric Acid</td>
<td>C_6H_8O_7</td>
<td>( 1.4 \times 10^{-5} )</td>
</tr>
</tbody>
</table>

- Writing \( K_c \) Reactions

<table>
<thead>
<tr>
<th>Substance</th>
<th>Formula</th>
<th>( K_c )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetic Acid</td>
<td>CH_3COOH</td>
<td>( 2.4 \times 10^{-5} )</td>
</tr>
<tr>
<td>Benzoic Acid</td>
<td>C_6H_5COOH</td>
<td>( 3.1 \times 10^{-5} )</td>
</tr>
<tr>
<td>Citric Acid</td>
<td>C_6H_8O_7</td>
<td>( 2.3 \times 10^{-5} )</td>
</tr>
</tbody>
</table>
• Dimethylamine becomes dimethylammonium ion:
  \[(\text{CH}_3\text{H}_2\text{NH}_2 + \text{H}_2\text{O}) \rightarrow (\text{CH}_3\text{H}_2\text{NH}_3^+ + \text{OH}^-)\]

• Pyridine becomes pyridinium ion:
  \[\text{C}_5\text{H}_5\text{NH}^+ + \text{H}_2\text{O} \rightarrow \text{C}_5\text{H}_5\text{NH}_3^+ + \text{OH}^-\]

• Hydrazine becomes hydrazinium ion:
  \[\text{N}_2\text{H}_4 + \text{H}_2\text{O} \rightarrow \text{N}_2\text{H}_5^+ + \text{OH}^-\]

We can be given pH, initial concentration, and \(K_b\).

From the pH, we can find first \([\text{H}_3\text{O}^+]\) and then \([\text{OH}^-]\). Using what is given, we can find the other quantities.

We can also use a simplifying assumption: When \([\text{B}]_0 / K_b > 10^3\), the expression \((\text{B})_0 - x \approx [\text{B}]_0\).

A Problem To Consider

• What is the pH of a 0.20 M solution of pyridine, \(\text{C}_5\text{H}_5\text{N}\), in aqueous solution? The \(K_b\) for pyridine is \(1.4 \times 10^{-9}\).

  As before, we will follow the three steps in solving an equilibrium.
  
  1. Write the equation and make a table of concentrations.
  2. Set up the equilibrium constant expression.
  3. Solve for \(x = [\text{OH}^-]\).

  
  Using our simplifying assumption that the \(x\) in the denominator is negligible, we get

  \[
  \frac{x^2}{(0.20)} \approx 1.4 \times 10^{-9}
  \]

  Solving for \(x\) we get

  \[
  x \approx (0.20) \times (1.4 \times 10^{-9})
  \]

  \[
  x = [\text{OH}^-] \approx \sqrt{(0.20) \times (1.4 \times 10^{-9})} = 1.7 \times 10^{-5}
  \]
Solving for pOH
\[ \text{pOH} = -\log[\text{OH}^-] = -\log(1.7 \times 10^{-5}) = 4.8 \]

Since \( \text{pH} + \text{pOH} = 14.00 \)
\[ \text{pH} = 14.00 - \text{pOH} = 14.00 - 4.8 = 9.2 \]

Work exercise 17.6 See problems 17.47&48

- Since \( \text{pH} + \text{pOH} = 14.00 \)
- Solving for pOH

\[ \text{pOH} = -\log[\text{OH}^-] = -\log(1.7 \times 10^{-5}) = 4.8 \]

\[ \text{pH} = 14.00 - \text{pOH} = 14.00 - 4.8 = 9.2 \]

Sodium ion, Na\(^+\), is unreactive with water, but the cyanide ion, CN\(^-\), reacts to produce HCN and \( \text{OH}^- \).

\[ \text{CN}^- (aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{HCN}(aq) + \text{OH}^-(aq) \]

- From the Brønsted-Lowry point of view, the CN\(^-\) ion acts as a base, because it accepts a proton from \( \text{H}_2\text{O} \).

\[ \text{CN}^- (aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{HCN}(aq) + \text{OH}^-(aq) \]

- You can also see that \( \text{OH}^- \) ion is a product, so you would expect the solution to have a basic pH. This explains why NaCN solutions are basic.

\[ \text{CN}^- (aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{HCN}(aq) + \text{OH}^-(aq) \]

- The reaction of the CN\(^-\) ion with water is referred to as the hydrolysis of CN\(^-\).
- The CN\(^-\) ion hydrolyzes to give the conjugate acid and hydroxide.

\[ \text{CN}^- (aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{HCN}(aq) + \text{OH}^-(aq) \]

- The hydrolysis reaction for CN\(^-\) has the form of a base ionization so you write the \( K_b \) expression for it.

\[ \text{CN}^- (aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{HCN}(aq) + \text{OH}^-(aq) \]

- The \( \text{NH}_4^+ \) ion hydrolyzes to the conjugate base (\( \text{NH}_3 \)) and hydronium ion.

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

- This equation has the form of an acid ionization so you write the \( K_a \) expression for it.

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

- The hydrolysis reaction for \( \text{NH}_4^+ \) has the form of a base ionization so you write the \( K_b \) expression for it.

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

- The \( \text{NH}_4^+ \) ion hydrolyzes to the conjugate base (\( \text{NH}_3 \)) and hydronium ion.

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

- This equation has the form of an acid ionization so you write the \( K_a \) expression for it.

\[ \text{NH}_4^+ (aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{NH}_3(aq) + \text{H}_3\text{O}^+(aq) \]
Predicting Whether a Salt is Acidic, Basic, or Neutral

- How can you predict whether a particular salt will be acidic, basic, or neutral?
  - The Brønsted-Lowry concept illustrates the inverse relationship in the strengths of conjugate acid-base pairs.
  - Consequently, the anions of weak acids (poor proton donors) are good proton acceptors.
  - Anions of weak acids therefore, are basic.

- One the other hand, the anions of strong acids (good proton donors) have virtually no basic character, that is, they do not hydrolyze.
  - For example, the Cl^- ion, which is conjugate to the strong acid HCl, shows no appreciable reaction with water.

\[
\text{Cl}^- (\text{aq}) + \text{H}_2\text{O}(l) \rightarrow \text{no reaction}
\]

- Conversely, the cations of weak bases are acidic.
  - One the other hand, the cations of strong bases have virtually no acidic character, that is, they do not hydrolyze. For example,

\[
\text{Na}^+ (\text{aq}) + \text{H}_2\text{O}(l) \rightarrow \text{no reaction}
\]

Predicting Whether a Salt is Acidic, Basic, or Neutral

- To predict the acidity or basicity of a salt, you must examine the acidity or basicity of the ions composing the salt.
  - Consider potassium acetate, KC\textsubscript{2}H\textsubscript{3}O\textsubscript{2}.
    The potassium ion is the cation of a strong base (KOH) and does not hydrolyze.

\[
\text{K}^+ (\text{aq}) + \text{H}_2\text{O}(l) \rightarrow \text{no reaction}
\]

- Consider potassium acetate, KC\textsubscript{2}H\textsubscript{3}O\textsubscript{2}.
  The acetate ion, however, is the anion of a weak acid (HC\textsubscript{2}H\textsubscript{3}O\textsubscript{2}) and is basic.

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

A solution of potassium acetate is predicted to be basic.

Do Exercise 16.6

See Problems 16.53-54

Predicting Whether a Salt is Acidic, Basic, or Neutral

- These rules apply to normal salts (those in which the anion has no acidic hydrogen)

1. A salt of a strong base and a strong acid.
   The salt has no hydrolyzable ions and so gives a neutral aqueous solution.

   An example is NaCl.

2. A salt of a strong base and a weak acid.
   The anion of the salt is the conjugate of the weak acid. It hydrolyzes to give a basic solution.

   An example is NaCN.

3. A salt of a weak base and a strong acid.
   The cation of the salt is the conjugate of the weak base. It hydrolyzes to give an acidic solution.

   An example is NH\textsubscript{4}Cl.
The pH of a Salt Solution

- To calculate the pH of a salt solution would require the $K_a$ of the acidic cation or the $K_b$ of the basic anion. (see Figure 17.8)
  - The ionization constants of ions are not listed directly in tables because the values are easily related to their conjugate species.
  - Thus the $K_b$ for CN$^-$ is related to the $K_a$ for HCN.

How about?

4. A salt of a weak base and a weak acid.

Both ions hydrolyze. You must compare the $K_a$ of the cation with the $K_b$ of the anion. If the $K_a$ of the cation is larger the solution is acidic. If the $K_b$ of the anion is larger, the solution is basic.

- The conjugate acid of a weak base reacts with water to form an acidic solution:
  - $\text{NH}_4^+ + \text{H}_2\text{O} \rightleftharpoons \text{NH}_3 + \text{H}_3\text{O}^+$
- The conjugate base of a weak acid reacts with water to form a basic solution:
  - $\text{F}^- + \text{H}_2\text{O} \rightleftharpoons \text{HF} + \text{OH}^-$

We classify each salt by examining its cation and its anion, and then combining the result.

- NaBr (Where did it come from?)
  - Na$^+$ is the conjugate acid of NaOH, a strong base. It does not react with water, so it is neutral.
  - Br$^-$ is the conjugate base of HBr, a strong acid. It does not react with water, so is neutral.
  - The cation is neutral; the anion is neutral.
  - NaBr is neutral.

- NaC$_2$H$_3$O$_2$
  - Na$^+$ is the conjugate acid of NaOH, a strong base. It does not react with water, so it is neutral.
  - C$_2$H$_3$O$_2^-$ is the conjugate base of HC$_2$H$_3$O$_2^-$, a weak acid. It reacts with water to give a basic solution.
  - The cation is neutral; the anion is basic.
  - NaC$_2$H$_3$O$_2$ is basic.

- The conjugate acid of a strong base is very weak and does not react with water. It is therefore considered to be neutral.
  - Na$^+$ + H$_2$O $\rightarrow$ No Reaction (NR)

- The conjugate base of a strong acid is very weak and does not react with water. It is therefore considered to be neutral.
  - Cl$^- + \text{H}_2\text{O} \rightarrow$ NR

• NaC$_2$H$_3$O$_2$
• Na$^+$ is the conjugate acid of NaOH, a strong base. It does not react with water, so it is neutral.
• C$_2$H$_3$O$_2^-$ is the conjugate base of HC$_2$H$_3$O$_2^-$, a weak acid. It reacts with water to give a basic solution.
• The cation is neutral; the anion is basic.
• NaC$_2$H$_3$O$_2$ is basic.
• **NH₄Cl**
  - NH₄⁺ is the conjugate acid of NH₃, a weak base. It reacts with water to give an **acidic** solution.
  - Cl⁻ is the conjugate base of HCl, a strong acid. It does not react with water, so it is **neutral**.
  - The cation is acidic; the anion is neutral.
  - **NH₄Cl is acidic.**

• **NH₄F**
  - NH₄⁺ is the conjugate acid of NH₃, a weak base. It reacts with water to give an **acidic** solution.
  - F⁻ is the conjugate base of HF, a weak acid. It does not react with water, so it is **basic**.
  - The cation is acidic; the anion is basic. We need more information in this case. We compare \( K_a \) for HF to \( K_b \) for NH₃.

• If \( K_a > K_b \), the solution is acidic. If \( K_a < K_b \), the solution is basic. If \( K_a = K_b \), the solution is neutral.

  - For NH₄⁺: \( K_a = \frac{K_w}{K_b} = \frac{1.0 \times 10^{-14}}{1.8 \times 10^{-5}} = 5.6 \times 10^{-10} \)
  - For F⁻: \( K_b = \frac{K_w}{K_a} = \frac{1.0 \times 10^{-14}}{6.8 \times 10^{-11}} = 1.5 \times 10^{-11} \)

  - \( K_a \) for NH₄⁺ > \( K_b \) for F⁻

  - **NH₄F is acidic.**

• **Ammonium nitrate, NH₄NO₃**, is administered as an intravenous solution to patients whose blood pH has deviated from the normal value of 7.40.

• Would this substance be used for acidosis (blood pH < 7.40) or alkalosis (blood pH > 7.40)?

• NH₄⁺ is the conjugate acid of NH₃, a weak base. NH₄⁺ is acidic.

• NO₃⁻ is the conjugate base of HNO₃, a strong acid. NO₃⁻ is neutral.

• **NH₄NO₃ is acidic, so it could be used for alkalosis.**

• The hydrolysis equilibrium constant can be used in problems to determine the pH of a salt solution. To use the hydrolysis equilibrium, we need to compute the \( K \) value for it.
We can determine \( K \) for the reaction of the ion with water (hydrolysis reaction):

\[
\text{NH}_4^+ + \text{H}_2\text{O} \leftrightarrow \text{NH}_3 + \text{H}_3\text{O}^+
\]

is the sum of

\[
\text{NH}_4^+ + \text{OH}^- \leftrightarrow \text{NH}_3 + \text{H}_2\text{O}; \quad K_1 = 1/K_b
\]

\[
2\text{H}_2\text{O} \leftrightarrow \text{H}_3\text{O}^+ + \text{OH}^-; \quad K_2 = K_w
\]

Overall reaction

\[
\text{NH}_4^+ + \text{H}_2\text{O} \leftrightarrow \text{NH}_3 + \text{H}_3\text{O}^+
\]

\[
K_a = K_1 K_2 = \frac{K_a}{K_b}
\]

What is \( K_b \) for the \( \text{F}^- \) ion, the ion added to the public water supply to protect teeth?

For HF, \( K_a = 6.8 \times 10^{-4} \).

Overall reaction:

\[
\text{F}^- + \text{H}_2\text{O} \leftrightarrow \text{HF} + \text{OH}^-
\]

Is the sum of

\[
\text{H}_3\text{O}^+ + \text{F}^- \leftrightarrow \text{HF} + \text{H}_2\text{O}; \quad K_1 = 1/K_a
\]

\[
2\text{H}_2\text{O} \leftrightarrow \text{H}_3\text{O}^+ + \text{OH}^-; \quad K_2 = K_w
\]

Overall reaction:

\[
\text{F}^- + \text{H}_2\text{O} \leftrightarrow \text{HF} + \text{OH}^-
\]

\[
K_b = K_1 K_2 = \frac{K_a}{K_b} = \frac{1.0 \times 10^{-14}}{6.8 \times 10^{-10}} = 1.5 \times 10^{-11}
\]

Household bleach is a 5% solution of sodium hypochlorite, \( \text{NaClO} \). This corresponds to a molar concentration of about 0.70 M \( \text{NaClO} \).

What is the \([\text{OH}^-]\) and the pH of the solution?

For \( \text{HClO} \), \( K_a = 3.5 \times 10^{-8} \).

We are told that \( K_a = 3.5 \times 10^{-8} \). That means that \( K_b = 2.9 \times 10^{-7} \).

This allows us to substitute into the \( K_b \) expression to solve for \( x \).

\[
\frac{0.70 - x}{x} = \frac{2.9 \times 10^{-7}}{2.9 \times 10^{-7}}\times 0.70
\]

\[
x = 0.70 - 0.45
\]

\[x = 0.25\]

\[
\text{For F}^-, K_b = 1.5 \times 10^{-11}
\]
• The question asks for $[\text{OH}^-]$ and the pH:

$$[\text{OH}^-] = x = 4.5 \times 10^{-4} \text{ M}$$

$$\text{pH} = 14.00 = \text{pOH} = 14.00 - \log [\text{OH}^-]$$

$$\text{pH} = 14.00 - \log (4.5 \times 10^{-4})$$

$$\text{pH} = 14.00 - 3.35$$

$$\text{pH} = 10.65$$

---

The pH of a Salt Solution

• For a solution of a salt in which only one ion hydrolyzes, the calculation of equilibrium composition follows that of weak acids and bases.

  - The only difference is first obtaining the $K_a$ or $K_b$ for the ion that hydrolyzes.

  - The next example illustrates the reasoning and calculations involved.

---

A Problem To Consider

• What is the pH of a 0.10 M NaCN solution at 25 °C? The $K_a$ for HCN is $4.9 \times 10^{-10}$.

  - Only the CN⁻ ion hydrolyzes.

  - The CN⁻ ion is acting as a base, so first, we must calculate the $K_b$ for CN⁻.

$$K_b = \frac{K_w}{K_a} = \frac{1.0 \times 10^{-14}}{4.9 \times 10^{-10}} = 2.0 \times 10^{-5}$$
Now we can proceed with the equilibrium calculation.

Let \( x = [\text{OH}^-] = [\text{HCN}] \), then substitute into the equilibrium expression.

\[
\frac{[\text{HCN}][\text{OH}^-]}{[\text{CN}^-]} = K_b
\]

\[
\frac{x^2}{(0.10 - x)} = 2.0 \times 10^{-5}
\]

Solving the equation, you find that

\[
x = [\text{OH}^-] = 1.4 \times 10^{-3}
\]

Hence,

\[
pH = 14.00 - p\text{OH} = 14.00 + \log(1.4 \times 10^{-3}) = 11.2
\]

As expected, the solution has a pH greater than 7.0.

**Common-Ion Effect**

The common-ion effect is the shift in an ionic equilibrium caused by the addition of a solute that takes part in the equilibrium.

**Buffers**

A buffer solution is characterized by the ability to resist changes in pH when limited amounts of acid or base are added to it.

A buffer is made by combining a weak acid with its conjugate base or a weak base with its conjugate acid.

The Common Ion Effect

- The common-ion effect is the shift in an ionic equilibrium caused by the addition of a solute that provides an ion common to the equilibrium.

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

- Consider a solution of acetic acid (\(\text{HC}_2\text{H}_3\text{O}_2\)), in which you have the following equilibrium.
- If we were to add \(\text{NaC}_2\text{H}_3\text{O}_2\) to this solution, it would provide \(\text{C}_2\text{H}_3\text{O}_2^-\) ions which are present on the right side of the equilibrium.

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

- The equilibrium composition would shift to the left and the degree of ionization of the acetic acid is decreased.
- This repression of the ionization of acetic acid by sodium acetate is an example of the common-ion effect.
A Problem To Consider

- An aqueous solution is 0.025 M in formic acid, HCHO, and 0.018 M in sodium formate, NaCHO. What is the pH of the solution. The Ka for formic acid is $1.7 \times 10^{-4}$.

  - Consider the equilibrium below.

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

  | Starting | 0.025 | 0.018 |
  | Change   | -x    | +x    |
  | Equilibrium | 0.025-x | x | 0.018+x |

  - The equilibrium constant expression is:

  $$\frac{[\text{H}_2\text{O}^+][\text{CHO}^-]}{[\text{HCHO}]} = K_a$$

  - Substituting into this equation gives:

  $$x(0.018 + x) = 1.7 \times 10^{-4}$$

  - Assume that x is small compared with 0.018 and 0.025. Then

  $$(0.018 + x) \approx 0.018$$

  $$(0.025 - x) \approx 0.025$$

  - The equilibrium equation becomes

  $$x(0.018) \approx 1.7 \times 10^{-4}$$

  - Hence,

  $$x \approx (1.7 \times 10^{-4}) \times \frac{0.025}{0.018} = 2.4 \times 10^{-4}$$

  - Note that x was much smaller than 0.018 or 0.025.

  $\text{pH} = -\log(2.4 \times 10^{-4}) = 3.63$

  - For comparison, the pH of 0.025 M formic acid is 2.69.

  Do Exercise 17.9,10,11

Buffers

- A buffer is a solution characterized by the ability to resist changes in pH when limited amounts of acid or base are added to it.

  - Buffers contain either a weak acid and its conjugate base or a weak base and its conjugate acid.

  - Thus, a buffer contains both an acid species and a base species in equilibrium.
Buffer capacity depends on the **amount** of acid and conjugate base present in the solution.

The next example illustrates how to calculate the pH of a buffer.

- **How do you prepare a buffer of given pH?**
  - A buffer must be prepared from a conjugate acid-base pair in which the $K_a$ of the acid is approximately equal to the desired $H_3O^+$ concentration.
  - To illustrate, consider a buffer of a weak acid $HA$ and its conjugate base $A^-$. The acid ionization equilibrium is:

$$HA(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + A^-(aq)$$

- Taking the negative logarithm of both sides of the equation we obtain:

$$-\log[H_3O^+] = -\log(K_a) - \log\left[\frac{HA}{A^-}\right]$$

- The previous equation can be rewritten

$$pH = pK_a + \log\left[\frac{A^-}{HA}\right]$$

Henderson-Hasselbalch Equation

- **How do you prepare a buffer of given pH?**
  - More generally, you can write

$$pH = pK_a + \log\left[\frac{[\text{base}]}{[\text{acid}]}\right]$$

- This equation relates the pH of a buffer to the concentrations of the conjugate acid and base. It is known as the **Henderson-Hasselbalch equation**.

The problem involves dilution first. Once we know the concentrations of benzoic acid and benzoate ion, we can use the acid equilibrium to solve for $x$.

We will use HBz to represent benzoic acid and Bz$^-$ to represent benzoate ion.
The Henderson-Hassellbalch Equation

• How do you prepare a buffer of given pH?
  
  – So to prepare a buffer of a given pH (for example, pH 4.90) we need a conjugate acid-base pair with a $pK_a$ close to the desired pH.
  
  – The $K_a$ for acetic acid is $1.7 \times 10^{-5}$, and its $pK_a$ is 4.77.
  
  – You could get a buffer of pH 4.90 by increasing the ratio of [base]/[acid].

Instructions for making a buffer say to mix 60 mL of 0.100 M NH$_3$ with 40 mL of 0.100 M NH$_4$Cl. What is the pH of the solution?

**Example 16.11**

\[
\begin{align*}
\text{NH}_3(aq) & \rightleftharpoons \text{NH}_4^+(aq) + \text{OH}^-(aq) \\
\end{align*}
\]

1. How many moles of NH$_3$ and NH$_4^+$ are added?

2. Fill in the concentration table.

\[
\begin{align*}
\text{Start} & \\
\text{Change} & \\
\text{Equilibrium} & \\
\end{align*}
\]

3. Substitute in to equilibrium constant equation.

\[
\begin{align*}
\text{NH}_3(aq) + \text{H}_2\text{O}(l) & \rightleftharpoons \text{NH}_4^+(aq) + \text{OH}^-(aq) \\
\end{align*}
\]

4. Solve the equation (assume $x$ is small compared with the molar concentrations).

\[
\begin{align*}
\text{pH} = 9.43 \\
\end{align*}
\]

Do Exercise 16.12

See problems 16.75-76
Acid-Ionization Titration Curves

• An \textbf{acid-base titration curve} is a plot of the pH of a solution of acid (or base) against the volume of added base (or acid).

  – Such curves are used to gain insight into the titration process.

  – You can use titration curves to choose an \textbf{appropriate indicator} that will show when the titration is complete.

\textbf{Titrination of a Strong Acid by a Strong Base}

• Figure 16.12 shows a curve for the titration of HCl with NaOH.

  – At the equivalence point, the pH of the solution is 7.0 because it contains a \textbf{salt, NaCl, that does not hydrolyze}.

  – However, the pH changes rapidly from a pH of about 3 to a pH of about 11.

  – To detect the equivalence point, you need an \textbf{acid-base indicator} that changes color within the pH range 3-11.

  – Phenolphthalein can be used because it changes color in the pH range 8.2-10. (see Figure 15.10)

\textbf{A Problem To Consider}

• Calculate the pH of a solution in which 10.0 mL of 0.100 M NaOH is added to 25.0 mL of 0.100 M HCl.

  – Because the reactants are a strong acid and a strong base, the reaction is essentially complete.

  \begin{align*}
  \text{H}_3\text{O}^+ (\text{aq}) + \text{OH}^- (\text{aq}) & \rightarrow \text{H}_2\text{O}(\ell) + \text{H}_3\text{O}^+(\ell) \\
  \end{align*}

  – We get the amounts of reactants by multiplying the volume of each (in liters) by their respective molarities.
\[
\text{Mol H}_3\text{O}^+ = 0.0250\text{L} \times 0.100\text{mol/L} = 0.00250\text{ mol}
\]
\[
\text{Mol OH}^- = 0.0100\text{L} \times 0.100\text{mol/L} = 0.00100\text{ mol}
\]
- All of the OH\(^-\) reacts, leaving an excess of H\(_3\)O\(^+\)

\[
\text{Excess H}_3\text{O}^+ = (0.00250 - 0.00100)\text{mol}
\]
\[
= 0.00150\text{ mol H}_3\text{O}^+
\]
- You obtain the H\(_3\)O\(^+\) concentration by dividing the mol H\(_3\)O\(^+\) by the total volume of solution (=0.0250 L + 0.0100 L=0.0350 L)

\[
[H_3O^+] = \frac{0.00150}{0.0350} \text{ mol} = 0.0429\text{ M}
\]

- Calculate the pH of a solution in which 10.0 mL of 0.100 M NaOH is added to 25.0 mL of 0.100 M HCl.
- Hence,

\[
\text{pH} = -\log(0.0429) = 1.368
\]

---

Figure 17.13: Curve for the titration of a weak acid by a strong base.

A Problem To Consider

- Calculate the pH of the solution at the equivalence point when 25.0 mL of 0.10 M acetic acid is titrated with 0.10 M sodium hydroxide. The \(K_a\) for acetic acid is \(1.7 \times 10^{-5}\).
- At the equivalence point, equal molar amounts of acetic acid and sodium hydroxide react to give sodium acetate.
- First, calculate the concentration of the acetate ion.
- In this case, 25.0 mL of 0.10 M NaOH is needed to react with 25.0 mL of 0.10 M acetic acid.

- The molar amount of acetate ion formed equals the initial molar amount of acetic acid.

\[
25\times10^{-3}\text{ L soln} \times \frac{0.10\text{ mol acetic ion}}{1\text{ L soln}} = 2.5\times10^{-3}\text{ mol acetate ion}
\]
- The total volume of the solution is 50.0 mL. Hence,

\[
\text{Molar concentration} = \frac{2.5\times10^{-3}\text{ mol}}{50\times10^{-3}\text{ L}} = 0.050\text{ M}
\]
- The hydrolysis of the acetate ion follows the method given in an earlier section of this chapter.
- You find the \(K_b\) for the acetate ion to be \(5.9 \times 10^{-10}\) and that the concentration of the hydroxide ion is \(5.4 \times 10^{-6}\). The pH is 8.73

---

Titration of a Weak Acid by a Strong Base

- The titration of a weak acid by a strong base gives a somewhat different curve.
- The pH range of these titrations is shorter.
- The equivalence point will be on the basic side since the salt produced contains the anion of a weak acid.
- Figure 17.13 shows the curve for the titration of nicotinic acid with NaOH.

---
The titration of a weak base with a strong acid is a reflection of our previous example.

– Figure 17.14 shows the titration of NH₃ with HCl.
– In this case, the pH declines slowly at first, then falls abruptly from about pH 7 to pH 3.
– Methyl red, which changes color from yellow at pH 6 to red at pH 4.8, is a possible indicator.

What would the titration of a weak acid with a weak base appear?

What would the titration of a weak base with a weak acid appear?

Look at examples 16.13 and 14
Do exercises 16.13, 14, 15, and 16
Look at problems 16.85-92

Operational Skills

• Determining $K_a$ (or $K_b$) from the solution pH
• Calculating the concentration of a species in a weak acid solution using $K_a$
• Calculating the concentration of a species in a weak base solution using $K_b$
• Predicting whether a salt solution is acidic, basic, or neutral
• Obtaining $K_a$ from $K_b$ or $K_b$ from $K_a$
• Calculating concentrations of species in a salt solution

Figure 16.14: Curve for the titration of a weak base by a strong acid.

Operational Skills

• Calculating the common-ion effect on acid ionization
• Calculating the pH of a buffer from given volumes of solution
• Calculating the pH of a solution of a strong acid and a strong base
• Calculating the pH at the equivalence point in the titration of a weak acid with a strong base

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