Reactions in Aqueous Solutions I: Acids, Bases & Salts
CHAPTER GOALS

1. Properties of Aqueous Solutions of Acids and Bases
2. The Arrhenius Theory
3. The Hydronium Ion (Hydrated Hydrogen Ion)
4. The Brønsted-Lowry Theory
5. The Autoionization of Water
6. Amphoterism
7. Strengths of Acids
CHAPTER GOALS

8. Acid-Base Reactions in Aqueous Solutions
9. Acidic Salts and Basic Salts
10. The Lewis Theory
11. The Preparation of Acids
Properties of Aqueous Solutions of Acids and Bases

• Aqueous acidic solutions have the following properties:

1. They have a sour taste.
2. They change the colors of many indicators.
   - Acids turn blue litmus to red.
   - Acids turn bromothymol blue from blue to yellow.
3. They react with metals to generate hydrogen, \( \text{H}_2(\text{g}) \).
Properties of Aqueous Solutions of Acids and Bases

4. They react with metal oxides and hydroxides to form salts and water.
5. They react with salts of weaker acids to form the weaker acid and the salt of the stronger acid.
6. Acidic aqueous solutions conduct electricity.
Properties of Aqueous Solutions of Acids and Bases

- Aqueous basic solutions have the following properties:
  1. They have a bitter taste.
  2. They have a slippery feeling.
  3. They change the colors of many indicators:
     - Bases turn red litmus to blue.
     - Bases turn bromothymol blue from yellow to blue.
  4. They react with acids to form salts and water.
  5. Aqueous basic solutions conduct electricity.
The Arrhenius Theory

- Svante Augustus Arrhenius first presented this theory of acids and bases in 1884.
- Acids are substances that contain hydrogen and produce H⁺ in aqueous solutions.
- Two examples of substances that behave as Arrhenius acids:

  \[
  \text{HCl}_{(aq)} + \text{H}_2\text{O}_{(l)} \rightarrow \text{H}_3\text{O}^+_{(aq)} + \text{Cl}^-_{(aq)}
  \]

  \[
  \text{HCO}_2\text{H}_{(aq)} + \text{H}_2\text{O}_{(l)} \rightleftharpoons \text{H}_3\text{O}^+_{(aq)} + \text{HCO}_2^-_{(aq)}
  \]
The Arrhenius Theory

• Bases are substances that contain the hydroxyl, OH, group and produce hydroxide ions, OH\(^-\), in aqueous solutions.

• Two examples of substances that behave as Arrhenius bases:

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

\[
\text{Ca(OH)}_2 \leftrightharpoons \text{Ca}^{2+\text{(aq)}} + 2 \text{OH}^{-\text{(aq)}}
\]
The Arrhenius Theory

• Neutralization reactions are the combination of $\text{H}^+$ (or $\text{H}_3\text{O}^+$) with $\text{OH}^-$ to form $\text{H}_2\text{O}$.

• Strong acids are acidic substances that ionize 100% in water.
  – List of aqueous strong acids:
    – $\text{HCl}$, $\text{HBr}$, $\text{HI}$, $\text{H}_2\text{SO}_4$, $\text{HNO}_3$, $\text{HClO}_4$, $\text{HClO}_3$

• Strong bases are basic substances that ionize 100% in water.
  – List of aqueous strong bases:
    – $\text{LiOH}$, $\text{NaOH}$, $\text{KOH}$, $\text{RbOH}$, $\text{CsOH}$,
    – $\text{Ca(OH)}_2$, $\text{Sr(OH)}_2$, $\text{Ba(OH)}_2$
The Arrhenius Theory

• For a typical strong acid-strong base reaction, the formula unit, total ionic, and net ionic equations are given below.

• The formula unit equation is:

\[ \text{HCl}_{(aq)} + \text{NaOH}_{(aq)} \rightarrow \text{NaCl}_{(aq)} + \text{H}_2\text{O}_{(l)} \]

⇒ The total ionic equation is:

\[ \text{H}^+_{(aq)} + \text{Cl}^-_{(aq)} + \text{Na}^+_{(aq)} + \text{OH}^-_{(aq)} \rightarrow \text{Na}^+_{(aq)} + \text{Cl}^-_{(aq)} + \text{H}_2\text{O}_{(l)} \]

⇒ You do it!
The Arrhenius Theory

• What are the spectator ions in this reaction?

You do it!

Cl\textsuperscript{−}(aq) + Na\textsuperscript{+}(aq)

The net ionic equation is:

You do it!

H\textsuperscript{+}(aq) + OH\textsuperscript{−}(aq) → H\textsubscript{2}O\textsuperscript{(l)}

All strong acid-strong base reactions have this net ionic equation.
The Hydronium Ion (Hydrated Hydrogen Ion)

- The protons that are generated in acid-base reactions are not present in solution by themselves.
- Protons are surrounded by several water molecules.
  - How many varies from solution to solution.
- $H^+_{\text{(aq)}}$ is really $H(H_2O)_n^+$
  - Where $n$ is a small integer.
- Chemists normally write the hydrated hydrogen ion as $H_3O^+$ and call it the hydronium ion.
The Brønsted-Lowry Theory

- J.N. Brønsted and T.M. Lowry developed this more general acid-base theory in 1923.
- An acid is a proton donor (H\(^+\)).
- A base is a proton acceptor.
- Two examples to illustrate this concept.

\[ \text{HBr}_3 + \text{H}_2\text{O} \rightarrow \text{NH}_4^+ + \text{OBr}^- \]
The Brønsted-Lowry Theory

- Acid-base reactions are the transfer of a proton from an acid to a base.

\[
\text{HCl} + \text{NH}_3 \rightarrow \text{NH}_4^+ + \text{Cl}^-
\]

- Note that coordinate covalent bonds are often made in these acid-base reactions.
The Brønsted-Lowry Theory

• An important part of Brønsted-Lowry acid-base theory is the idea of **conjugate acid-base pairs**.
  – Two species that differ by a proton are called acid-base conjugate pairs.

• For example we can use this reaction:

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

1. Identify the reactant acid and base.  
   **You do it!**

2. Find the species that differs from the acid by a proton, that is the conjugate base.  
   **You do it!**
3. Find the species that differs from the base by a proton, that is the conjugate acid.

You do it!

- HNO₃ is the acid, conjugate base is NO₃⁻
- H₂O is the base, conjugate acid is H₃O⁺
The Brønsted-Lowry Theory

- Conjugate acid-base pairs are species that differ by a proton.
  - Some examples:
The Brønsted-Lowry Theory

• Standard format for writing conjugate acid-base pairs.

\[ HF + H_2O \rightleftharpoons H_3O^+ + F^- \]

acid\_1 base\_2 acid\_2 base\_1

HF - acid\_1 F^- - base\_1

The subscript 1's indicate the 1\textsuperscript{st} pair.

H\textsubscript{2}O - base\_2 H\textsubscript{3}O\textsuperscript{+} - acid\_2

The subscript 2's indicate the 2\textsuperscript{nd} pair.
The Brønsted-Lowry Theory

- The major differences between Arrhenius and Brønsted-Lowry theories.
  1. The reaction does not have to occur in an aqueous solution.
  2. Bases are not required to be hydroxides.
The Brønsted-Lowry Theory

• An important concept in Brønsted-Lowry theory involves the relative strengths of acid-base pairs.
  • Weak acids have strong conjugate bases.
  • Weak bases have strong conjugate acids.
  • The weaker the acid or base, the stronger the conjugate partner.
  • The reason why a weak acid is weak is because the conjugate base is so strong it reforms the original acid.
  • Similarly for weak bases.
The Brønsted-Lowry Theory

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

• Since \( \text{NH}_3 \) is a weak base, \( \text{NH}_4^+ \) must be a strong acid.
  – \( \text{NH}_4^+ \) gives up \( \text{H}^+ \) to reform \( \text{NH}_3 \).

• Compare that to
  \[
  \text{NaOH} \rightarrow \text{Na}^+ \text{(aq)} + \text{OH}^- \text{(aq)}
  \]
  – \( \text{Na}^+ \) must be a weak acid or it would recombine to form \( \text{NaOH} \)

• Remember \( \text{NaOH} \) ionizes 100%.
  \( \text{NaOH} \) is a strong base.
The Brønsted-Lowry Theory

- Amines are weak bases that behave similarly to ammonia.
- The functional group for amines is an \(-\text{NH}_2\) group attached to other organic groups.

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

\[
\text{CH}_3\text{NH}_2 + \text{H}_2\text{O} \rightleftharpoons \text{CH}_3\text{NH}_3^+ + \text{OH}^-
\]
The Autoionization of Water

• Water can be either an acid or base in Bronsted-Lowry theory.
• Consequently, water can react with itself.
  – This reaction is called autoionization.
• One water molecule acts as a base and the other as an acid.

\[
\begin{align*}
\text{H}_2\text{O} & \quad + \quad \text{H}_2\text{O} \quad \Leftrightarrow \quad \text{H}_3\text{O}^+ & \quad + \quad \text{OH}^- \\
\text{base}_1 & \quad \text{acid}_2 & \quad \text{acid}_1 & \quad \text{base}_2
\end{align*}
\]
The Autoionization of Water

- Water does not do this extensively.
  \[ [H_3O^+] = [OH^-] \approx 1.0 \times 10^{-7} \, M \]
- Autoionization is the basis of the pH scale which will be developed in Chapter 18.
Amphoterism

• Other species can behave as both acids and bases.
• Species that can behave as an acid or base are called **amphoteric**.
• Proton transfer reactions in which a species behaves as either an acid or base is called **amphiprotic**.
Amphoterism

• Examples of amphoteric species are hydroxides of elements with intermediate electronegativity.
  – Zn and Al hydroxides for example.
• Zn(OH)$_2$ behaves as a base in presence of strong acids.
Molecular equation for the reaction of zinc hydroxide with nitric acid.

\[ \text{Zn(OH)}_2 + 2 \text{HNO}_3 \rightarrow \text{Zn(NO}_3)_2 + 2 \text{H}_2\text{O} \]

- Total ionic equation – **You do it!**

\[ \text{Zn(OH)}_2 + 2\text{H}^+ + 2\text{NO}_3^- \rightarrow \text{Zn}^{2+} + 2\text{NO}_3^- + 2\text{H}_2\text{O} \]

- Net ionic equation - **You do it!**

\[ \text{Zn(OH)}_2 + 2\text{H}^+ \rightarrow \text{Zn}^{2+} + 2\text{H}_2\text{O} \]
Amphoterism

• Look at this reaction in more structural detail.
Amphoterism

- Zn(OH)$_2$ behaves as an acid in presence of strong bases.
- Molecular equation
  \[\text{Zn(OH)}_2 + 2\text{KOH} \rightarrow \text{K}_2\text{Zn(OH)}_4\]
  Zn(OH)$_2$ is insoluble until it reacts with KOH

- Total ionic equation – **You do it!**
  \[\text{Zn(OH)}_2 + 2\text{K}^+ + 2\text{OH}^- \rightarrow 2\text{K}^+ + \text{Zn(OH)}_4^{2-}\]
Amphoterism

- Net ionic equation – **You do it!**

\[
\text{Zn(OH)}_2 + 2\text{OH}^- \rightarrow \text{Zn(OH)}_4^{2-}
\]

- In more structural detail.
Strengths of Acids

- For **binary acids**, acid strength increases with decreasing H-X bond strength.
- For example, the hydrohalic binary acids
- Bond strength has this periodic trend.
  \[ \text{HF} > \text{HCl} > \text{HBr} > \text{HI} \]
- Acid strength has the reverse trend.
  \[ \text{HF} < \text{HCl} < \text{HBr} < \text{HI} \]
Strengths of Acids

• The same trend applies to the VIA hydrides.
• Their bond strength has this trend.
  \[ \text{H}_2\text{O} \gg \text{H}_2\text{S} > \text{H}_2\text{Se} > \text{H}_2\text{Te} \]
• The acid strength is the reverse trend.
  \[ \text{H}_2\text{O} \ll \text{H}_2\text{S} < \text{H}_2\text{Se} < \text{H}_2\text{Te} \]
Strengths of Acids

• The acid leveling effect masks the differences in acid strength of the hydrohalic acids.
  – The strongest acid that can exist in water is H$_3$O$^+$. 
• Acids that are stronger than H$_3$O$^+$ merely react with water to produce H$_3$O$^+$.
• Consequently all strong soluble acids have the same strength in water.

$$\text{HI} + \text{H}_2\text{O} \rightarrow \text{H}_3\text{O}^+ + \text{I}^-$$

essentially 100%
Strengths of Acids

• HBr, which should be a weaker acid, has the same strength in water as HI.

\[
\text{HBr} + \text{H}_2\text{O} \rightarrow \text{H}_3\text{O}^+ + \text{Br}^-
\]

essentially 100%

• Acid strength differences for strong acids can only be distinguished in nonaqueous solutions like acetic acid, acetone, etc.
Using our knowledge of Brønsted-Lowry theory, it is possible to construct a relative ranking of acid and base strengths (and their conjugate partners.)

<table>
<thead>
<tr>
<th>Strongest Acid</th>
<th>Weakest Base</th>
</tr>
</thead>
<tbody>
<tr>
<td>HClO₄</td>
<td>ClO₄⁻</td>
</tr>
<tr>
<td>H₃O⁺</td>
<td>H₂O</td>
</tr>
<tr>
<td>CH₃COOH</td>
<td>CH₃COO⁻</td>
</tr>
<tr>
<td>HCN</td>
<td>CN⁻</td>
</tr>
<tr>
<td>H₂O</td>
<td>OH⁻</td>
</tr>
<tr>
<td>NH₃</td>
<td>NH₂⁻</td>
</tr>
</tbody>
</table>

- HClO₄ is the strongest acid and ClO₄⁻ is the weakest base.
- H₃O⁺ is the acid that loses H⁺ and H₂O is the base that gains H⁺.
Strengths of Acids

- It is possible to do this for essentially every acid and base (and their partners).

<table>
<thead>
<tr>
<th>Acid</th>
<th>Base</th>
</tr>
</thead>
<tbody>
<tr>
<td>HClO₄</td>
<td>ClO₄⁻</td>
</tr>
<tr>
<td>HI</td>
<td>I⁻</td>
</tr>
<tr>
<td>HBr</td>
<td>Br⁻</td>
</tr>
<tr>
<td>HCl</td>
<td>Cl⁻</td>
</tr>
<tr>
<td>HNO₃</td>
<td>NO₃⁻</td>
</tr>
</tbody>
</table>

**TABLE 10-2  Relative Strengths of Conjugate Acid–Base Pairs**

- Acid loses H⁺ when it is complete.
- Base gains H⁺ when it is complete.

<table>
<thead>
<tr>
<th>Acid</th>
<th>Base</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₃O⁺</td>
<td>H₂O</td>
</tr>
<tr>
<td>HF</td>
<td>F⁻</td>
</tr>
<tr>
<td>CH₃COOH</td>
<td>CH₃COO⁻</td>
</tr>
<tr>
<td>HCN</td>
<td>CN⁻</td>
</tr>
<tr>
<td>NH₄⁺</td>
<td>NH₃</td>
</tr>
<tr>
<td>H₂O</td>
<td>OH⁻</td>
</tr>
<tr>
<td>NH₃</td>
<td>NH₂⁻</td>
</tr>
</tbody>
</table>

Equilibrium mixture of nonionized molecules of acid, conjugate base, and H⁺(aq).
Strengths of Acids

• The strongest acid that can exist in water is $\text{H}_3\text{O}^+$. 

\[
\text{HCl} + \text{H}_2\text{O} \rightarrow \text{H}_3\text{O}^+ + \text{Cl}^-
\]
– HCl is strong enough that it forces water to accept $\text{H}^+$.

• The strongest base that can exist in water is $\text{OH}^-$. 

\[
\text{NH}_2^- + \text{H}_2\text{O} \rightarrow \text{NH}_3 + \text{OH}^-
\]
– $\text{NH}_2^-$ is strong enough to remove $\text{H}^+$ from water.

• The reason that stronger acids and bases cannot exist in water is that water is amphiprotic.
Strengths of Acids

• Ternary acids are hydroxides of nonmetals that produce $\text{H}_3\text{O}^+$ in water.
  – Consist of H, O, and a nonmetal.

• $\text{HClO}_4$  
  
• $\text{H}_3\text{PO}_4$  

![Ternary acid structures](image-url)
Strengths of Acids

- $\text{HClO}_4$
- $\text{H}_3\text{PO}_4$

Bonds which must break for these compounds to be acidic

Acidic protons
Strengths of Acids

- It is a very common mistake for students to not realize that the H’s are attached to O atoms in ternary acids.
  - Just because chemists write them as $\text{HClO}_4$. 

![Chemical structures](image)
Strengths of Acids

• Remember that for binary acids, acid strength increased with decreasing H-X bond strength.
• Ternary acids have the same periodic trend.
• Strong ternary acids have weaker H-O bonds than weak ternary acids.
• For example, compare acid strengths:
  \[ \text{HNO}_2 < \text{HNO}_3 \quad \text{H}_2\text{SO}_3 < \text{H}_2\text{SO}_4 \]
• This implies that the H-O bond strength is:
  \[ \text{You do it!} \]
  \[ \text{HNO}_2 > \text{HNO}_3 \quad \text{H}_2\text{SO}_3 > \text{H}_2\text{SO}_4 \]
Strengths of Acids

• Ternary acid strength usually increases with:
  1. an increasing number of O atoms on the central atom and
  2. an increasing oxidation state of central atom.
• Effectively, these are the same phenomenon.
  – Every additional O atom increases the oxidation state of the central atom by 2.
Strengths of Acids

• For ternary acids having the same central atom:
  the **highest oxidation state** of the central atom is **usually strongest acid**.

• For example, look at the strength of the Cl ternary acids.

  \[
  \text{HClO} < \text{HClO}_2 < \text{HClO}_3 < \text{HClO}_4
  \]

  weakest                      strongest

  Cl oxidation states

  \[
  +1 \quad +3 \quad +5 \quad +7
  \]
There are four acid-base reaction combinations that are possible:
1. Strong acids – strong bases
2. Weak acids – strong bases
3. Strong acids – weak bases
4. Weak acids – weak bases

Let us look at one example of each acid-base reaction.
Acid-Base Reactions in Aqueous Solutions

1. Strong acids - strong bases
   - forming soluble salts

   • This is one example of several possibilities
     hydrobromic acid + calcium hydroxide

   • The molecular equation is:

     \[ 2 \text{HBr}_{\text{aq}} + \text{Ca(OH)}_{2\text{aq}} \rightarrow \text{CaBr}_2_{\text{aq}} + 2 \text{H}_2\text{O}_{(\ell)} \]
Acid-Base Reactions in Aqueous Solutions

• The total ionic equation is:

   \[
   2\text{H}^+_{(aq)} + 2\text{Br}^-_{(aq)} + \text{Ca}^{2+}_{(aq)} + 2\text{OH}^-_{(aq)} \rightarrow \text{Ca}^{2+}_{(aq)} + 2\text{Br}^-_{(aq)} + 2\text{H}_2\text{O}_{(l)}
   \]

• The net ionic equation is:

   \[
   2\text{H}^+_{(aq)} + 2\text{OH}^-_{(aq)} \rightarrow 2\text{H}_2\text{O}_{(l)}
   \]

   or

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

This net ionic equation is the same for all strong acid - strong base reactions that form soluble salts.
1. Strong acids-strong bases
   - forming **insoluble** salts

- There is only one reaction of this type:
  sulfuric acid + barium hydroxide

- The molecular equation is:

  \[
  \text{You do it!} \\
  \text{H}_2\text{SO}_4(aq) + \text{Ba(OH)}_2(aq) \rightarrow \text{BaSO}_4(s) + 2\text{H}_2\text{O}(l)
  \]
Acid-Base Reactions in Aqueous Solutions

• The total ionic equation is:

You do it!

\[ 2\text{H}^+_{(aq)} + \text{SO}_4^{2-}_{(aq)} + \text{Ba}^{2+}_{(aq)} + 2\text{OH}^-_{(aq)} \rightarrow \text{BaSO}_4(s) + 2\text{H}_2\text{O}(l) \]

• The net ionic equation is:

You do it!

\[ 2\text{H}^+_{(aq)} + \text{SO}_4^{2-}_{(aq)} + \text{Ba}^{2+}_{(aq)} + 2\text{OH}^-_{(aq)} \rightarrow \text{BaSO}_4(s) + 2\text{H}_2\text{O}(l) \]
2. Weak acids - strong bases
   – forming soluble salts

• This is one example of many possibilities: nitrous acid + sodium hydroxide

• The molecular equation is:

   \[
   \text{HNO}_2(\text{aq}) + \text{NaOH}(\text{aq}) \rightarrow \text{NaNO}_2(\text{aq}) + \text{H}_2\text{O}(\ell)
   \]
Acid-Base Reactions in Aqueous Solutions

• The total ionic equation is:
  – Reminder – there are 3 types of substances that are written as ionized in total and net ionic equations.
    1. Strong acids
    2. Strong bases
    3. Strongly water soluble salts

  You do it!

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

• The net ionic equation is:

  You do it!

  \[
  \text{HNO}_2(aq) + \text{OH}^-(aq) \rightarrow \text{NO}_2^-(aq) + \text{H}_2\text{O}(	ext{l})
  \]
3. Strong acids - weak bases
   - forming soluble salts

   • This is one example of many.
     nitric acid + ammonia

   • The molecular equation is:

     \[
     \text{HNO}_3(aq) + \text{NH}_3(aq) \rightarrow \text{NH}_4\text{NO}_3(aq)
     \]
Acid-Base Reactions in Aqueous Solutions

• The total ionic equation is:

\[ \text{You do it!} \]

\[ \text{H}^+_{(aq)} + \text{NO}_3^{-}_{(aq)} + \text{NH}_3_{(aq)} \rightarrow \text{NH}_4^+_{(aq)} + \text{NO}_3^{-}_{(aq)} \]

• The net equation is:

\[ \text{You do it!} \]

\[ \text{H}^+_{(aq)} + \text{NH}_3_{(aq)} \rightarrow \text{NH}_4^+_{(aq)} \]
Acid-Base Reactions in Aqueous Solutions

4. Weak acids - weak bases
   – forming soluble salts

• This is one example of many possibilities.
  acetic acid + ammonia

• The molecular equation is:

  \[ \text{CH}_3\text{COOH}_{(aq)} + \text{NH}_3_{(aq)} \rightarrow \text{NH}_4\text{CH}_3\text{COO}_{(aq)} \]

You do it!
Acid-Base Reactions in Aqueous Solutions

• The total ionic equation is:

You do it!

$$\text{CH}_3\text{COOH}_{(aq)} + \text{NH}_3_{(aq)} \rightarrow \text{NH}_4^+_{(aq)} + \text{CH}_3\text{COO}^-_{(aq)}$$

• The net ionic equation is:

You do it!

$$\text{CH}_3\text{COOH}_{(aq)} + \text{NH}_3_{(aq)} \rightarrow \text{NH}_4^+_{(aq)} + \text{CH}_3\text{COO}^-_{(aq)}$$
Acidic Salts and Basic Salts

- Acidic salts are formed by the reaction of polyprotic acids with less than the stoichiometric amount of base.
- For example, if sulfuric acid and sodium hydroxide are reacted in a 1:1 ratio.
  \[ \text{H}_2\text{SO}_4(\text{aq}) + \text{NaOH}(\text{aq}) \rightarrow \text{NaHSO}_4(\text{aq}) + \text{H}_2\text{O}(\ell) \]
  The acidic salt sodium hydrogen sulfate is formed.
- If sulfuric acid and sodium hydroxide are reacted in a 1:2 ratio.
  \[ \text{H}_2\text{SO}_4(\text{aq}) + 2\text{NaOH}(\text{aq}) \rightarrow \text{Na}_2\text{SO}_4(\text{aq}) + 2\text{H}_2\text{O}(\ell) \]
  The normal salt sodium sulfate is formed.
Acidic Salts and Basic Salts

• Similarly, basic salts are formed by the reaction of polyhydroxy bases with less than the stoichiometric amount of acid.

• If barium hydroxide and hydrochloric acid are reacted in a 1:1 ratio.

\[
\text{Ba(OH)}_2(\text{aq}) + \text{HCl}(\text{aq}) \rightarrow \text{Ba(OH)Cl}(\text{aq}) + \text{H}_2\text{O}(\ell)
\]

The basic salt is formed.

• If the reaction is in a 1:2 ratio.

\[
\text{Ba(OH)}_2(\text{aq}) + 2\text{HCl}(\text{aq}) \rightarrow \text{BaCl}_2(\text{aq}) + 2\text{H}_2\text{O}(\ell)
\]

The normal salt is formed.
Acidic Salts and Basic Salts

• Both acidic and basic salts can neutralize acids and bases.
  – However the resulting solutions are either acidic or basic because they form conjugate acids or bases.
    • Another example of Brønsted-Lowry theory.
    • This is an important concept in understanding buffers.

• An acidic salt neutralization example is:
  \[ \text{NaHSO}_4(\text{aq}) + \text{NaOH}(\text{aq}) \rightarrow \text{Na}_2\text{SO}_4(\text{aq}) + \text{H}_2\text{O}(\ell) \]

• A basic salt neutralization example is:
  \[ \text{Ba(OH)Cl}(\text{aq}) + \text{HCl}(\text{aq}) \rightarrow \text{BaCl}_2(\text{aq}) + \text{H}_2\text{O}(\ell) \]
The Lewis Theory

• Developed in 1923 by G.N. Lewis.
  – This is the most general of the present day acid-base theories.
  – Emphasis on what the electrons are doing as opposed to what the protons are doing.

• Acids are defined as **electron pair acceptors**.
• Bases are defined as **electron pair donors**.
• Neutralization reactions are accompanied by coordinate covalent bond formation.
The Lewis Theory

• One Lewis acid-base example is the ionization of ammonia.

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

base acid
The Lewis Theory

- Look at this reaction in more detail paying attention to the electrons.

Base - it donates the electron pair

Acid - it accepts the electron pair

Notice that a coordinate covalent bond is formed on the ammonium ion.
The Lewis Theory

• A second example is the ionization of HBr.

\[ \text{HBr} + \text{H}_2\text{O} \rightarrow \text{H}_3\text{O}^+ + \text{Br}^- \]

acid base
The Lewis Theory

• Again, a more detailed examination keeping our focus on the electrons.

Acid - it accepts the electron pair
Base - it donates the electron pair

covalent coordinate bond formed
The Lewis Theory

- A third Lewis example is the autoionization of water.

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

You do it

acid     base
The Lewis Theory

• The reaction of sodium fluoride and boron trifluoride provides an example of a reaction that is only a Lewis acid-base reaction.
  – It does not involve H⁺ at all, thus it cannot be an Arrhenius nor a Brønsted-Lowry acid-base reaction.
    \[ \text{NaF} + \text{BF}_3 \rightarrow \text{Na}^+ + \text{BF}_4^- \]

• You must draw the detailed picture of this reaction to determine which is the acid and which is the base.
The Lewis Theory

Base - it donates the electron pair
Acid - it accepts the electron pair
coordinate covalent bond formed
The Lewis Theory

- BF$_3$ is a strong Lewis acid. Another example of it reacting with NH$_3$ is shown in this movie.
Acid-Base Theories

- Look at the reaction of ammonia and hydrobromic acid.
  \[ \text{NH}_3 + \text{HBr} \rightarrow \text{NH}_4^+ + \text{Br}^- \]
- Is this reaction an example of:
  1. Arrhenius acid-base reaction,
  2. Brønsted-Lowry acid base reaction,
  3. Lewis acid-base reaction,
  4. or a combination of these?

  **You do it!**

- It is a Lewis and Brønsted-Lowry acid base reaction but not Arrhenius.
Acid-Base Theories

• Arrhenius, Brønsted-Lowry, and Lewis Acid-Base Theories expand on one another.
The Preparation of Acids

• The binary acids are prepared by reacting the nonmetallic element with \( \text{H}_2 \).

\[
\text{H}_2(\text{g}) + \text{Cl}_2(\text{g}) \rightarrow 2\text{HCl}(\text{g})
\]

This reaction is performed in the presence of UV light.

• Volatile acids, ones with low boiling points, are prepared by reacting salts with a nonvolatile acid like sulfuric or phosphoric.

\[
\text{NaCl}_(\text{s}) + \text{H}_2\text{SO}_4(\text{conc.}) \rightarrow \text{NaHSO}_4(\text{s}) + \text{HCl}(\text{g})
\]

\[
\text{NaF}_(\text{s}) + \text{H}_2\text{SO}_4(\text{conc.}) \rightarrow \text{NaHSO}_4(\text{s}) + \text{HF}(\text{g})
\]
The Preparation of Acids

• We must use phosphoric acid to make HBr and HI.

\[
\text{NaBr}_\text{(s)} + \text{H}_3\text{PO}_4\text{(conc.)} \rightarrow \text{NaH}_2\text{PO}_4\text{(s)} + \text{HBr}_\text{(g)}
\]

\[
\text{NaI}_\text{(s)} + \text{H}_3\text{PO}_4\text{(conc.)} \rightarrow \text{NaH}_2\text{PO}_4\text{(s)} + \text{HI}_\text{(g)}
\]
The Preparation of Acids

- Ternary acids are made by reacting nonmetal oxides (acid anhydrides) with water.
  \[ \text{SO}_2(g) + \text{H}_2\text{O}(\ell) \rightarrow \text{H}_2\text{SO}_3(\text{aq}) \]
  \[ \text{N}_2\text{O}_5(g) + \text{H}_2\text{O}(\ell) \rightarrow 2 \text{HNO}_3(\text{aq}) \]

- Some nonmetal halides and oxyhalides react with water to give both a binary and a ternary acid.
  \[ \text{PCl}_5(s) + 4 \text{H}_2\text{O}(\ell) \rightarrow \text{H}_3\text{PO}_4(\text{aq}) + 5 \text{HCl}(\text{aq}) \]
  \[ \text{POCl}_3(\ell) + 3 \text{H}_2\text{O}(\ell) \rightarrow \text{H}_3\text{PO}_4(\text{aq}) + 3 \text{HCl}(\text{aq}) \]
Synthesis Question

• One method of increasing the solubility and the absorption of a medication is to convert weakly acidic drugs into sodium salts before making the pills that will be ingested. How does this preparation method enhance the drug’s solubility in the stomach?
• The sodium salt of a weakly acidic compound is a strong conjugate base. In the presence of stomach fluids, ~ 1.0 M HCl, the conjugate base readily reacts with the HCl generating the active and soluble form of the medication.
• Medicines that are weakly basic are not absorbed well into the bloodstream. One method to increase their absorption is to take an antacid at the same time that the medicine is administered. How does this method increase the absorption?
10
Reactions in Aqueous Solutions I: Acids, Bases & Salts