Chapter 16: Acid-Base and Solubility Equilibria: 
Reactions in Soil and Water 
Problems: 16.2-16.86

16.1 ACIDS AND BASES: THE BRØNSTED-LOWRY MODEL

PROPERTIES OF ACIDS & BASES

Acids
- produce hydrogen ions, \( H^+ \)
- taste sour
- turn blue litmus paper red
- e.g. citrus fruits, vinegar, coffee

Bases
- produce hydroxide ions, \( OH^- \)
- taste bitter; feels soapy, slippery
- turn red litmus paper blue
- e.g. bleach, drain cleaner, baking soda

Arrhenius Definitions:

**Arrhenius acid:** A substance that *releases* \( H^+ \) when dissolved in water
- Some acids are *monoprotic* (release only one \( H^+ \) per molecule)
  - e.g. HCl, HBr, HI, HNO₃, HClO₄
- Some acids are *polyprotic* (release more than one \( H^+ \) per molecule)
  - e.g. H₂SO₄ and H₂CO₃ are both diprotic; H₃PO₄ is triprotic.

\[
\begin{align*}
\text{HCl(aq)} + \text{H₂O(l)} & \rightarrow \text{H₃O⁺(aq)} + \text{Cl⁻(aq)} \\
\text{HC₂H₃O₂(aq)} + \text{H₂O(l)} & \rightleftharpoons \text{H₃O⁺(aq)} + \text{C₂H₃O₂⁻(aq)}
\end{align*}
\]

Note: \( \text{H₃O⁺} \) is the *hydronium ion*, a hydrated proton: \( H^+ + H₂O = H₃O⁺ \)

**Arrhenius base:** A substance that *releases* \( OH^- \) when dissolved in water
- Any ionic compound containing hydroxide ion (\( OH^- \))

\[
\text{NaOH(aq)} \rightarrow \text{Na⁺(aq)} + \text{OH⁻(aq)}
\]

The general equation for an **Arrhenius acid-base neutralization reaction** is shown below:

\[
\text{HX(aq)} + \text{MOH(aq)} \rightarrow \text{H₂O(l)} + \text{MX}
\]

Thus, in an Arrhenius acid-base neutralization reaction the \( H^+ \) from the acid reacts with the \( OH^- \)
from the base to produce \( H₂O \), and the *cation from the base* reacts with the *anion from the acid* to
form the *salt* (MX).
**Brønsted-Lowry (B-L) Definitions:**
Danish chemist Johannes Brønsted and English chemist Thomas Lowry developed the following model for acids and bases in 1923:

**Brønsted-Lowry acid:** A substance that donates a proton ($H^+$) — i.e., a **proton donor**

**Brønsted-Lowry base:** A substance that accepts a proton ($H^+$) — i.e., a **proton acceptor**

- Unlike an Arrhenius base, a B-L base need not contain $OH^-$.  

According to Brønsted-Lowry, an **acid-base reaction simply involves a proton ($H^+$) transfer**, not necessarily the formation of water and a salt.

For example, the ionization of HCl can be viewed at the molecular level as follows:

In this example, the HCl donates a $H^+$ ion to the H$_2$O molecule.

$\rightarrow$ HCl is the **proton donor = acid** and H$_2$O is the **proton acceptor = base**

Note: The Brønsted-Lowry base (or proton acceptor) must have a lone pair of electrons to form the bond with the $H^+$ ion.

**Conjugate Acid-Base Pairs:** a Brønsted-Lowry acid/base and its conjugate differ by a $H^+$

- For the reaction above, when HCl donates $H^+$ to H$_2$O, it leaves behind Cl$^-$.  
- An acid and base that differ only in the presence/absence of $H^+$ are called **conjugate acid-base pairs**.
- Thus, HCl is the conjugate acid of Cl$^-$, and Cl$^-$ is the conjugate base of HCl.

Example: Indicate the other conjugate acid-base pair in the reaction above: ________________
In the general reaction for the dissociation (or ionization) of an acid below the double-arrow indicates both the forward and reverse reactions can occur:

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

Brønsted-Lowry acid = ____________  Brønsted-Lowry base= ____________

Also, \( \text{H}_2\text{O} \) is the conjugate ________ of \( \text{H}_3\text{O}^+ \), and \( \text{A}^- \) is the conjugate ________ of ________.

Example: Label the Brønsted-Lowry acid and base in each of the following reactions, and fill in the blanks below to indicate the conjugate acid/base pairs shown:

a. \( \text{F}^-(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{OH}^-(aq) + \text{HF}(aq) \)

\( \text{F}^- \) is the conjugate ________ of __________; \( \text{H}_2\text{O} \) is the conjugate ________ of ____________.

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

\( \text{NH}_4^+ \) is the conjugate ________ of __________; \( \text{OH}^- \) is the conjugate ________ of __________.

c. \( \text{CH}_3\text{COOH}(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{H}_3\text{O}^+(aq) + \text{CH}_3\text{COO}^-(aq) \)

\( \text{CH}_3\text{COO}^- \) is the conjugate ______ of ____________; \( \text{H}_3\text{O}^+ \) is the conjugate ______ of ________.
A substance that can both accept and donate a proton—i.e. act as an acid or as a base—is amphoteric.
- e.g., H₂O is amphoteric.

\[
\begin{align*}
\text{HNO}_3(\text{aq}) + \text{H}_2\text{O}(l) & \rightarrow \text{H}_3\text{O}^+(\text{aq}) + \text{NO}_3^-(\text{aq}) \\
\text{NH}_3(\text{aq}) + \text{H}_2\text{O}(l) & \rightleftharpoons \text{NH}_4^+(\text{aq}) + \text{OH}^-(\text{aq})
\end{align*}
\]

Relative Strengths of Acids and Bases

The strength of an acid is defined by the equilibrium position for its dissociation (or ionization) reaction:

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

A strong acid ionizes almost completely.
- The equilibrium lies far to the right.
- A forward arrow (not double arrow) is used for the dissociation of a strong acid like HNO₃ since all the HNO₃ molecules ionize to H⁺ and NO₃⁻, leaving no HNO₃ molecules in water.

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

All strong acids ionize completely in water to produce H₃O⁺ ions, the strongest acid.
- Water has a leveling effect for strong acids.
- 1 mole of any strong acid in water would produce 1 mole of H₃O⁺.
- Strong acids of equal concentration are indistinguishable—i.e. level—in water.

In contrast, a weak acid ionizes only to a very small extent.
- The equilibrium lies far to the left.
- Thus, a double arrow is used for the dissociation of a weak acid like HF(aq) since mostly HF exists at equilibrium, with very few H⁺ or F⁻ ions in solution.

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

Similar to a strong acid, a strong base dissociates (breaks up) almost completely.
- The equilibrium lies far to the right.
- A forward arrow is used for the dissociation of a strong base like Ca(OH)₂ (aq) since virtually all the Ca(OH)₂ ionizes to Ca²⁺ and OH⁻, leaving almost no Ca(OH)₂.

\[
\text{Ca(OH)}_2(\text{aq}) \rightarrow \text{Ca}^2+(\text{aq}) + 2 \text{OH}^-(\text{aq})
\]
Know the following acids and bases. All other acids and bases are weak!

<table>
<thead>
<tr>
<th>Strong Acids</th>
<th>Strong Bases</th>
</tr>
</thead>
<tbody>
<tr>
<td>HCl, HBr, HI, HNO₃, HClO₄, H₂SO₄</td>
<td>LiOH, NaOH, KOH, Ca(OH)₂, Sr(OH)₂, Ba(OH)₂</td>
</tr>
</tbody>
</table>

Note: H₂SO₄(aq) is a strong acid and diprotic (able to release 2 H⁺ ions), but it generally ionizes to release only one H⁺, as follows:

\[ \text{H}_2\text{SO}_4(aq) \rightarrow \text{H}^+(aq) + \text{HSO}_4^-(aq) \]

The resulting HSO₄⁻(aq) is a weak acid:

\[ \text{HSO}_4^-(aq) \rightleftharpoons \text{H}^+(aq) + \text{SO}_4^{2-}(aq) \]

16.3 CALCULATIONS INVOLVING pH, Kₐ, and Kₐ

Given the ionization (or dissociation) reaction of an acid, HA,

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

the equilibrium expression for the reaction can be written as

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

where \( K_a \) is the acid dissociation constant.

Example: For the following acids, write equation for the acid dissociation (including the reaction with water), then write the equilibrium expression for its acid dissociation constant, \( K_a \).

a. hydrobromic acid

b. nitrous acid

c. ammonium ion
Ex. 1: Consider the following trends for acid strength and base strength.

a. List the 4 strongest acids in the list:

b. List the four weakest bases in the list:

c. As the strength of an acid decreases, the strength of its conjugate base _________.
   
   increases   decreases

d. Thus, there is a __________ correlation between the strength of an acid and the strength of its conjugate base.
   
   positive   negative

Thus, the strength of an acid is **inversely related** to the strength of its conjugate base.

→ Weaker an acid, stronger its conjugate base.

   – The **conjugate bases of weak acids** (F–, NO2–, C2H3O2–, etc.) are much stronger bases compared to H2O.

   → These bases can react with a H2O molecule, removing a H+ ion from the water to produce its conjugate acid and OH–.

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

   – The **conjugate bases of strong acids** (Cl–, Br–, I–, NO3–, ClO3–, ClO4–) are much weaker bases compared to H2O.

   → These bases are not strong enough to react with a H2O molecule.

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

Ex. 1: Write the hydrolysis reaction for acetate ion:
Ex. 2: Write the hydrolysis reaction (reaction with water) for each of the following ions:

a. cyanide ion

b. perchlorate ion

c. nitrite ion

d. bromide ion

16.5 ACID STRENGTH AND MOLECULAR STRUCTURE

Any molecules with a hydrogen atom can potentially be an acid, so why do many of these molecules display no acidic properties?
- e.g., \( \text{CH}_4 \) produces no \( \text{H}^+ \) ions in water;
  - \( \text{NH}_3 \) is a weak base that removes \( \text{H}^+ \) ions from \( \text{H}_2\text{O} \) molecules to form \( \text{OH}^- \);
  - \( \text{HF} \) produces very few \( \text{H}^+ \) ions in water; and
  - \( \text{HCl} \) dissociates completely to produce many \( \text{H}^+ \) ions in water.

Consider the two hydrogen halides, \( \text{HF} \) and \( \text{HCl} \).
- How \textit{likely is the H–F molecule to ionize} (i.e., break up by donating its proton) \textit{in water}?
- How \textit{likely is the H–Cl molecule to ionize} \textit{in water}?
Ex. 1: Both examples above involve a Brønsted-Lowry acid donating a proton to \( \text{H}_2\text{O} \). What bond is made in each example?

Ex. 2 Consider the table below showing bond strengths and differences in electronegativity (EN) values indicating bond polarity:

<table>
<thead>
<tr>
<th>H–X Bond</th>
<th>Bond Strength (kJ/mol)</th>
<th>Difference in EN Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>H–F</td>
<td>565</td>
<td>4.0 – 2.1 = 1.9</td>
</tr>
<tr>
<td>H–Cl</td>
<td>427</td>
<td>3.0 – 2.1 = 0.9</td>
</tr>
<tr>
<td>H–Br</td>
<td>363</td>
<td>2.8 – 2.1 = 0.7</td>
</tr>
<tr>
<td>H–I</td>
<td>295</td>
<td>2.5 – 2.1 = 0.4</td>
</tr>
<tr>
<td>H–O</td>
<td>467</td>
<td>3.5 – 2.1 = 1.4</td>
</tr>
<tr>
<td>H–N</td>
<td>391</td>
<td>3.0 – 2.1 = 0.9</td>
</tr>
<tr>
<td>H–C</td>
<td>413</td>
<td>2.5 – 2.1 = 0.4</td>
</tr>
</tbody>
</table>

Given the bond strengths for the H–F, H–Cl, and H–O bonds, explain why HF is a weak acid while HCl is a strong acid. (Hint: Compare the bonds broken with the bonds made.)

Ex. 3: A molecule is more likely to dissociate if its H–X bond is ______ polar. more less Explain.

Ex. 4: Even though the bond polarities are the same for H–I and H–C, explain why HI is a strong acid while \( \text{CH}_4 \) displays no acidic properties.
Ex. 5: a. Draw the Lewis structures for HOCl and HOBr below:

b. Given that chlorine’s EN value is 3.0, bromine’s is 2.8, and oxygen’s is 3.5, explain why the acid dissociation constant, $K_a$, is $2.9 \times 10^{-8}$ for HOCl and $2.1 \times 10^{-9}$ for HOBr.

Ex. 6: a. Draw the Lewis structures for HNO$_2$ and HNO$_3$. Next, determine the molecular geometry around each atom, and indicate the dipoles for each polar covalent bond:

b. Explain why one of these is a strong acid while the other is weak based on their structures.

c. A ternary oxyacid’s dissociation constant will increase as the number of oxygen atoms atoms around the central atom ______. ↑ ↓

Thus, the tendency for a molecule to donate a proton depends on two things:
1. the strength of the $H$–$X$ bond
2. the polarity of the $H$–$X$ bond.
17.1 LEWIS ACIDS AND BASES

In the early 1920's, Gilbert N. Lewis proposed a more general model for acid-base behavior.

**Lewis base:** electron-pair donor
   – needs to have a lone pair of electrons to donate

**Lewis acid:** electron-pair acceptor
   – needs an unoccupied atomic orbital that can hold a pair of electrons donated by a Lewis base

In the example above, NH$_3$ donates a pair of electrons to BF$_3$ to form a coordinate covalent bond and give BF$_3$ and octet, so NH$_3$ is the Lewis base and BF$_3$ is the Lewis acid.

Ex. 1: Draw the Lewis structures for the reactants and products in the reactions below, and indicate the Lewis acid and Lewis base for each reaction.

a. \[ \text{H}^+ + \text{H}_2\text{O} \quad \rightleftharpoons \quad \text{H}_3\text{O}^+ \]

b. \[ \text{NH}_3 + \text{H}_2\text{O} \quad \rightleftharpoons \quad \text{NH}_4^+ + \text{OH}^- \]
Thus, nitrogen-containing compounds usually have a lone pair of electron on the N atom.

→ **Nitrogen-containing compounds act as Lewis bases** (to donate a pair of electrons) or **Bronsted-Lowry bases** (to accept a $\text{H}^+$).

- NH$_3$, CH$_3$NH$_2$, C$_5$H$_5$N, etc., are all examples of Lewis and B-L bases.

In addition, **highly charged cations** (e.g. Al$^{3+}$, Cu$^{2+}$, etc.) can act as **Lewis acids** in water.

- In the example below, Al$^{3+}$ attracts the negative (oxygen) end of six polar water molecules to become a hydrated complex ion, Al(H$_2$O)$_6^{3+}$.

- The complex ion, Al(H$_2$O)$_6^{3+}$, can then donate a $\text{H}^+$ to a H$_2$O molecule to form H$_3$O$^+$, making Al(H$_2$O)$_6^{3+}$ an Arrhenius, B-L, and Lewis acid and H$_2$O a B-L and Lewis base.

![Diagram showing the reaction of Al$^{3+}$ with water to form Al(H$_2$O)$_6^{3+}$ and H$_3$O$^+$](image)

### 16.2 pH and the AUTOIONIZATION OF WATER

**Water as an acid and a base**

- Water is **amphoteric**; it can behave as an acid or a base.

Consider the **autoionization** of water,

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

which has the equilibrium expression: $K_w = [\text{H}_3\text{O}^+] [\text{OH}^-] = [\text{H}^+] [\text{OH}^-]$

where $K_w$ is called the **ion-product constant** or **dissociation constant** for water.

Experiment shows that at 25°C, $[\text{H}_3\text{O}^+] = [\text{OH}^-] = 1.0 \times 10^{-7}$ M

so $K_w = [\text{H}_3\text{O}^+] [\text{OH}^-] = (1.0 \times 10^{-7})(1.0 \times 10^{-7}) = 1.0 \times 10^{-14}$. 
This is true for any aqueous solution at 25°C, no matter what ions or compounds are present.

→ For **neutral** solutions, \([H_3O^+] = [OH^-]\).
→ For **acidic** solutions, \([H_3O^+] > [OH^-]\).
→ For **basic** solutions, \([H_3O^+] < [OH^-]\).

Ex. 1: Calculate the hydrogen or hydroxide ion concentration for each of the following, and indicate if the solution is acidic, basic, or neutral.

a. milk, \([H_3O^+] = 3.0 \times 10^{-7} \) M \([OH^-] = \) ___________ acidic basic neutral

b. eggs, \([OH^-] = 6.3 \times 10^{-7} \) M \([H_3O^+] = \) ___________ acidic basic neutral

c. urine, \([H_3O^+] = 1.8 \times 10^{-5} \) M \([OH^-] = \) ___________ acidic basic neutral

Ex. 2: At 60°C the value of \(K_w\) is \(1 \times 10^{-13}\). Compare this to \(K_w\) at 25°C, then indicate if the autoionization of water is endothermic or exothermic. Explain why.

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**Reviewing Logarithms**

Logarithms provide a more convenient way to deal with very large and very small numbers.

→ e.g., using log (or \(\log_{10} = \log\text{ base-10}\)) the number \(2.50 \times 10^6\) can be expressed as

\[
\log 2.50 \times 10^6 = 6.39794\ldots \quad \text{or} \quad 10^{6.39794\ldots} = 2.50 \times 10^6
\]

The components of a logarithm are called the **character** and the **mantissa**.

→ In the example above, the **character is 6**, corresponding to the **exponent** of the number when it’s expressed in scientific notation, and the **mantissa is 39794…**, which

→ When a number is expressed in scientific notation,

→ The **exponent** in scientific notation = the **character** of the logarithm, and the **digit term** in scientific notation = the **mantissa** of the logarithm.

Consider the following examples,

\[
\begin{align*}
\log 2.50 \times 10^3 & = 3.39794\ldots \quad \log 2.50 \times 10^{-1} = 0.39794\ldots - 1 \\
\log 2.50 \times 10^2 & = 2.39794\ldots \quad \log 2.50 \times 10^{-2} = 0.39794\ldots - 2 \\
\log 2.50 \times 10^1 & = 1.39794\ldots \quad \log 2.50 \times 10^{-3} = 0.39794\ldots - 3 \\
\log 2.50 \times 10^0 & = 0.39794\ldots \quad \log 2.50 \times 10^{-4} = 0.39794\ldots - 4 \\
& \quad \log 2.50 \times 10^{-5} = 0.39794\ldots - 5 \\
& \quad \log 2.50 \times 10^{-6} = 0.39794\ldots - 6
\end{align*}
\]

→ Note that the **digit term of 2.50** in all of these examples always has the same **mantissa**, 0.39794… for non-negative exponents, and for negative exponents, the mantissa is the difference between the negative of the exponent and 0.39794….
Thus, when dealing with logarithms, the **number of significant figures** is determined by the number of digits in the mantissa.

→ For example, \( \log 2.50 \times 10^6 = 6.398 \) and \( 10^{3.18} = 1.5 \times 10^3 \)

**The pH Scale**

The value of \( K_w \) at 25°C (1.0 \( \times \) 10\(^{-14} \)) is so small, indicating very few water molecules ionize to form \( H^+ \) and \( OH^- \).

→ The hydrogen ion concentration, \([H^+]\), is typically quite small, so the **pH scale** provides a convenient **measure of a solution's acidity**.

The pH is a \( \log_{10} \) scale and is defined as \( pH = -\log [H_3O^+] \)  so \( [H_3O^+] = 10^{-pH} \)

Similarly, \( pOH = -\log [OH^-] \) and \( [OH^-] = 10^{-pOH} \)

\( pK = -\log K \) and \( K = 10^{-pK} \)

On the pH scale,

- acidic: \( pH < 7 \)
- neutral: \( pH = 7 \)
- basic: \( pH > 7 \)

Furthermore,

- strongly acidic: \( pH \leq 2 \)
- strongly basic: \( pH \geq 12 \)
- weakly acidic: \( 2 < pH < 7 \)
- weakly basic: \( 7 < pH < 12 \)

Ex. 1: Calculate the measurement indicated for the following substances:

a. saliva, \([H_3O^+] = 2.818 \times 10^{-7} \), \( pH = \) ____________

b. coffee, \([H_3O^+] = 1.6 \times 10^{-5} \), \( pH = \) ____________

c. egg white, \( pH = 8.0 \) \( [H_3O^+] = \) ____________
   Classification: strong weak acid base neutral

d. blood, \( pH = 7.50 \) \( [H_3O^+] = \) ____________

e. gastric juice, \( pOH = 12.20 \) \( [OH^-] = \) ____________ and
   \( [H_3O^+] = \) ____________ and \( pH = \) ____________
   Classification: strongly weakly acidic basic neutral
16.3 CALCULATIONS INVOLVING pH, $K_a$, and $K_b$

To understand what occurs in acid-base equilibria, one must recognize the ions and compounds present in solution.

→ **major species:** ions and/or compounds present in **relatively large amounts**

→ **minor species:** ions and/or compounds present in **very small amounts**

Example: Draw the major species present for 1 molecule of acid or 1 formula unit of the **ionic compound** in each beaker below, then list the major and minor species.

- **hydrochloric acid**
  - major species: ________________
  - minor species: ________________

- **sodium hydroxide**
  - major species: ________________
  - minor species: ________________

- **acetic acid**
  - major species: ________________
  - minor species: ________________

- **calcium hydroxide**
  - major species: ________________
  - minor species: ________________

- **hydrofluoric acid**
  - major species: ________________
  - minor species: ________________

- **sulfuric acid**
  - major species: ________________
  - minor species: ________________

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Calculating pH, pOH, $[H_3O^+]$, and $[OH^-]$ for STRONG ACIDS AND STRONG BASES

Ex. 1  Indicate the molarity of each ion in the solutions indicated below:

a. In 0.500M NaOH($aq$) solution, the $[Na^+] = \underline{\hspace{2cm}}$ and $[OH^-] = \underline{\hspace{2cm}}$.

b. In 0.250M nitric acid, the $[H_3O^+] = \underline{\hspace{2cm}}$ and $[NO_3^-] = \underline{\hspace{2cm}}$.

c. In 0.100M Ca(OH)$_2$(aq) solution, the $[Ca^{2+}] = \underline{\hspace{2cm}}$ and $[OH^-] = \underline{\hspace{2cm}}$.

d. Indicate the concentration of the major species present in a 0.150M sulfuric acid solution.

Ex. 2  Calculate the pH for each of the solutions in Ex. 1 above.

a. 

b. 

c. 

d. 

Ex. 3  Calculate the pH for a 2.00M hydrochloric acid solution.
Thus, **a negative value of pH is possible.** It simply means $[H^+]$ is greater than 1M, which is common for strong acid solutions—e.g. 6M HCl(aq), 2M H$_2$SO$_4$(aq), etc.

Since most strong acids and strong bases dissociate completely and pH meters are not reliable for very high H$_3$O$^+$ concentrations, we generally don’t worry about the pH of these solutions.

Ex. 4: Calculate the pH of a solution prepared by mixing 50.0 mL of a 1.50M nitric acid with 150.0 mL of 0.250M perchloric acid.

Ex. 5: Calculate the pH of a solution prepared by mixing 100.0 mL of a 0.500M sodium hydroxide solution with 50.0 mL of 1.00M of strontium hydroxide.
CALCULATING THE pH OF WEAK ACID SOLUTIONS

A weak acid barely ionizes or dissociates; thus, the equilibrium for its dissociation,

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

lies far to the left.

→ The major species in solution is HA, with very few H\(^+\) and A\(^-\) present.

However, water also dissociates to produce \(\text{H}^+\) ions:

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

If \([\text{H}_3\text{O}^+] = 10^{-7}\text{M}\) in water, water’s contribution to the \([\text{H}_3\text{O}^+]\) is negligible when \([\text{H}_3\text{O}^+] \geq 10^{-6}\text{M}\).

→ Only the \(\text{H}_3\text{O}^+\) ions produced by the weak acid have an effect on the solution’s pH when \([\text{H}_3\text{O}^+] \geq 10^{-6}\text{M}\).

Guidelines for Determining the pH of a Weak Acid at Equilibrium

1. Write the net ionic equation for the weak acid’s dissociation.
2. Write the equilibrium expression for the weak acid’s dissociation.
3. Determine the initial concentrations of the weak acid ([HA]\(_0\)), hydronium ion ([H\(_3\)O\(^+\)]\(_0\)), and the conjugate base ([A\(^-\)]\(_0\)).
4. Set up the ICE table, and solve for the unknown \(x\) using the acid dissociation constant, \(K_a\), given for the acid.
5. Use the value for \(x\) to solve for the \([\text{H}_3\text{O}^+]\), then solve for the pH.

Example: A sample of vinegar, which is typically about 5.0% acetic acid, was analyzed and determined to be 0.87M acetic acid.

a. Calculate the pH of the vinegar solution. For acetic acid, \(K_a = 1.8 \times 10^{-5}\).
b. For acetic acid $K_a = 1.8 \times 10^{-5}$ is very small. Make the approximation that the original acid concentration is much greater than $x$, so to simplify the calculation, if $x =$ change in concentration, we can assume $[HA]_0 - x \approx [HA]_0$.

Calculate the pH of the vinegar solution.

c. Compare the pH determined in parts a and b above.

The $K_a$ for weak acids is generally only known to an accuracy of ±5%. If we let $[HA]_0 =$ initial concentration of weak acid and $x =$ change in concentration, we can assume $[HA]_0 - x \approx [HA]_0$ is valid if the change, $x$, is less than 5% of the original acid concentration:

$$\frac{x}{[HA]} < 5\%$$

PERCENT DISSOCIATION (or PERCENT IONIZATION)

$$\text{Percent Dissociation} = \frac{[H_3O^+ \text{ at equilibrium}]}{[HA]_0} \times 100\%$$

Example: Calculate the percent dissociation for the vinegar solution in the example above.
Ex. 1: If hydrocyanic acid’s $K_a = 4.9 \times 10^{-10}$ at 25°C, calculate the pH of a 0.50M hydrocyanic acid solution.

Ex. 2: If hydrofluoric acid’s $K_a = 7.1 \times 10^{-4}$ at 25°C, calculate the pH of a 0.035M hydrofluoric acid solution.

**Method of Successive Approximations**

- Can be used for a much faster calculation compared to the quadratic equation when the change in concentration is greater than 5%
- In the initial equilibrium calculation, make the approximation that $[HA]_0 - x \approx [HA]_0$, and solve for $x$, then repeat the calculation, substituting the calculated value for $x$ to get a more accurate value for $x$ until the calculated value for $x$ can be substituted back into the equilibrium expression to solve for $K_a$ within 5% of the reported value of $K_a$. 
Ex. 2 (Continued): If hydrofluoric acid’s $K_a = 7.1 \times 10^{-4}$ at 25°C, calculate the pH of a 0.035M hydrofluoric acid solution.
Calculating $K_a$ from pH or Percent Dissociation

Ex. 1: Calculate the acid ionization constant for ascorbic acid, $C_6H_8O_6$, at 25°C given that a 0.20M ascorbic acid solution is 2.0% dissociated at 25°C.

Ex. 2: Calculate the acid ionization constant for hypoiodous acid, HOI, at 25°C given that a 0.15M hypoiodous acid solution has a pH of 5.73 at 25°C.

Ex. 3: Calculate the acid ionization constant for propanoic acid, HC$_3$H$_5$O$_2$, at 25°C given that a 0.10M propanoic acid solution is 1.14% dissociated at 25°C.
BASES

The reaction of a weak base, like ammonia, with water can be shown as follows,

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

and the equilibrium expression for the reaction can be written as

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

where \( K_b \) is the base dissociation constant.

Example: Write the reaction for the following weak bases with water, then write the equilibrium expression for its base-dissociation constant, \( K_b \).

a. fluoride ion

b. acetate ion

c. formate ion, HCOO

d. ethylamine, \( \text{C}_2\text{H}_5\text{NH}_2 \)

e. nitrite ion
Calculating the pH of Weak Bases

Ex. 1: Calculate the pH of a 0.50M ammonia solution given \( K_b \) is \( 1.8 \times 10^{-5} \) at 25°C.

Ex. 2: Calculate the pH of a 0.25M caffeine (\( \text{C}_8\text{H}_{10}\text{N}_4\text{O}_2 \)) solution given \( K_b \) is \( 4.1 \times 10^{-4} \) at 25°C.
16.6 pH (and ACIDIC AND BASIC PROPERTIES) OF SALT SOLUTIONS

Relating $K_a$ and $K_b$

Consider the ionization of hydrofluoric acid, $\text{HF}(aq) \ ⇄ \ H^+(aq) + F^-(aq)$.

and its corresponding equilibrium expression,

$$K_a = \frac{[H^+][F^-]}{[\text{HF}]}$$

Consider fluoride ion reacting with water, $F^-(aq) + H_2O(l) \ ⇄ \ HF(aq) + OH^-(aq)$.

and its corresponding equilibrium expression,

$$K_b = \frac{[HF][OH^-]}{[F^-]}$$

The product of the two ionization constants can be shown as

$$K_a \cdot K_b = \frac{[H^+][F^-]}{[\text{HF}]} \times \frac{[HF][OH^-]}{[F^-]} = [H^+][OH^-] = K_w \quad \rightarrow \quad K_w = K_a \cdot K_b$$

Ex. 1: Calculate the pH of a 0.50M sodium acetic solution given the $K_a$ for acetic acid is $1.8 \times 10^{-5}$ at 25°C.
Ex. 2: Calculate the pH of a 0.15M ammonium nitrate solution given the $K_b$ for ammonia is $1.8 \times 10^{-5}$ at 25°C.

**ACIDIC, BASIC, AND NEUTRAL SALTS**

- **A salt** is simply an *ionic compound*.
- When soluble salts dissolve in water, they form ions.

**Salts** that produce *Weakly Acidic Solutions*

- **react with water to produce $H^+$ ions**
  1. When the cation is the conjugate acid of a weak base: $NH_4^+$
  2. When the cation is a highly charged (+2, +3) metal ion: $Al^{3+}$, $Zn^{2+}$, $Mg^{2+}$, etc.
    - These form hydrated metal ions—e.g. $Al(H_2O)_6^{3+}$—that can donate a proton, $H^+$.
    - Exceptions are the cations of strong bases ($Li^+$, $Na^+$, $K^+$, $Ca^{2+}$, $Sr^{2+}$, $Ba^{2+}$) which do not react with water.

**Salts** that produce *Weakly Basic Solutions*

- **react with water to produce $OH^-$ ions**
  - When the anion is the conjugate base of a weak acid
    - Essentially every anion except those derived from strong acids
      (e.g. $Cl^-$, $Br^-$, $I^-$, $NO_3^-$, $ClO_3^-$, $ClO_4^-$)
    - Note: Sulfate ion ($SO_4^{2-}$) reacts with water to form $HSO_4^{2-}$ and $OH^-$.

**Salts** that produce *Neutral Solutions*

- **does not react with water to produce $H^+$ or $OH^-$ ions**
  - When the cation is the cation of a strong base ($Li^+$, $Na^+$, $K^+$, $Ca^{2+}$, $Sr^{2+}$, $Ba^{2+}$) and the anion is the conjugate base of a strong acid ($Cl^-$, $Br^-$, $I^-$, $NO_3^-$, $ClO_3^-$, $ClO_4^-$).
Ex. 1: Predict whether each of the following salts will result in an **acidic**, **basic**, or **neutral** solution. Explain why for each.

<table>
<thead>
<tr>
<th>Salt</th>
<th>Acidic, Basic, Neutral?</th>
<th>Explanation</th>
</tr>
</thead>
<tbody>
<tr>
<td>a. NaCl</td>
<td></td>
<td></td>
</tr>
<tr>
<td>b. Al(NO₃)₃</td>
<td></td>
<td></td>
</tr>
<tr>
<td>c. KC₂H₃O₂</td>
<td></td>
<td></td>
</tr>
<tr>
<td>d. NH₄Br</td>
<td></td>
<td></td>
</tr>
<tr>
<td>d. Sr(NO₂)₂</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Ex. 2: Ammonium fluoride is soluble. Will it result in an acidic, basic, or neutral solution?

Compare the cation’s $K_a$ with the anion’s $K_b$.
- For NH₄F,
  
  $K_a = \frac{K_w}{K_b} = \frac{1.0 \times 10^{-14}}{1.8 \times 10^{-5}} = 5.6 \times 10^{-10}$

  $K_b = \frac{K_w}{K_a} = \frac{1.0 \times 10^{-14}}{7.2 \times 10^{-4}} = 1.4 \times 10^{-11}$

<table>
<thead>
<tr>
<th>Table of $K_a$ and $K_b$ values at 25°C</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Value of $K_a$</strong></td>
</tr>
<tr>
<td>HClO₂</td>
</tr>
<tr>
<td>HCOOH</td>
</tr>
<tr>
<td>HF</td>
</tr>
<tr>
<td>HNO₂</td>
</tr>
<tr>
<td>HC₃H₅O₂ (or CH₃COOH)</td>
</tr>
<tr>
<td>HClO</td>
</tr>
<tr>
<td>HCN</td>
</tr>
</tbody>
</table>
Combining an Acidic Cation and a Basic Anion

- If $K_a > K_b$, then $[H_3O^+] > [OH^-]$ in solution $\rightarrow$ The salt and resulting solution are *acidic*.
- If $K_a < K_b$, then $[H_3O^+] < [OH^-]$ in solution $\rightarrow$ The salt and resulting solution are *basic*.
- If $K_a = K_b$, then $[H_3O^+] = [OH^-]$ in solution $\rightarrow$ The salt and resulting solution are *neutral*.

Example: Use the Table of $K_a$ and $K_b$ values to classify each of the following salts as acidic, basic, or neutral.

a. NH$_4$F where NH$_4^+$'s $K_a=5.6\times10^{-10}$ and F$^-$'s $K_b=1.4\times10^{-11}$

b. ammonium cyanide

c. zinc nitrite

d. aluminum acetate
16.4 Polyprotic Acids

Some acids are polyprotic—i.e. they have more than one ionizable H atom.
– e.g., H₂SO₄ and H₂CO₃ are both diprotic, and H₃PO₄ is triprotic.

Polyprotic acids always dissociate in a stepwise manner—i.e., one proton at a time.
– e.g., sulfurous acid, H₂SO₃(aq), dissociates according to the following steps at 25°C, where
  the successive acid dissociation constants are designated Kₐ₁ and Kₐ₂:

\[
\begin{align*}
\text{H}_2\text{SO}_3(aq) + \text{H}_2\text{O}(l) & \rightleftharpoons \text{H}^+(aq) + \text{HSO}_3^-(aq) & K_{a1} &= \frac{[\text{H}_3\text{O}^+][\text{HSO}_3^-]}{[\text{H}_2\text{SO}_3]} = 1.5 \times 10^{-2} \\
\text{HSO}_3^-(aq) + \text{H}_2\text{O}(l) & \rightleftharpoons \text{H}^+(aq) + \text{SO}_3^{2-}(aq) & K_{a2} &= \frac{[\text{H}_3\text{O}^+][\text{SO}_3^{2-}]}{[\text{HSO}_3^-]} = 6.3 \times 10^{-8}
\end{align*}
\]

Experimentally, this can be demonstrated by carrying out a titration of a polyprotic acid, where
  the protons are titrated in succession.
– The anion formed in one step is then ionized in the next step.
– With each successive step, the ionization constant becomes much smaller, usually by several
  orders of magnitude.
→ It is much more difficult to remove a proton from a positively charged ion.
→ \( K_{a1} > K_{a2} \) for all polyprotic acids.
→ Essentially all the of the H⁺ ions in solution come from the dissociation of
  the first acid.

Ex. 1: Calculate the pH of a 0.700M sulfurous acid solution.
  a. First, calculate the [H₃O⁺] after the dissociation of the first acid, H₂SO₃.
Ex. 1 (Continued): Calculate the pH of a 0.700M sulfurous acid solution.

b. Next, calculate the [H\(^+\)] resulting from the dissociation of the second acid, HSO\(_3\)\(^-\), where the initial concentration of HSO\(_3\)\(^-\), [HSO\(_3\)\(^-\)]\(_0\), is equal to the [H\(^+\)] from part a (since [H\(^+\)] = [HSO\(_3\)\(^-\)] = x).

c. How do the hydrogen ion concentrations compare after the first dissociation and the second dissociation?

d. Calculate the [SO\(_3\)\(^2-\)] at equilibrium?

Thus, because the contribution of H\(_3\)O\(^+\) ions from the second dissociation step is negligible compared to the [H\(_3\)O\(^+\)] after the first dissociation step, [H\(_3\)O\(^+\)] = [HSO\(_3\)\(^-\)].

Substituting into the \(K_{a2}\) expression, \[ K_{a2} = \frac{[H^+][SO_3^{2-}]}{[HSO_3^-]} = 6.3 \times 10^{-8} \rightarrow [SO_3^{2-}] = K_{a2}. \]