Chapter 10  Reactions in Aqueous Solutions I: Acids, Bases + Salts

This chapter is a continuation of Chapter 4 in the discussion of acids and bases. It emphasizes the opposite nature of acids and bases in the discussion of different theories to explain what acids and bases are and how they react.

Let us consider properties of acids and bases

aqueous solutions of acids (containing H⁺)
  • sour taste (vinegar is dilute acetic acid, CH₃COOH)
  • change colors of indicators
  • non-oxidizing acids react with active metals to liberate H₂
  • react with metal oxides, metal hydroxides, yielding salt and water
  • react with carbonates, yielding CO₂ (test for carbonate minerals)
  • conduct electricity, because they ionize in water

aqueous solutions of bases (containing OH⁻)
  • bitter taste (Alka-Seltzer and other antacids, baking soda)
  • slimy to touch (base + natural oils on fingers → soap)
  • change colors of indicators
  • neutralize protonic acids, yielding salt and water
  • conduct electricity, because they ionize in water

One primary chemical property of acids and bases is that they react together - neutralize each other - to yield a salt and water (only salt if base is NH₃). So all of the theories define acids and bases in the same general context, as we shall see.

The 3 theories we will be discussing include

1. Arrhenius (1884)  most simplistic - solvent must be H₂O
2. Bronsted-Lowry (1923) involves protons
3. Lewis (1923) involves electron pairs
1. **Arrhenius Theory of Acid-Base Behavior**

**Examples**
- HCl, CH₃COOH
- NaOH, Cu(OH)₂

**acid:** species that contains H and produces H⁺ in aqueous solution

**base:** species that contains OH and produces OH⁻ in aqueous solution

**acid-base reaction:** reaction where H⁺ and OH⁻ combine to form H₂O.

(neutralization)

\[ H^+(aq) + OH^-(aq) \rightarrow H_2O(l) \]

**Note:** it is realized now that H⁺(aq) does not exist as such. It is hydrated in water:

\[ H^+ + nH₂O \rightarrow H^+(H₂O)_n \]

We represent this in equations by using the hydronium ion, H₃O⁺.

(In all of our balancing equations, though, it is easier to use H⁺.)

2. **Bronsted-Lowry Theory**

**acid:** a substance that donates a proton, H⁺ i.e. a proton donor

:**any substance containing hydrogen is a B.-L. acid.**

**base:** a substance that accepts a proton i.e. a proton acceptor.

**acid-base reaction:** reaction in which a proton is transferred from an acid to a base.

Bronsted-Lowry theory is more general than Arrhenius theory: NH₃ is considered a base even though it has no OH group, because it accepts H⁺.

\[ \text{Reaction} \]

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

Bronsted-Lowry acid-base reactions can be described in terms of CONJUGATE ACID-BASE PAIRS. These are species on opposite sides of the equation that differ by a proton (H⁺).
\[ HF (g) + H_2O (l) \rightarrow H_3O^+ + F^- \]

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

\[ \therefore \text{HF, } F^- \text{ and } H_3O^+, H_2O \text{ are conjugate acid base pairs.} \]

\[ \therefore \text{NH}_3, \text{NH}_4^+ \text{ and } H_2O, \text{OH}^- \text{ are also conjugate acid base pairs.} \]

**Note:** water can act as a base and as an acid in aqueous solution. It is called **AMPHOTERIC**. When the transfer involves a proton, the term is amphiprotic.

**IONIZATION OF WATER**

\[ H_2O + H_2O \rightleftharpoons H_3O^+ + OH^- \]

(examples of autoionization)

<table>
<thead>
<tr>
<th>ACID</th>
<th>CONJUGATE BASE</th>
</tr>
</thead>
<tbody>
<tr>
<td>HCl</td>
<td>Cl^-</td>
</tr>
<tr>
<td>CH₃COOH</td>
<td>CH₃COO⁻</td>
</tr>
<tr>
<td>H₂SO₄</td>
<td>HSO₄⁻</td>
</tr>
<tr>
<td>HClO₄</td>
<td>ClO₄⁻</td>
</tr>
<tr>
<td>H₂O</td>
<td>OH⁻</td>
</tr>
<tr>
<td>H₃O⁺</td>
<td>H₂O (not exist)</td>
</tr>
<tr>
<td>NH₃</td>
<td>NH₂⁻ (in water)</td>
</tr>
<tr>
<td>NH₄⁺</td>
<td>NH₃</td>
</tr>
<tr>
<td>HSO₄⁻</td>
<td>SO₄²⁻</td>
</tr>
</tbody>
</table>

Examples of conjugate acid-base pairs:

See also Table 10-1

How strong are these acids and their conjugate bases?

The stronger the acid, the more it wants to donate a proton.

The stronger the base, the more it wants to accept a proton.

**Generalization:** The weaker an acid is, the greater is the base strength of its conjugate base. The weaker a base is, the greater is the acid strength of its conjugate acid.
Example: \( \text{HF} \) is a weak acid \( \rightarrow \) \( \text{F}^- \) is a stronger base (it wants an \( \text{H}^+ \))
\( \text{HNO}_3 \) is a strong acid \( \rightarrow \) \( \text{NO}_3^- \) is a very weak base (it does not want \( \text{H}^+ \))

\( \text{NH}_3 \) is a weak base \( \rightarrow \) \( \text{NH}_4^+ \) is a stronger acid (it wants to lose \( \text{H}^+ \))
\( \text{OH}^- \) is a strong base \( \rightarrow \) \( \text{H}_2\text{O} \) is a very weak acid (does not want to lose \( \text{H}^+ \))

**Relative Strengths of Binary (2 element) Acids**

Strong acids want to lose (donate) protons \( \rightarrow \) they ionize \( \approx 100\% \)
\( \therefore \) therefore the \( \text{H-X} \) bond is very weak, and breaks in aqueous solution

Bond strength can be predicted from the electronegativity difference of the two atoms.

<table>
<thead>
<tr>
<th>( \text{H-F} )</th>
<th>( \text{H-Cl} )</th>
<th>( \text{H-Br} )</th>
<th>( \text{H-I} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \Delta\text{EN} )</td>
<td>1.9</td>
<td>0.9</td>
<td>0.7</td>
</tr>
</tbody>
</table>

order of bond strength: \( \text{HF} \gg \text{HCl} > \text{HBr} > \text{HI} \)

order of acid strength: \( \text{HF} \ll \text{HCl} < \text{HBr} < \text{HI} \)

similarly,

order of acid strength: \( \text{H}_2\text{O} \ll \text{H}_2\text{S} < \text{H}_2\text{Se} < \text{H}_2\text{Te} \)

**Reactions of Acids and Bases**

Let us first review formula unit, total ionic and net ionic equations.
Recall: the only substances that dissociate totally into ions are the strong electrolytes: strong acids, strong soluble bases, soluble salts. (Chapter 4)

**Example:** reaction of nitric acid and copper(II) hydroxide

- *strong acid*  \( 2\text{HNO}_3(\text{aq}) + \text{Cu(OH)}_2(\text{s}) \rightarrow \text{Cu(NO}_3)_2(\text{aq}) + 2\text{H}_2\text{O( l)} \)
- *insoluble base*  \( \text{Cu(OH)}_2(\text{s}) \)
- *soluble salt*  \( \text{Cu(NO}_3)_2(\text{aq}) \)

*Total Ionic:*  \( 2\text{H}^+(\text{aq}) + 2\text{NO}_3^-(\text{aq}) + \text{Cu(OH)}_2(\text{s}) \rightarrow \text{Cu}^{2+}(\text{aq}) + 2\text{NO}_3^-(\text{aq}) + 2\text{H}_2\text{O(l)} \)

*Net Ionic:*  \( 2\text{H}^+(\text{aq}) + \text{Cu(OH)}_2(\text{s}) \rightarrow \text{Cu}^{2+}(\text{aq}) + 2\text{H}_2\text{O(l)} \)

(spectator ions are cancelled out)
These acid-base stoichiometric reactions yielded normal salts, containing no unreacted \( \text{H}^+ \) or \( \text{OH}^- \) ions. If amounts of acids and bases are combined in proportions other than stoichiometric amounts, acidic salts or basic salts are the result (Nomenclature: Chapter 7).

**Acidic Salt**: (acidic because it can neutralize a base)

\[
\begin{align*}
\text{H}_3\text{PO}_4 + \text{NaOH} & \rightarrow \text{NaH}_2\text{PO}_4 + \text{H}_2\text{O} \\
1\text{ mol} + 1\text{ mol} & \rightarrow \text{NaH}_2\text{PO}_4 + \text{H}_2\text{O} \\
\text{sodium dihydrogen phosphate} & \text{acidic salt}
\end{align*}
\]

\[
\begin{align*}
\text{H}_3\text{PO}_4 + 2\text{NaOH} & \rightarrow \text{Na}_2\text{HPO}_4 + 2\text{H}_2\text{O} \\
1\text{ mol} + 2\text{ mol} & \rightarrow \text{Na}_2\text{HPO}_4 + 2\text{H}_2\text{O} \\
\text{sodium hydrogen phosphate} & \text{acidic salt}
\end{align*}
\]

\[
\begin{align*}
\text{H}_3\text{PO}_4 + 3\text{NaOH} & \rightarrow \text{Na}_3\text{PO}_4 + 3\text{H}_2\text{O} \\
1\text{ mol} + 3\text{ mol} & \rightarrow \text{Na}_3\text{PO}_4 + 3\text{H}_2\text{O} \\
\text{sodium phosphate} & \text{normal salt}
\end{align*}
\]

**Basic Salt**: (basic because it can neutralize an acid)

\[
\begin{align*}
\text{Al(OH)}_3(s) + \text{HCl} & \rightarrow \text{Al(OH)}_2\text{Cl} + \text{H}_2\text{O} \\
1\text{ mol} + 1\text{ mol} & \rightarrow \text{Al(OH)}_2\text{Cl} + \text{H}_2\text{O} \\
\text{aluminum dihydroxide chloride} & \text{basic salt}
\end{align*}
\]

\[
\begin{align*}
\text{Al(OH)}_3 + 2\text{HCl} & \rightarrow \text{Al(OH)}_2\text{Cl}_2 + 2\text{H}_2\text{O} \\
1\text{ mol} + 2\text{ mol} & \rightarrow \text{Al(OH)}_2\text{Cl}_2 + 2\text{H}_2\text{O} \\
\text{aluminum hydroxide chloride} & \text{basic salt}
\end{align*}
\]

\[
\begin{align*}
\text{Al(OH)}_3 + 3\text{HCl} & \rightarrow \text{AlCl}_3 + 3\text{H}_2\text{O} \\
1\text{ mol} + 3\text{ mol} & \rightarrow \text{AlCl}_3 + 3\text{H}_2\text{O} \\
\text{aluminium chloride} & \text{normal salt}
\end{align*}
\]
In this reaction, Al(OH)₃ (s) is acting like a base. However, if placed in a strong, soluble base solution, it will dissolve and react with the base as if it were an acid. Therefore, Al(OH)₃ (s) is called an amphoteric metal hydroxide.

**Formula unit:**  \[ \text{Al(OH)}_3 (s) + \text{NaOH(aq)} \rightarrow \text{NaAl(OH)}_4 (aq) \]

**Net ionic:**  \[ \text{Al(OH)}_3 (s) + \text{OH}^- (aq) \rightarrow \text{Al(OH)}_4^- (aq) \]

Generally, it is elements of intermediate electronegativity that form insoluble amphoteric hydroxides (Table 10-2) e.g. Cr(OH)₃, Zn(OH)₂, Sn(OH)₂, Sn(OH)₄.

**Note:** Elements of low electronegativity form basic hydroxides (O-H bond is strong)

- e.g. NaOH, Ba(OH)₂

Elements of high electronegativity form acidic hydroxides = acids

- e.g. \( \text{SO}_2 \text{(OH)}_2 \equiv \text{H}_2\text{SO}_4 \)
- \( \text{NO}_2 \text{(OH)} \equiv \text{HNO}_3 \)

**Relative Strengths of Ternary (3 element - nonmetal + H + O) Acids**

1. For ternary acids with the same central nonmetal: generally, acid strength increases with increasing oxidation state of central element and with increasing numbers of oxygen atoms.

\[
\begin{align*}
\text{H}_2\text{SO}_3 & < \text{H}_2\text{SO}_4 \\
\text{HNO}_2 & < \text{HNO}_3 \\
\text{HClO} & < \text{HClO}_2 < \text{HClO}_3 < \text{HClO}_4
\end{align*}
\]

Consider HClO₄. The oxygen atoms pull electron density away from O-H bond thereby weakening it and making HClO₄ a stronger acid.
For ternary acids with different nonmetal central atoms in the same oxidation state with similar structures: generally, acid strengths increase with increasing electronegativity of central atom.

\[ \text{E.N. Se: 2.4, S: 2.5} \]

Using Bronsted-Lowry terminology for binary and ternary acids:

<table>
<thead>
<tr>
<th></th>
<th>Increasing strength of acid</th>
<th>Increasing strength of conjugate base</th>
</tr>
</thead>
<tbody>
<tr>
<td>HF</td>
<td>F^-</td>
<td>HBrO_2</td>
</tr>
<tr>
<td>HCl</td>
<td>Cl^-</td>
<td>HBrO_3</td>
</tr>
<tr>
<td>HBr</td>
<td>Br^-</td>
<td>HBrO_4</td>
</tr>
<tr>
<td>HI</td>
<td>I^-</td>
<td></td>
</tr>
</tbody>
</table>

Lewis Theory of Acids and Bases

acid: any species that can accept an electron pair for sharing.

base: any species that can donate an electron pair for sharing.

acid-base (neutralization) reaction: the formation of a special bond—called a coordinate covalent bond—in which both electrons are furnished by one atom belonging to the base.

Example: \( \text{BF}_3 + \text{NH}_3 \rightarrow \text{F}_3\text{B}:\text{NH}_3 \)

\[ \begin{align*}
\text{BF}_3 & \quad \text{NH}_3 \\
\text{acid} & \quad \text{base} \\
\text{sp}^3 & \quad \text{sp}^3
\end{align*} \]
Example: $\text{SnCl}_2 + 2 \text{Cl}^- \rightarrow \text{SnCl}_4^{2-}$

\[ \text{acid} \quad \text{base} \quad \text{complex} \]

(sp$^3$) (sp$^3$) (sp$^3d$)