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
   – 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
   – 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.
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.

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.

\[
HA(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + A^-(aq)
\]
• Acetic acid is a weak acid. It reacts with water as follows:
  \[
  \text{HC}_2\text{H}_3\text{O}_2(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{H}_3\text{O}^+(\text{aq}) + \text{C}_2\text{H}_5\text{O}_2^-(\text{aq})
  \]

• The equilibrium constant for the reaction of a weak acid with water is called the **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. **WHY?**

**Acid-Ionization Equilibria**

• **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.

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

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

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

  - Consider the generic monoprotic acid, 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.

<table>
<thead>
<tr>
<th>Substance</th>
<th>Formula</th>
<th>( K_a )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetic acid</td>
<td>CH₃CO₂H</td>
<td>1.7 × 10⁻⁵</td>
</tr>
<tr>
<td>Benzoic acid</td>
<td>C₆H₅CO₂H</td>
<td>6.3 × 10⁻⁵</td>
</tr>
<tr>
<td>Formic acid</td>
<td>HCO₂H</td>
<td>5.9 × 10⁻⁴</td>
</tr>
<tr>
<td>Carbamic acid</td>
<td>H₂CO₃</td>
<td>4.3 × 10⁻⁷</td>
</tr>
<tr>
<td>Cyanic acid</td>
<td>HOCN</td>
<td>4.8 × 10⁻⁷</td>
</tr>
<tr>
<td>Formic acid</td>
<td>HCO₂H</td>
<td>3.5 × 10⁻⁵</td>
</tr>
<tr>
<td>Formic acid</td>
<td>HCO₂H</td>
<td>1.7 × 10⁻⁵</td>
</tr>
<tr>
<td>Hydrosulfonic acid</td>
<td>H₂S</td>
<td>4.9 × 10⁻¹⁰</td>
</tr>
<tr>
<td>Nitric acid</td>
<td>HNO₃</td>
<td>6.8 × 10⁻⁵</td>
</tr>
<tr>
<td>Hydrogen sulfide</td>
<td>H₂S</td>
<td>1.1 × 10⁻⁹</td>
</tr>
<tr>
<td>Nitric acid</td>
<td>HNO₃</td>
<td>8.9 × 10⁻⁵</td>
</tr>
<tr>
<td>Hypochlorous acid</td>
<td>HClO</td>
<td>1.2 × 10⁻³¹</td>
</tr>
<tr>
<td>Nitric acid</td>
<td>HNO₂</td>
<td>3.5 × 10⁻⁵</td>
</tr>
<tr>
<td>Acetic acid</td>
<td>CH₃CO₂H</td>
<td>4.5 × 10⁻⁵</td>
</tr>
<tr>
<td>Oxalic acid</td>
<td>H₂C₂O₄</td>
<td>5.6 × 10⁻⁵</td>
</tr>
<tr>
<td>Oxalic acid</td>
<td>H₂C₂O₄</td>
<td>5.1 × 10⁻⁵</td>
</tr>
</tbody>
</table>
In order of decreasing $K_a$:

<table>
<thead>
<tr>
<th></th>
<th>$K_a$</th>
<th>Highest pH</th>
<th>Lowest pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>HF</td>
<td>$6.8 \times 10^{-4}$</td>
<td>HCN</td>
<td></td>
</tr>
<tr>
<td>HNO$_2$</td>
<td>$4.5 \times 10^{-4}$</td>
<td>HC$_2$H$_3$O$_2$</td>
<td></td>
</tr>
<tr>
<td>HC$_2$H$_3$O$_2$</td>
<td>$1.7 \times 10^{-5}$</td>
<td>HNO$_2$</td>
<td></td>
</tr>
<tr>
<td>HCN</td>
<td>$4.9 \times 10^{-10}$</td>
<td>HF</td>
<td></td>
</tr>
</tbody>
</table>

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.
We can be given pH, percent or degree ionization, initial concentration, and $K_a$.

From pH, we can find $[H_3O^+]$.

From percent or degree ionization, we can find $K_a$.

Using what is given, we can find the other quantities.

A Problem To Consider

• Nicotinic acid is a weak monoprotic acid with the formula $HC_6H_4NO_2$. 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.

\[
HNic(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + Nic^-(aq)
\]

<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:

\[
K_a = \frac{[H_3O^+][Nic^-]}{[HNic]}
\]

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.

\[
x = [H_3O^+] = \text{antilog}(-pH)
\]

\[
x = \text{antilog}(−3.39)
\]

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

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

Note first, however, that

\[
(0.012 − x) = (0.012 − 0.00041) = 0.01159 ≈ 0.012
\]

the concentration of unionized acid remains virtually unchanged.

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

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

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%.

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?
\[
\begin{array}{c|c|c|c}
\text{HC}_6\text{H}_5\text{O}(aq) + \text{H}_2\text{O}(l) & \text{H}_3\text{O}^+(aq) + \text{C}_6\text{H}_5\text{O}^-(aq) \\
\hline
\text{Initial} & 0.10 & 0 & 0 \\
\text{Change} & -x & +x & +x \\
\text{Equilibrium} & 0.10 - x & x & x \\
\end{array}
\]

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

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

- Finally, we write the expression for \(K_a\) and substitute the concentrations we now know.
  - \(\text{HC}_6\text{H}_5\text{O} + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{C}_6\text{H}_5\text{O}^-\)
  - \([\text{H}_3\text{O}^+] = [\text{C}_6\text{H}_5\text{O}^-] = 3.7 \times 10^{-6} \text{ M} \)
  - \([\text{HC}_6\text{H}_5\text{O}] = 0.10 \text{ M} \)
  - \(K_a = \frac{[\text{H}_3\text{O}^+][\text{C}_6\text{H}_5\text{O}^-]}{[\text{HC}_6\text{H}_5\text{O}]} = \frac{(3.7 \times 10^{-6})^2}{0.10} \)
  
  \[K_a = 1.4 \times 10^{-10}\]

- The degree of ionization is the ratio of ionized concentration to original concentration:
  
  \[
  \text{Degree of ionization} = \frac{x}{0.10} = \frac{3.7 \times 10^{-6}}{0.10} \]

  \[\text{Degree of ionization} = 3.7 \times 10^{-5}\]

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

  \[\text{Percent ionization} = 3.7 \times 10^{-5}\% \text{ or } 0.0037\%\]
**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 $[\text{HA}]$:
  
  $$(\text{[HA]}_0 - x) = \text{[HA]}_0$$

- 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.

---

**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 $2.6 \times 10^{-5}$.**

We will use the generic formula HA for para-hydroxybenzoic acid and the following equilibrium:

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

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

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

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

$$\frac{0.200}{2.6 \times 10^{-5}} > 1000, \text{ so } 0.200 - x \approx 0.200$$
\[ K_a = \frac{x^2}{0.200} \]

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

\[ x = 2.3 \times 10^{-3} \quad M = [H_3O^+] \]

\[ pH = -\log[H_3O^+] = -pH(2.3 \times 10^{-3}) \]

\[ pH = 2.64 \]

Calculations With \( K_a \)

- Once you know the value of \( K_a \), you can calculate the equilibrium concentrations of species \( HA \), \( A^- \), and \( H_3O^+ \) for solutions of different molarities.

- 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).
Calculations With $K_a$

- **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,

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

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

- 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), $\text{HC}_9\text{H}_7\text{O}_4$, a common headache remedy.
  - The molar mass of $\text{HC}_9\text{H}_7\text{O}_4$ 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 mol/0.500 L = **0.0036 M** (Retain two significant figures, the same number of significant figures in $K_a$).
Note that

\[
\frac{C_n}{K_a} = \frac{0.0036}{3.3 \times 10^{-4}} = 11
\]

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

Abbreviate the formula for acetylsalicylic acid as \( \text{HAc}_s \) and let \( x \) be the amount of \( \text{H}_3\text{O}^+ \) 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.

\[
\begin{array}{c|c|c|c|c}
\text{Starting} & 0.0036 & 0 & 0 \\
\text{Change} & -x & +x & +x \\
\text{Equilibrium} & 0.0036-x & x & x \\
\end{array}
\]

The equilibrium constant expression is

\[
\frac{[\text{H}_3\text{O}^+][\text{Ac}^-]}{[\text{HAc}_s]} = K_a
\]

If we substitute the equilibrium concentrations and the \( K_a \) into the equilibrium constant expression, we get

\[
\frac{[\text{H}_3\text{O}^+][\text{Ac}^-]}{[\text{HAc}_s]} = K_a
\]

\[
\frac{x^2}{(0.0036-x)} = 3.3 \times 10^{-4}
\]

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.

\[ x = \frac{-(3.3 \times 10^{-4}) \pm \sqrt{(3.3 \times 10^{-4})^2 - 4(1.2 \times 10^{-7})}}{2} \]

– The lower sign in ± gives a negative root which we can ignore
– Taking the upper sign, we get

\[ x = [\text{H}_3\text{O}^+] = 9.4 \times 10^{-4} \]

– Now we can calculate the pH.

\[ \text{pH} = -\log(9.4 \times 10^{-4}) = 3.03 \]

Check your answer by substituting the hydrogen ion concentration into the equilibrium expression and calculate Ka

• **Polyprotic Acids**
  - A polyprotic acid has more than one acidic proton—for example, H\textsubscript{2}SO\textsubscript{4}, H\textsubscript{2}SO\textsubscript{3}, H\textsubscript{2}CO\textsubscript{3}, H\textsubscript{3}PO\textsubscript{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.
    \[
    \text{H}_2\text{SO}_4\text{(aq)} + \text{H}_2\text{O}\text{(l)} \rightarrow \text{H}_3\text{O}^+\text{(aq)} + \text{HSO}_4^-\text{(aq)}
    \]
    \[
    \text{HSO}_4^-\text{(aq)} + \text{H}_2\text{O}\text{(l)} \rightleftharpoons \text{H}_3\text{O}^+\text{(aq)} + \text{SO}_4^{2-}\text{(aq)}
    \]
  - 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$_2$CO$_3$, two simultaneous equilibria must be considered.
  \[
  \text{H}_2\text{CO}_3\text{(aq)} + \text{H}_2\text{O}\text{(l)} \rightleftharpoons \text{H}_3\text{O}^+\text{(aq)} + \text{HCO}_3^-\text{(aq)}
  \]
  \[
  \text{HCO}_3^-\text{(aq)} + \text{H}_2\text{O}\text{(l)} \rightleftharpoons \text{H}_3\text{O}^+\text{(aq)} + \text{CO}_3^{2-}\text{(aq)}
  \]
  - Each equilibrium has an associated acid-ionization constant.
    - For the loss of the **first** proton
      \[
      K_{a1} = \frac{[\text{H}_3\text{O}^+][\text{HCO}_3^-]}{[\text{H}_2\text{CO}_3]} = 4.3 \times 10^{-7}
      \]
    - For the loss of the **second** proton
      \[
      K_{a2} = \frac{[\text{H}_3\text{O}^+][\text{CO}_3^{2-}]}{[\text{HCO}_3^-]} = 4.8 \times 10^{-11}
      \]
  - 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$_3$PO$_4$, 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, \( \text{H}_2\text{C}_6\text{H}_6\text{O}_6 \). What is the pH of a 0.10 M solution? What is the concentration of the ascorbate ion, \( \text{C}_6\text{H}_6\text{O}_6^{2-} \)?

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 \( \text{H}_2\text{Asc} \), then the first ionization is:

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

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

<table>
<thead>
<tr>
<th>Starting</th>
<th>Change</th>
<th>Equilibrium</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.10</td>
<td>-x</td>
<td>0.10-x</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>0</th>
<th>0</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>+x</td>
<td>+x</td>
</tr>
<tr>
<td></td>
<td>x</td>
<td>X</td>
</tr>
</tbody>
</table>

The equilibrium constant expression is

\[
\frac{[\text{H}_3\text{O}^+][\text{HAsc}^-]}{[\text{H}_2\text{Asc}]} = K_{a1}
\]
Substituting into the equilibrium expression
\[
x^2 = 7.9 \times 10^{-5}
\]
\[
(0.10 - x)
\]
Assuming that \( x \) is much smaller than 0.10, you get
\[
x^2 \approx (7.9 \times 10^{-5}) \times (0.10)
\]
\[
x \approx 2.8 \times 10^{-3} = 0.0028
\]
The hydronium ion concentration is 0.0028 M, so
\[
pH = -\log(0.0028) = 2.55
\]

The ascorbate ion, \( \text{Asc}^2- \), which we will call \( y \), is produced only in the second ionization of \( \text{H}_2\text{Asc} \).

\[
\text{HAsc}^- (aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{H}_3\text{O}^+ (aq) + \text{Asc}^2- (aq)
\]

Assume the starting concentrations for \( \text{HAsc}^- \) and \( \text{H}_3\text{O}^+ \) to be those from the first equilibrium.

| Starting \( \text{HAsc}^- \) | 0.0028 | \( y = 0 \) |
| Change \(-y\) | +y | +y |
| Equilibrium \( \text{HAsc}^- \) | 0.0028-y | y |

The equilibrium constant expression is
\[
\frac{[\text{H}_3\text{O}^+][\text{Asc}^2-]}{[\text{HAsc}^-]} = K_{a2}
\]
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,

\[ y \equiv [\text{Asc}^{2-}] = 1.6 \times 10^{-12} \]

- 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 \([\text{C}_4\text{H}_4\text{O}_6^{2-}]\).

<table>
<thead>
<tr>
<th>( \text{H}_2\text{A}(\text{aq}) )</th>
<th>( \text{H}_2\text{O}(l) )</th>
<th>( \text{H}_3\text{O}^-(\text{aq}) + )</th>
<th>( \text{HA}^- (\text{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>

\[ K_{a1} = \frac{[\text{H}_3\text{O}^-][\text{HA}^-]}{[\text{H}_2\text{A}]} \]

\[ 9.2 \times 10^{-4} = \frac{x^2}{0.10 \ - \ x} \]

\[ \frac{0.10}{9.2 \times 10^{-4}} < 100 \]

We cannot use the simplifying assumption.
\[
9.2 \times 10^{-4}(0.10 - x) = x^2 \\
9.2 \times 10^{-5} - 9.2 \times 10^{-4}x = x^2 \\
x^2 + 9.2 \times 10^{-4}x - 9.2 \times 10^{-5} = 0
\]

\[
a = 1 \\
b = 9.2 \times 10^{-4} \\
c = -9.2 \times 10^{-5}
\]

\[
x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}
\]

\[
x = \frac{-(9.2 \times 10^{-4}) \pm \sqrt{(9.2 \times 10^{-4})^2 - 4(1)(-9.2 \times 10^{-5})}}{2(1)}
\]

\[
x = \frac{-(9.2 \times 10^{-4}) \pm (1.92 \times 10^{-3})}{2} = -4.6 \times 10^{-4} \pm 9.6 \times 10^{-3}
\]

\[x = 9.1 \times 10^{-3}\] and \[x = -1.0 \times 10^{-2}\]

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

\([H_3O^+] = 9.1 \times 10^{-3} \, M \] \[\quad [H_2A] = 9.0 \times 10^{-4} \, M\]

\([HA^-] = 9.1 \times 10^{-3} \, M\]

Now we use these for the second acid ionization equilibrium.

<table>
<thead>
<tr>
<th>HA (aq)</th>
<th>H₂O(l) ➔</th>
<th>H₃O⁺(aq) +</th>
<th>A²⁻(aq)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial</td>
<td>0.0091</td>
<td>0.0091</td>
<td>0</td>
</tr>
<tr>
<td>Change</td>
<td>−x</td>
<td>+x</td>
<td>+x</td>
</tr>
<tr>
<td>Equilibrium</td>
<td>0.0091 − x</td>
<td>0.0091 + x</td>
<td>x</td>
</tr>
</tbody>
</table>

\[K_{a2} = \frac{[H_2O^+][A^{2-}]}{[HA^-]} \]

\[4.3 \times 10^{-5} = \frac{(0.0091 + x)x}{(0.0091 - x)}\]

We can assume that
\[0.0091 + x = 0.0091\] and \[0.0091 - x = 0.0091\]
Base-Ionization Equilibria

- Equilibria involving weak bases are treated similarly to those for weak acids.
  - Ammonia, for example, ionizes in water as follows.

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

- The corresponding equilibrium constant is:

\[
K_e = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3][\text{H}_2\text{O}]}
\]

- The concentration of water is nearly constant.

\[
K_b = [\text{H}_2\text{O}]K_e = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]}
\]

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

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

has a base ionization constant equal to

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

Table 17.2 lists ionization constants for some weak bases.
• 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:
    \[ \text{NH}_3 + \text{H}_2\text{O} \rightarrow \text{NH}_4^+ + \text{OH}^- \]
  
  • Ethylamine becomes ethyl ammonium ion:
    \[ \text{C}_2\text{H}_5\text{NH}_2 + \text{H}_2\text{O} \rightarrow \text{C}_2\text{H}_5\text{NH}_3^+ + \text{OH}^- \]

  • Dimethylamine becomes dimethylammonium ion:
    \[ (\text{CH}_3)_2\text{NH}_2 + \text{H}_2\text{O} \rightarrow (\text{CH}_3)_2\text{NH}_3^+ + \text{OH}^- \]

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

  • 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 $(\text{[B]}_0 - x) = [\text{B}]_0$.

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Figure 16.12: Curve for the titration 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 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 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)

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.

\[
\text{H}_3\text{O}^+ (\text{aq}) + \text{OH}^- (\text{aq}) \rightarrow \text{H}_2\text{O}(1) + \text{H}_2\text{O}(1)
\]

- We get the amounts of reactants by multiplying the volume of each (in liters) by their respective molarities.

\[
\begin{align*}
\text{Mol H}_3\text{O}^+ &= 0.0250\text{L} \times 0.100\text{ mol/L} = 0.00250\text{ mol} \\
\text{Mol OH}^- &= 0.0100\text{L} \times 0.100\text{ mol/L} = 0.00100\text{ mol}
\end{align*}
\]

- All of the OH\(^-\) reacts, leaving an excess of H\(_3\)O\(^+\)

Excess H\(_3\)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)

\[
[\text{H}_3\text{O}^+] = \frac{0.00150\text{ mol}}{0.0350\text{ L}} = 0.0429\text{ M}
\]
• 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,

\[
pH = -\log(0.0429) = 1.368
\]

---

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.

---

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.

$$25 \times 10^{-3} \text{ L soln} \times \frac{0.10 \text{ mol acetate ion}}{1 \text{ L soln}} = 2.5 \times 10^{-3} \text{ mol acetate ion}$$

- The total volume of the solution is 50.0 mL. Hence,

$$\text{molar concentration} = \frac{2.5 \times 10^{-3} \text{ mol}}{50 \times 10^{-3} \text{ L}} = 0.050 \text{ M}$$

- 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 Strong Acid by a Weak Base

- The titration of a weak base with a strong acid is a reflection of our previous example.
  - Figure 17.14 shows the titration of $\text{NH}_3$ 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?

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

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
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