ACIDS and BASES

Models of Acids and Bases

- **Arrhenius Concept**: Acids produce H\(^+\) in solution, bases produce OH\(^-\) ion.
- **Brounsted-Lowry**: Acids are H\(^+\) donors, bases are proton acceptors.
- Review Chapter 4 – Acids & Bases, Section 4.8

\[ \text{HCl} + \text{H}_2\text{O} \rightarrow \text{Cl}^- + \text{H}_3\text{O}^+ \]

The reaction of an acid HA with water to form H\(_3\)O\(^+\) and a conjugate base A\(^-\).

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

Conjugate Acid/Base Pairs

- **HA(aq) + H\(_2\)O(l) ↔ H\(_3\)O\(^+\)(aq) + A\(^-\)(aq)**
- conjugate base: everything that remains of the acid molecule after a proton is lost.
- conjugate acid: formed when the proton is transferred to the base.

Acid Dissociation Constant \( (K_a) \)

- **HA(aq) + H\(_2\)O(l) ↔ H\(_3\)O\(^+\)(aq) + A\(^-\)(aq)**

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

Representation of the reaction H\(_3\)O\(^+\) + NH\(_3\).
Concept Check 16.1

Chemists in the seventeenth century discovered that the substance that gives red ants their irritating bite is an acid with the formula HCHO₃. They called this substance formic acid after the ant, whose Latin name is formica rufas. Formic acid has the following structural formula and molecular model:

\[
\begin{array}{c}
\text{O} \\
- \text{C} \text{–} \text{O} \quad \text{H}
\end{array}
\]

Write the acid-base equilibria connecting all components in the aqueous solution. Now list all of the species present.

\[
\text{HCOOH} \quad \text{+} \quad \text{H}_2\text{O} \quad \text{⇌} \quad \text{HCOO}^- \quad \text{+} \quad \text{H}_3\text{O}^+
\]

formic acid \hspace{1cm} \text{water} \hspace{1cm} \text{formate ion} \hspace{1cm} \text{hydronium ion}

Acid Strength

Strong Acid:

\(\text{HNO}_3\)

- Its equilibrium position lies far to the right.
- Yields a weak conjugate base. (NO\(_3^–\))

\[
\text{HNO}_3 (aq) + \text{H}_2\text{O} (l) \rightarrow \text{H}_3\text{O}^+ (aq) + \text{NO}_3^– (aq)
\]

\(K_a >> 1\) We do not usually consider the reactants in reactions because the are present in very small amounts!

Weak Acid:

\(\text{CH}_3\text{COOH}\)

- Its equilibrium lies far to the left.
- Yields a much stronger (it is relatively strong) conjugate base than water. (CH\(_3\text{COO}^–\))

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

\(K_a << 1\) Equilibrium favors reactants – but the solution is still acidic – so acetic acid IS an acid!

Weak & Strong Acids: (a) A strong acid HA is completely ionized in water. (b) A weak acid HB exists mostly as undissociated HB molecules in water. Note that the water molecules are not shown in this figure.
Figure 14.4: Graphic representation of the behavior of acids of different strengths in aqueous solution. (a) A strong acid. (b) A weak acid.

Figure 14.5: The relationship of acid strength and conjugate base strength for the reaction

In general, the strength of a weak acid is inversely related to the strength of its conjugate base.

Bases

• “Strong” and “weak” are used in the same sense for bases as for acids.

• Strong = complete dissociation (hydroxide ion supplied to solution)

  \[ \text{NaOH} (s) \rightarrow \text{Na}^+ (aq) + \text{OH}^- (aq) \]

  \[ K_b \gg 1 \]

• Weak = very little dissociation (or reaction with water)

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

  \[ K_b << 1 \]

Kₐ = [OH⁻][BH⁺]/[B]
Acetate ion! Acetic Acid: \( K_a = 1.8 \times 10^{-5} \) Formic Acid: \( K_a = 1.8 \times 10^{-4} \) Acetate ion: \( K_b = 5 \times 10^{-10} \) Formate ion: \( K_b = 5 \times 10^{-11} \)

**Self-ionization of Water**

- These ions are produced in equal numbers in pure water, so if we let \( x = [H^+] = [OH^-] \)

\[
1.0 \times 10^{-14} = (x)(x) \quad \text{at 25 } ^\circ \text{C}
\]

\[
x = \sqrt{1.0 \times 10^{-14}} = 1.0 \times 10^{-7}
\]

- Thus, the concentrations of \( H^+ \) and \( OH^- \) in pure water are both \( 1.0 \times 10^{-7} \) M.
- If you add acid or base to water they are no longer equal but the \( K_w \) expression still holds.

**Solutions of Strong Acid or Base**

- As an example, calculate the concentration of \( OH^- \) ion in 0.10 M HCl. Because you started with 0.10 M HCl (a strong acid) the reaction will produce 0.10 M H\(^+\)(aq).

\[
\text{HCl(aq)} \rightarrow \text{H}^+ \text{(aq)} + \text{Cl}^- \text{(aq)}
\]

- Substituting \([H^+]=0.10\) into the ion-product expression, we get:

\[
1.0 \times 10^{-14} = (0.10)[OH^-]
\]
Solutions of Strong Acid or Base

- As an example, calculate the concentration of OH⁻ ion in 0.10 M HCl. Because you started with 0.10 M HCl (a strong acid) the reaction will produce 0.10 M H⁺(aq).

  \[ \text{HCl(aq)} \rightarrow \text{H}^+(aq) + \text{Cl}^-(aq) \]

- Substituting [H⁺]=0.10 into the ion-product expression, we get:

  \[ [\text{OH}^-] = \frac{1.0 \times 10^{-14}}{0.10} = 1.0 \times 10^{-13} M \]

- Similarly, in a solution of a strong base you can normally ignore the self-ionization of water as a source of OH⁻(aq).

Solutions of Strong Acid or Base

- As an example, calculate the concentration of H⁺ ion in 0.010 M NaOH. Because you started with 0.010 M NaOH (a strong base) the reaction will produce 0.010 M OH⁻(aq).

  \[ \text{NaOH(s)} \rightarrow \text{Na}^+(aq) + \text{OH}^- (aq) \]

- Substituting [OH⁻]=0.010 into the ion-product expression, we get:

  \[ [\text{H}^+] = \frac{1.0 \times 10^{-14}}{0.010} = 1.0 \times 10^{-12} M \]

- At 25 °C, you observe the following conditions.

  - In an acidic solution, [H⁺] > 1.0 × 10⁻⁷ M.
  - In a neutral solution, [H⁺] = 1.0 × 10⁻⁷ M.
  - In a basic solution, [H⁺] < 1.0 × 10⁻⁷ M.

The pH Scale

- pH ≈ −log[H⁺]
- pH in water ranges from 0 to 14.
- \( K_w = 1.00 \times 10^{-14} = [\text{H}^+] [\text{OH}^-] \)
- \( pK_w = 14.00 = \text{pH} + \text{pOH} \)
- As pH rises, pOH falls (sum = 14.00).
The pH of a Solution

- For a solution in which the hydrogen-ion concentration is $1.0 \times 10^{-3}$, the pH is:
  $$pH = -\log(1.0 \times 10^{-3}) = 3.00$$
- Note that the number of decimal places in the pH equals the number of significant figures in the hydrogen-ion concentration.

- In a neutral solution, whose hydrogen-ion concentration is $1.0 \times 10^{-7}$, the pH = 7.00.
- For acidic solutions, the hydrogen-ion concentration is greater than $1.0 \times 10^{-7}$, so the pH is less than 7.00.
- Similarly, a basic solution has a pH greater than 7.00.
- Figure 16.6 shows a diagram of the pH scale and the pH values of some common solutions.

A Problem to Consider

- A sample of orange juice has a hydrogen-ion concentration of $2.9 \times 10^{-4}$ M. What is the pH?
  $$pH = -\log[H^+]$$
  $$pH = -\log(2.9 \times 10^{-4})$$
  $$pH = 4.54$$

A Problem to Consider

- The pH of human arterial blood is 7.40. What is the hydrogen-ion concentration?
  $$[H^+] = \text{antilog}(-\text{pH})$$
  $$[H^+] = \text{antilog}(-7.40)$$
  $$[H^+] = 10^{-7.40} = 4.0 \times 10^{-8} \text{ M}$$

The pH of a Solution

- A measurement of the hydroxide ion concentration, similar to pH, is the pOH.
- The pOH of a solution is defined as the negative logarithm of the molar hydroxide-ion concentration.
  $$\text{pOH} = -\log[OH^-]$$
The pH of a Solution

• A measurement of the hydroxide ion concentration, similar to pH, is the pOH.
• Then because $K_w = [H^+][OH^-] = 1.0 \times 10^{-14}$ at 25°C, you can show that

$$\text{pH} + \text{pOH} = 14.00$$

A Problem to Consider

• An ammonia solution has a hydroxide-ion concentration of $1.9 \times 10^{-3}$ M. What is the pH of the solution?
  You first calculate the pOH:
  $$\text{pOH} = -\log(1.9 \times 10^{-3}) = 2.72$$
  Then the pH is:
  $$\text{pH} = 14.00 - 2.72 = 11.28$$

The pH of a Solution

• The pH of a solution can accurately be measured using a pH meter (see Figure 14.9).
  • Although less precise, acid-base indicators are often used to measure pH because they usually change color within a narrow pH range.
  • Figure 16.8 shows the color changes of various acid-base indicators.

Figure 14.9: pH meters are used to measure acidity.

Figure 16.8: Color changes of some acid-based indicators.

<table>
<thead>
<tr>
<th>Indicator name</th>
<th>pH range for color change</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methyl violet</td>
<td>0  2  4  6  8  10  12</td>
</tr>
<tr>
<td>Thymol blue (acidic)</td>
<td>yellow</td>
</tr>
<tr>
<td>Bromphenol blue</td>
<td>yellow, blue</td>
</tr>
<tr>
<td>Methyl orange</td>
<td>red, yellow</td>
</tr>
<tr>
<td>Bromcresol green</td>
<td>yellow, blue</td>
</tr>
<tr>
<td>Methyl red</td>
<td>yellow</td>
</tr>
<tr>
<td>Bromthymol blue</td>
<td>yellow, blue</td>
</tr>
<tr>
<td>Thymol blue (basic)</td>
<td>yellow, blue</td>
</tr>
<tr>
<td>Phenolphthalein</td>
<td>colorless, pink</td>
</tr>
<tr>
<td>Alizarin yellow R</td>
<td>yellow, red</td>
</tr>
</tbody>
</table>

Percent Dissociation (Degree of Ionization)

$$\% \text{ dissociation} = \frac{\text{amount dissociated}(M)}{\text{initial concentration}(M)} \times 100\%$$

Weak acids and bases have low values for % dissociation - their degree of ionization is small.
A Problem To Consider

- Nicotinic acid is a weak monoprotic acid with the formula $\text{HC}_6\text{H}_4\text{NO}_2$. A 0.012 M solution of nicotinic acid has a pH of 3.39 at 25 °C.
  
  $[\text{H}^+] = 10^{-3.39} = 0.00041$

- 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%.

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A Problem To Consider

- Nicotinic acid is a weak monoprotic acid with the formula $\text{HC}_6\text{H}_4\text{NO}_2$. 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.

- 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.

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A Problem To Consider

- Nicotinic acid is a weak monoprotic acid with the formula $\text{HC}_6\text{H}_4\text{NO}_2$. A 0.012 M solution of nicotinic acid has a pH of 3.39 at 25 °C. We can obtain the value of $x$ from the given pH.

\[
\begin{align*}
x &= [\text{H}_3\text{O}^+] = \text{anti log}(-\text{pH}) \\
x &= \text{anti log}(-3.39) \\
x &= 4.1 \times 10^{-4} = 0.00041
\end{align*}
\]

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A Problem To Consider

- Nicotinic acid is a weak monoprotic acid with the formula $\text{HC}_6\text{H}_4\text{NO}_2$. 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.

- Substituting the expressions for the equilibrium concentrations, we get:

\[
K_a = \frac{[\text{H}_3\text{O}^+][\text{Nic}^-]}{[\text{HNic}]} = \frac{x^2}{(0.012 - x)}
\]
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.

• Substitute this value of \( x \) in our equilibrium expression.

• Note first, however, that

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

the concentration of unionized acid remains virtually unchanged.

Solving Weak Acid Equilibrium Problems

1. List major species in solution.
2. Choose species that can produce H⁺ and write reactions.
3. Based on \( K_a \) values, decide on dominant equilibrium.
4. Write equilibrium expression for dominant equilibrium.
5. List initial concentrations in dominant equilibrium.

Calculations With \( K_a \)

• If you know the value of \( K_a \), you can calculate the equilibrium concentrations of species HA, A⁻, and H⁺ for solutions of different molarities.

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.
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, if \[ \frac{C_a}{K_a} > 100 \]
  then this simplifying assumption of ignoring the subtracted $x$ gives an acceptable error of less than 5%.

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

A Problem To Consider

- What is the pH at 25 °C of a solution obtained by dissolving 0.325 g of acetylsalicylic acid (aspirin), $\text{HC}_9\text{H}_7\text{O}_4$, in 0.500 L of water? The acid is monoprotic and $K_a = 3.3 \times 10^{-4}$ at 25 °C.

  - 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.

  - 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.

A Problem To Consider

- What is the pH at 25 °C of a solution obtained by dissolving 0.325 g of acetylsalicylic acid (aspirin), $\text{HC}_9\text{H}_7\text{O}_4$, in 0.500 L of water? The acid is monoprotic and $K_a = 3.3 \times 10^{-4}$ at 25 °C.

  - The molar mass of $\text{HC}_9\text{H}_7\text{O}_4$ is 180.2 g.
  - 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 $K_a$).

A Problem To Consider

- What is the pH at 25 °C of a solution obtained by dissolving 0.325 g of acetylsalicylic acid (aspirin), $\text{HC}_9\text{H}_7\text{O}_4$, in 0.500 L of water? The acid is monoprotic and $K_a = 3.3 \times 10^{-4}$ at 25 °C.

  - We will abbreviate the formula for acetylsalicylic acid as $\text{HAcs}$ 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.
A Problem To Consider

• What is the pH at 25 °C of a solution obtained by dissolving 0.325 g of acetylsalicylic acid (aspirin), HC₉H₇O₄, in 0.500 L of water? The acid is monoprotic and K_a = 3.3 x 10^{-4} at 25 °C.

These data are summarized below:

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

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

A Problem To Consider

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

\[
\frac{[\text{H}_3\text{O}^+][\text{Acs}^-]}{[\text{HAcs}]} = K_a
\]

• Rearranging the preceding equation to put it in the form ax^2 + bx + c = 0, we get

\[
x^2 + (3.3 \times 10^{-3})x - (1.2 \times 10^{-6}) = 0
\]

• The lower sign in ± gives a negative root which we can ignore.

A Problem To Consider

• What is the pH at 25 °C of a solution obtained by dissolving 0.325 g of acetylsalicylic acid (aspirin), HC₉H₇O₄, in 0.500 L of water? The acid is monoprotic and K_a = 3.3 x 10^{-4} at 25 °C.

Now substitute into the quadratic formula.

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

A Problem To Consider

• What is the pH at 25 °C of a solution obtained by dissolving 0.325 g of acetylsalicylic acid (aspirin), HC₉H₇O₄, in 0.500 L of water? The acid is monoprotic and K_a = 3.3 x 10^{-4} at 25 °C.

• 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 ± gives a negative root which we can ignore.
A Problem To Consider

What is the pH at 25 °C of a solution obtained by dissolving 0.325 g of acetylsalicylic acid (aspirin), HC9H7O4, in 0.500 L of water? The acid is monoprotic and Ka=3.3 x 10^-4 at 25 °C.

Taking the upper sign, we get

\[ x = [H_3O^+] = 9.4 \times 10^{-4} \]

Now we can calculate the pH.

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

A Problem To Consider

What is the pH of a 0.20 M solution of pyridine, C5H5N, in aqueous solution? The Kb for pyridine is 1.4 x 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 \( x = [OH^-] \).

A Problem To Consider (Weak Base)

What is the pH of a 0.20 M solution of pyridine, C5H5N, in aqueous solution? The Kb for pyridine is 1.4 x 10^-9.

Pyridine ionizes by picking up a proton from water (as ammonia does).

\[
\text{C}_5\text{H}_5\text{N(aq)} + \text{H}_2\text{O(l)} \rightleftharpoons \text{C}_5\text{H}_5\text{NH}^+(aq) + \text{OH}^-(aq)
\]

| Initial | 0.20 | 0 | 0 |
| Change  | -x   | +x | +x |
| Equilibrium | 0.20-x | x | x |

Note that

\[
\frac{C_5H_5N}{K_b} = \frac{0.20}{1.4 \times 10^{-9}} = 1.4 \times 10^8
\]

which is much greater than 100, so we may use the simplifying assumption that \((0.20-x) \approx (0.20)\).

A Problem To Consider

What is the pH of a 0.20 M solution of pyridine, C5H5N, in aqueous solution? The Kb for pyridine is 1.4 x 10^-9.

The equilibrium expression is

\[
\frac{[C_5H_5NH^+] [OH^-]}{[C_5H_5N]} = K_b
\]

If we substitute the equilibrium concentrations and the Kb into the equilibrium constant expression, we get

\[
\frac{x^2}{(0.20 - x)} = 1.4 \times 10^{-9}
\]
A Problem To Consider

• What is the pH of a 0.20 M solution of pyridine, C₅H₅N, in aqueous solution? The $K_b$ for pyridine is $1.4 \times 10^{-9}$.
• Using our simplifying assumption that the $x$ in the denominator is negligible, we get

$$\frac{x^2}{(0.20)} \cong 1.4 \times 10^{-9}$$

A Problem To Consider

• What is the pH of a 0.20 M solution of pyridine, C₅H₅N, in aqueous solution? The $K_b$ for pyridine is $1.4 \times 10^{-9}$.
• Solving for $x$ we get

$$x \cong \sqrt{(0.20) \times (1.4 \times 10^{-9})} = 1.7 \times 10^{-5}$$

• Solving for pOH

$$pOH = -\log[OH^-] = -\log(1.7 \times 10^{-5}) = 4.8$$
• Since $pH + pOH = 14.00$

$$pH = 14.00 - pOH = 14.00 - 4.8 = 9.2$$

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.

$$\text{H}_2\text{SO}_4(aq) + \text{H}_2\text{O}(l) \rightarrow \text{H}_3\text{O}^+(aq) + \text{HSO}_4^-(aq)$$

• The first proton is lost completely followed by a weak ionization of the hydrogen sulfate ion, \( \text{HSO}_4^- \).

$$(\text{H}_3\text{O}_2\text{O}^+(aq) + \text{SO}_4^{2-}(aq)$$

• For a weak diprotic acid like carbonic acid, \( \text{H}_2\text{CO}_3 \), two simultaneous equilibria must be considered.

$$\text{H}_2\text{CO}_3(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{H}_3\text{O}^+(aq) + \text{HCO}_3^-(aq)$$

$$\text{HCO}_3^-(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{H}_3\text{O}^+(aq) + \text{CO}_3^{2-}(aq)$$
Polyprotic Acids

• Some acids have two or more protons (hydrogen ions) to donate in aqueous solution. These are referred to as polyprotic acids.

• Each equilibrium has an associated acid-ionization constant.

For the loss of the first proton

\[ K_{a1} = \frac{[H_3O^+][HCO_3^-]}{[H_2CO_3]} = 4.3 \times 10^{-7} \]

Polyprotic Acids

• Some acids have two or more protons (hydrogen ions) to donate in aqueous solution. These are referred to as polyprotic acids.

• The second ionization constant, \( K_{a2} \), for a polyprotic acid is always 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, \( K_{a2} \).

Polyprotic Acids

• Some acids have two or more protons (hydrogen ions) to donate in aqueous solution. These are referred to as polyprotic acids.

For the loss of the second proton

\[ K_{a2} = \frac{[H_3O^+][CO_3^{2-}]}{[HCO_3^-]} = 4.8 \times 10^{-11} \]

Brønsted-Lowry Concept of Acids and Bases

• Some species can act as an acid or a base.

• An amphoteric species is a species that can act either as an acid or a base (it can gain or lose a proton).

• For example, \( HCO_3^- \) acts as a proton donor (an acid) in the presence of \( OH^- \):

\[ HCO_3^- (aq) + OH^- (aq) \rightarrow CO_3^{2-} (aq) + H_2O(l) \]

Bronsted-Lowry Concept of Acids and Bases

• Some species can act as an acid or a base.

• An amphoteric species is a species that can act either as an acid or a base (it can gain or lose a proton).

Alternatively, \( HCO_3^- \) can act as a proton acceptor (a base) in the presence of \( HF \):

\[ HCO_3^- (aq) + HF(aq) \rightarrow H_2CO_3(aq) + F^- (aq) \]
**Brønsted-Lowry Concept of Acids and Bases**

- The amphoteric characteristic of water is important in the acid-base properties of aqueous solutions.
- Water can also react as a base with the acid HF.

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

**Acid-Base Properties of a Salt Solution**

- One of the successes of the Brønsted-Lowry concept of acids and bases was in pointing out that some ions can act as acids or bases.
- Consider a solution of sodium cyanide, NaCN.

\[
\text{NaCN}(s) + \text{H}_2\text{O}(l) \rightarrow \text{Na}^+(aq) + \text{CN}^- (aq)
\]

- A 0.1 M solution has a pH of 11.1 and is therefore fairly basic.

**Acid-Base Properties of a Salt Solution**

- The hydrolysis of an ion is the reaction of an ion with water to produce the conjugate acid and hydroxide ion or the conjugate base and hydronium ion.
- The NH\text{4}^+ ion hydrolyzes to the conjugate base (NH\text{3}) and hydronium ion.

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

**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.
Predicting Whether a Salt is Acidic, Basic, or Neutral

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

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.
   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.

4. A salt of a weak base and a weak acid.
   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.
The pH of a Salt Solution

To see the relationship between $K_a$ and $K_b$ for conjugate acid-base pairs, consider the acid ionization of HCN and the base ionization of CN$^-$. 

\[
\begin{align*}
&\text{HCN}(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + \text{CN}^- (aq) \quad K_a \\
&\text{CN}^- (aq) + H_2O(l) \rightleftharpoons \text{HCN}(aq) + OH^- (aq) \quad K_b \\
&2H_2O(l) \rightleftharpoons H_3O^+(aq) + OH^- (aq) \quad K_w
\end{align*}
\]

When these two reactions are added you get the ionization of water.

Therefore, 

\[
K_a \times K_b = K_w
\]

A Problem To Consider

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

Sodium cyanide gives Na$^+$ ions and CN$^-$ ions in solution. 

Only the CN$^-$ ion hydrolyzes. 

\[
\text{CN}^- (aq) + H_2O(l) \rightleftharpoons \text{HCN}(aq) + OH^- (aq)
\]
A Problem To Consider

- What is the pH of a 0.10 M NaCN solution at 25 °C? The $K_a$ for HCN is $4.9 \times 10^{-10}$.
- Let $x = [OH^-] = [HCN]$, then substitute into the equilibrium expression.

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

A Problem To Consider

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

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

Structure and Acid-Base Properties

- Two factors for acidity in binary compounds:
  - Bond Polarity (high is good)
  - Bond Strength (low is good)

Molecular Structure and Acid Strength

- Two factors are important in determining the relative acid strengths.
  - One is the polarity of the bond to which the hydrogen atom is attached.
  - The H atom should have a partial positive charge:

\[
\delta^+ \quad \delta^-
\]

- The X atom should have a partial negative charge:

\[
\delta^- \quad \delta^+
\]

- The more polarized the bond, the more easily the proton is removed and the greater the acid strength.

Molecular Structure and Acid Strength

- Two factors are important in determining the relative acid strengths.
  - The second factor is the strength of the bond. Or, in other words, how tightly the proton is held.
  - This depends on the size of atom X.

\[
\delta^+ \quad \delta^-
\]

- The larger atom X, the weaker the bond and the greater the acid strength.
Molecular Structure and Acid Strength
- Consider a series of binary acids from a given column of elements.
- As you go down the column of elements, the radius increases markedly and the H-X bond strength decreases.
- You can predict the following order of acidic strength:

\[
\text{HF} < \text{HCl} < \text{HBr} < \text{HI}
\]

Molecular Structure and Acid Strength
- As you go across a row of elements, the polarity of the H-X bond becomes the dominant factor.
- As electronegativity increases going to the right, the polarity of the H-X bond increases and the acid strength increases.
- You can predict the following order of acidic strength:

\[
\text{H}_3\text{N} < \text{H}_2\text{O} < \text{HF}
\]

Molecular Structure and Acid Strength
- Consider the oxoacids. An oxoacid has the structure: \(\text{H} - \text{O} - \text{Y}\)
- If the electronegativity of Y is large, then the O-H bond is relatively polar and the acid strength is greater.
- We can predict the acid strength for compounds with Y in the same group:

\[
\text{HOCl} > \text{HOBr} > \text{HOI}
\]
Molecular Structure and Acid Strength

- Consider the oxoacids. An oxoacid has the structure: \( H - O - Y - X \)
- Other groups, such as O atoms or O-H groups, may be attached to Y.
- With each additional O atom, Y becomes effectively more electronegative.

- As a result, the H atom becomes more acidic.
- The acid strengths of the oxoacids of chlorine increase in the following order:
  \( \text{HClO} < \text{HClO}_2 < \text{HClO}_3 < \text{HClO}_4 \)

- Consider polyprotic acids and their corresponding anions.
  - Each successive H atom becomes more difficult to remove.
  - Therefore the acid strength of a polyprotic acid and its anions decreases with increasing negative charge.
  \( \text{HPO}_4^{2-} < \text{H}_2\text{PO}_4^- < \text{H}_3\text{PO}_4 \)

Models of HClO, HClO₂, HClO₃, and HClO₄.

Figure 14.11: The effect of the number of attached oxygens on the O—H bond in a series of chlorine oxyacids.
Oxides

- Acidic Oxides (Acid Anhydrides):
  - \( O\)–\(X\) bond is strong and covalent.
  - \(\text{SO}_2, \text{NO}_2, \text{CrO}_3\)
- Basic Oxides (Basic Anhydrides):
  - \( O\)–\(X\) bond is ionic.
  - \(\text{K}_2\text{O}, \text{CaO}\)

Lewis Acids and Bases

- Lewis Acid: electron pair acceptor
- Lewis Base: electron pair donor

\[
\text{Al}^{3+} + 6 \left( \begin{array}{c} \text{H} \\ \text{O} \\ \text{H} \end{array} \right) \rightarrow \left[ \text{Al} \left( \begin{array}{c} \text{O} \\ \text{H} \end{array} \right)_6 \right]^{3+}
\]

**Lewis Concept of Acids and Bases**

- The Lewis concept defines an **acid as an electron pair acceptor** and a **base as an electron pair donor**.
- This concept broadened the scope of acid-base theory to include reactions that did not involve \(\text{H}^+\).
- The Lewis concept embraces many reactions that we might not think of as acid-base reactions.

\[
\text{Al}^{3+} + 6 \text{H}_2\text{O} \rightarrow \text{Al(OH)}_2(\text{OH})_6^{3+}
\]

---

**TABLE 14.10 Three Models for Acids and Bases**

<table>
<thead>
<tr>
<th>Model</th>
<th>Definition of Acid</th>
<th>Definition of Base</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acid-Lewis</td>
<td>(\text{H}^+) donor</td>
<td>(\text{OH}^-) acceptor</td>
</tr>
<tr>
<td>Basic-Lewis</td>
<td>(\text{H}^+) acceptor</td>
<td>(\text{OH}^-) donor</td>
</tr>
<tr>
<td>Lewis</td>
<td>electron pair acceptor</td>
<td>electron pair donor</td>
</tr>
</tbody>
</table>

A model of \(\text{A} \left( \text{OH}_2 \right)_6^{3+}\).

A lone pair from the oxygen atom in each water molecule is donated to the \(\text{Al}^{3+}\) to coordinate covalent bonds between the water molecules and aluminum ion.