CHAPTER 10

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
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, $\text{H}_2(\text{g})$.
  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 Three theories we will be discussing include:

<table>
<thead>
<tr>
<th>The Arrhenius Theory</th>
<th>The Brønsted-Lowry Theory</th>
<th>The Lewis Theory</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Acids are substances that contain hydrogen</strong></td>
<td><strong>An acid is a proton donor (H(^{+}))</strong></td>
<td><strong>Acids are electron pair acceptors</strong></td>
</tr>
<tr>
<td><strong>Bases are substances that contain hydroxyl, OH, group</strong></td>
<td><strong>A base is a proton acceptor</strong></td>
<td><strong>Bases are electron pair donors</strong></td>
</tr>
<tr>
<td>HCl and NaOH</td>
<td>NH(_3) and H(_2)O</td>
<td>BF(_3) and NH(_3)</td>
</tr>
</tbody>
</table>
The Arrhenius Theory

- Svante Augustus Arrhenius first presented this theory of acids and bases in 1884.
- Acids are substances that contain hydrogen and produces $\text{H}^+$ in aqueous solutions (HCl, CH$_3$COOH).
- Bases are substances that contain the hydroxyl, OH, group and produce hydroxide ions, OH$^-$, in aqueous solutions (NaOH).
The protons that are generated in acid-base reactions are not present in solution by themselves.

Protons are surrounded by several water molecules.

$H^+_{(aq)}$ is really $H(H_2O)_n^+$, where $n$ is a small integer.

Chemists normally write the hydrated hydrogen ion as $H_3O^+$ ($n = 1$) 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.

![Chemical diagram showing proton transfer between an acid and a base.](image)
The Brønsted-Lowry Theory

\[
\text{H}_2\text{O}(\ell) + \text{HF}(\text{aq}) \rightleftharpoons \text{H}_3\text{O}^+ + \text{F}^-(\text{aq})
\]
The Brønsted-Lowry Theory

$$\text{NH}_3(\text{aq}) + \text{H}_2\text{O}(\ell) \rightleftharpoons \text{NH}_4^+(\text{aq}) + \text{OH}^-(\text{aq})$$

- base$_1$
- acid$_2$
- acid$_1$
- base$_2$

- ammonia
- water
- ammonium ion
- hydroxide ion

Trigonal pyramidal molecule
Angular molecule
Tetrahedral ion
Linear ion
The Brønsted-Lowry Theory

- An important part of Brønsted-Lowry acid-base theory is the idea of \textit{conjugate acid-base pairs}.
- Two species that differ by a proton are called acid-base conjugate pairs.

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

1. Identify the reactant acid and base.
2. Find the species that differs from the acid by a proton, that is the conjugate base.
3. Find the species that differs from the base by a proton, that is the conjugate acid.

- \text{HNO}_3 \text{ is the acid, conjugate base is NO}_3^-
- \text{H}_2\text{O} \text{ is the base, conjugate acid is H}_3\text{O}^+
The Brønsted-Lowry Theory

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

- Standard format for writing conjugate acid-base pairs.

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

\[ \text{acid}_1 \text{ base}_2 \quad \text{acid}_2 \quad \text{base}_1 \]

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

The subscript 1's indicate the 1\(^{st}\) pair.

\[ H_2O - \text{base}_2 \quad H_3O^+ - \text{acid}_2 \]

The subscript 2's indicate the 2\(^{nd}\) 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.

\[ \text{NH}_3 + \text{HBr} \rightarrow \text{NH}_4^+ + \text{Br}^- \]
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 NH\textsubscript{3} is a weak base, NH\textsubscript{4}\textsuperscript{+} must be a strong acid.
- NH\textsubscript{4}\textsuperscript{+} gives up H\textsuperscript{+} to reform NH\textsubscript{3}.
- Compare that to

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

- Na\textsuperscript{+} must be a weak acid or it would recombine to form NaOH
- Remember NaOH ionizes 100\%. NaOH is a strong base.
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 (self-ionization).
- One water molecule acts as a base and the other as an acid.

\[
\text{H}_2\text{O} \quad + \quad \text{H}_2\text{O} \quad \overset{\text{\rightarrow}}{\text{\rightleftharpoons}} \quad \text{H}_3\text{O}^+ \quad + \quad \text{OH}^- \\
\text{base}_1 \quad \text{acid}_2 \quad \text{acid}_1 \quad \text{base}_2
\]
The Autoionization of Water

Autoionization is the basis of the pH scale which will be developed in Chapter 18.
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**.
The Lewis Theory

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

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

acid   base

You do it
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.

\[
\text{NaF} + \text{BF}_3 \rightarrow \text{Na}^+ + \text{BF}_4^-
\]
The Lewis Theory

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

A second example:
\[ \text{AlCl}_3 + \text{Cl}^- \rightarrow [\text{AlCl}_4]^- \]
The Lewis Theory

**BF₃** is a strong Lewis acid.

![Diagrams showing Lewis acid, Lewis base, and acid-base adduct reactions](image-url)
The Lewis Theory

- 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.
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.

\[ \text{HF} \gg \text{HCl} > \text{HBr} > \text{HI} \]

Acid strength has the reverse trend.

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

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.

\[ \text{H}_2\text{O} << \text{H}_2\text{S} < \text{H}_2\text{Se} < \text{H}_2\text{Te} \]
<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>
<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>

Acid strength increases from top to bottom, base strength increases from right to left.

Acid loses H⁺ when it donates a proton. Base gains H⁺ when it accepts a proton.

HClO₄⁻ is 100% ionized in dilute aqueous solution. There are no molecules of nonionized acid.

Negligible base strength in water.

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

Reacts completely with H₂O to form OH⁻; cannot exist in aqueous solution.
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.

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

- 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 $\text{HClO}_4$. 
**Strengths of Acids**

Ternary acids are hydroxides of nonmetals that produce $\text{H}_3\text{O}^+$ in water.

Bond that breaks to form $\text{H}^+$ and $\text{NO}_3^-$

Hydroxyl group

\[
\begin{align*}
\text{O} & \quad \text{N} \\
\text{O} & \quad \text{O} \quad \text{H}
\end{align*}
\]
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:
  \[ \text{HNO}_2 > \text{HNO}_3 \quad \text{H}_2\text{SO}_3 > \text{H}_2\text{SO}_4 \]
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

- 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 the strongest acid.

- For example, \( \text{HClO} < \text{HClO}_2 < \text{HClO}_3 < \text{HClO}_4 \)

  - weakest
  - strongest

  Cl oxidation states

  - +2
  - +4
  - +6
  - +8

  ![Molecular structures of HClO, HClO₂, HClO₃, HClO₄](images)
Strengths of Acids

- For most ternary acids containing different elements in the same group in the periodic table, acid strengths increase with increasing electronegativity of the central element.

- For example, \( \text{H}_2\text{SeO}_4 < \text{H}_2\text{SO}_4 \)
  \( \quad \text{H}_2\text{SeO}_3 < \text{H}_2\text{SO}_3 \)
  \( \quad \text{HBrO}_4 < \text{HClO}_4 \)
  \( \quad \text{HBrO}_3 < \text{HClO}_3 \)
Acid-Base Reactions in Aqueous Solutions

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.
1. **Strong acids - strong bases**

- forming **soluble** salts
- The molecular equation is:

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

- The total ionic equation is:
\[ 2H^+_{(aq)} + 2Br^-_{(aq)} + Ca^{2+}_{(aq)} + 2OH^-_{(aq)} \rightarrow Ca^{2+}_{(aq)} + 2Br^-_{(aq)} + 2H_2O_{(l)} \]

- The net ionic equation is:
\[ 2H^+_{(aq)} + 2OH^-_{(aq)} \rightarrow 2H_2O_{(l)} \]

or
\[ H^+_{(aq)} + OH^-_{(aq)} \rightarrow H_2O_{(l)} \]

This net ionic equation is the same for all strong acid - strong base reactions that form soluble salts.
Acid-Base Reactions in Aqueous Solutions

1. **Strong acids-strong bases**
   - forming **insoluble** salts
   - There is only one reaction of this type:
   - The molecular equation is:

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

- The total ionic equation is:

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

- The net ionic equation is:

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

2. Weak acids - strong bases
   - forming soluble salts
   - This is one example of many possibilities:
   - The molecular equation is:

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

The total ionic equation is:

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

The net ionic equation is:

\[ \text{HNO}_2(aq) + \text{OH}^-(aq) \rightarrow \text{NO}_2^-(aq) + \text{H}_2\text{O}(\ell) \]
Acid-Base Reactions in Aqueous Solutions

3. Strong acids - weak bases
   - forming **soluble** salts
   - This is one example of many.
   - 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:

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

- The net equation is:

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

4. Weak acids - weak bases
   - forming soluble salts
   - This is one example of many possibilities.

   The molecular equation is:

   $$\text{CH}_3\text{COOH}_{(aq)} + \text{NH}_3_{(aq)} \rightarrow \text{NH}_4\text{CH}_3\text{COO}_{(aq)}$$
Acid-Base Reactions in Aqueous Solutions

- The total ionic equation is:

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

- The net ionic equation is:

\[ \text{CH}_3\text{COOH}_{(aq)} + \text{NH}_3_{(aq)} \rightarrow \text{NH}_4^+_{(aq)} + \text{CH}_3\text{COO}^-_{(aq)} \]
Many medicines are deliberately made as conjugate acids or bases so that they become active ingredients after passage through the stomach.
Homework Assignment

One-line Web Learning (OWL):

Chapter 10 Exercises and Tutors –

Optional