10.1 Acids and Bases in Aqueous Solution

Arrhenius Definition of Acids and Bases

- An acid is a substance that gives hydrogen ions, $H^+$, when dissolved in water. In fact, $H^+$ reacts with water and produces $H_3O^+$.
- A base is a substance that gives hydroxide ions, $OH^-$, when dissolved in water.
- The neutralization reaction of an acid with a base yields water plus a salt.
10.2 Some Common Acids and Bases

Some common acids are:
- Sulfuric acid, $\text{H}_2\text{SO}_4$
- Hydrochloric acid, $\text{HCl}$
- Phosphoric acid, $\text{H}_3\text{PO}_4$
- Nitric acid, $\text{HNO}_3$
- Acetic acid, $\text{CH}_3\text{CO}_2\text{H}$

Some common bases are:
- Sodium hydroxide, $\text{NaOH}$
- Calcium hydroxide, $\text{Ca(OH)}_2$
- Magnesium hydroxide, $\text{Mg(OH)}_2$
- Ammonia, $\text{NH}_3$
The Bronsted-Lowry Definition of Acids and Bases

**Bronsted-Lowry Acids**: Any substance that is able to give a hydrogen ion, $H^+$, to another ion or molecule. $H^+$ ions are also known as a *proton*. Therefore, acids are those substances that can donate protons.
Monoprotic acid: Acids with one proton to donate, such as, hydrochloric acid, HCl; nitric acid, HNO₃

Diprotic acid: Acids with two protons to donate, such as sulfuric acid, H₂SO₄.

Triprotic acid: Acids with three protons to donate, such as phosphoric acid, H₃PO₄.

Bronsted-Lowry bases: Any substance that is able to accept a hydrogen ion, H⁺, from an acid. A base can be neutral or negatively charged, for example, ammonia, NH₃ and hydroxide ion, OH⁻.
Products of an acid-base reactions are themselves acids and bases.

*Conjugate acid-base pair:* Two substances whose formula differ by only a hydrogen ion, $H^+$.

*Conjugate base:* The substance formed by loss of $H^+$ from an acid.

*Conjugated base:* The substance formed by addition of $H^+$ to a base.
10.4 Water as Both an Acid and a Base

Water is neither an acid nor a base according to Arrhenius acid-base theory since water does not contain appreciable amount of $\text{H}_3\text{O}^+$ or $\text{OH}^-$. However, according to Bronsted-Lowry acid-base theory, water is both an acid and a base.

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

Acetate ion (base) + Water (acid) $\rightleftharpoons$ Acetic acid (acid) + Hydroxide ion (base)
10.5 Some Common Acid-Base Reactions

- **Reaction of Acids with Hydroxide Ion:**
  Acids react with metal hydroxides to produce water and a salt in a neutralization reaction.

- **Reactions of Acids with Bicarbonate and Carbonate Ion**
  Bicarbonate ion, $\text{HCO}_3^-$, reacts with acid by accepting $\text{H}^+$ to yield carbonic acid, $\text{H}_2\text{CO}_3$. Similarly, carbonate ion accepts two protons in its reaction with acid. $\text{H}_2\text{CO}_3$ reaction product is unstable, rapidly decomposing to yield carbon dioxide gas and water.
Reaction of Acids with Ammonia

Acids react with ammonia to yield ammonium salts, such as ammonium chloride. Most of the ammonium salts are water soluble.

Living organisms contain a group of compounds called amines, which contain ammonia-like nitrogen atoms bonded to carbon. Amines react with acids just as ammonia does, yielding water soluble salts.
10.6 Acid and Base Strength

Acids differ in their ability to give up a proton. Similarly, bases differ in their ability to accept a proton. Acids and bases are classified as follows:

- **Strong acid**: An acid that gives up $\text{H}^+$ easily and is essentially 100% dissociated (splits to produce $\text{H}^+$ and an anion) in water.
- **Weak acid**: An acid that gives up $\text{H}^+$ with difficulty and is less than 100% dissociated in water.
Strong base: A base that has a high affinity for $\text{H}^+$ and holds it tightly.

Weak base: A base that has only a slight affinity for $\text{H}^+$ and holds it weakly.

The stronger the acid, the weaker its conjugate base; the weaker the acid, the stronger its conjugate base.
### Table 10.1 Relative Strengths of Acids and Conjugate Bases

<table>
<thead>
<tr>
<th>Acid</th>
<th>Conjugate Base</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Increasing acid strength</strong></td>
<td><strong>Increasing base strength</strong></td>
</tr>
<tr>
<td>Strong acids: 100% dissociated</td>
<td>Water</td>
</tr>
<tr>
<td>Perchloric acid HClO₄</td>
<td>ClO₄⁻</td>
</tr>
<tr>
<td>Sulfuric acid H₂SO₄</td>
<td>HSO₄⁻</td>
</tr>
<tr>
<td>Hydriodic acid HI</td>
<td>I⁻</td>
</tr>
<tr>
<td>Hydrobromic acid HBr</td>
<td>Br⁻</td>
</tr>
<tr>
<td>Hydrochloric acid HCl</td>
<td>Cl⁻</td>
</tr>
<tr>
<td>Nitric acid HNO₃</td>
<td>NO₃⁻</td>
</tr>
<tr>
<td><strong>Hydronium ion H₃O⁺</strong></td>
<td><strong>H₂O</strong></td>
</tr>
<tr>
<td>Hydrogen sulfate ion HSO₄⁻</td>
<td>SO₄²⁻</td>
</tr>
<tr>
<td>Phosphoric acid H₃PO₄</td>
<td>H₂PO₄⁻</td>
</tr>
<tr>
<td>Nitrous acid HNO₂</td>
<td>NO₂⁻</td>
</tr>
<tr>
<td>Hydrofluoric acid HF</td>
<td>F⁻</td>
</tr>
<tr>
<td>Acetic acid CH₃COOH</td>
<td>CH₃COO⁻</td>
</tr>
<tr>
<td>Carbonic acid H₂CO₃</td>
<td>HCO₃⁻</td>
</tr>
<tr>
<td>Dihydrogen phosphate ion H₂PO₄⁻</td>
<td>HPO₄²⁻</td>
</tr>
<tr>
<td>Ammonium ion NH₄⁺</td>
<td>NH₃</td>
</tr>
<tr>
<td>Hydrocyanic acid HCN</td>
<td>CN⁻</td>
</tr>
<tr>
<td>Bicarbonate ion HCO₃⁻</td>
<td>CO₃²⁻</td>
</tr>
<tr>
<td>Hydrogen phosphate ion HPO₄⁻</td>
<td>PO₄³⁻</td>
</tr>
<tr>
<td><strong>Water</strong> H₂O</td>
<td><strong>OH⁻</strong></td>
</tr>
<tr>
<td><strong>Hydroxide ion</strong></td>
<td></td>
</tr>
</tbody>
</table>

**Very weak acids**

- Very weak bases

**Weak bases**

- Weak bases

**Strong bases**
10.7 Acid Dissociated Constants

The reaction of weak acid with water can be described by an equilibrium equation. Equilibrium constant, $K$, and water concentration $[H_3O^+]$ together makes the acid dissociation constant $k_a$. Acid dissociation constant is a measure of acid strength.
Strong acids have $k_a$ value much greater than 1.

Weak acids have $k_a$ value much less than 1.

Donation of each successive $H^+$ from a polyprotic acid is more difficult than the one before it, so $k_a$ value become successively smaller.

Most organic acids, which contains $-CO_2H$ group, have $k_a$ value near $10^{-5}$. 
Like all weak acids, water is slightly dissociated into $H^+$ and $OH^-$ ions. The concentrations of the two ions are identical. At 25°C, concentration of each ion is $1.00 \times 10^{-7}$.

Ion product constant for water, $k_w$:

$$k_w = k_a[H_2O] = [H_3O^+][OH^-] = [1.00 \times 10^{-7}][1.00 \times 10^{-7}] = 1.00 \times 10^{-14} \text{ at } 25^\circ \text{C}.$$  

Product of $[H_3O^+]$ and $[OH^-]$ is a constant. Therefore, in an acidic solution where $[H_3O^+]$ is large and $[OH^-]$ must be small.
10.9 Measuring Acidity in Aqueous Solution: pH

A pH value between 0 and 14 is used to indicate concentration of $\text{H}_3\text{O}^+$ or $\text{OH}^-$ in solution. Mathematically, the pH of a solution is defined as the negative common logarithm of the $\text{H}_3\text{O}^+$ concentration:

$$\text{pH} = -\log [\text{H}_3\text{O}^+] \quad \text{or} \quad [\text{H}_3\text{O}^+] = 10^{-\text{pH}}$$

- **Acidic solution:** pH $< 7$  \quad $[\text{H}_3\text{O}^+] > 1.00 \times 10^{-7}$ M
- **Neutral solution:** pH $= 7$  \quad $[\text{H}_3\text{O}^+] = 1.00 \times 10^{-7}$ M
- **Basic solution:** pH $> 7$  \quad $[\text{H}_3\text{O}^+] < 1.00 \times 10^{-7}$ M
Fig 10.2 The pH scale and pH of some common substances

Fig 10.3 relationship of pH to $H^+$ and $OH^-$ ion concentrations
10.10 Working with pH

Calculate \([H_3O^+]\) in blood that has a pH of 7.4.

\[-\log [H_3O^+] = \text{pH}; \text{ rearrangement of this equation gives } [H_3O^+] = \text{antilog pH}\]

Therefore, \([H_3O^+] = \text{antilog} (-7.4) = 4 \times 10^{-8}\]

Calculate pH of a solution that has \([H_3O^+]\) of 4.6 x 10^{-3}

\[-\log [H_3O^+] = \text{pH}\]

\[-\log (4.6 \times 10^{-3}) = - (-2.34) = 2.34\]
The simplest but least accurate way to measure the pH of a solution is to use an acid-base indicator that changes color depending on the pH of the solution. For example:

- *Litmus* is red below pH 4.8 but blue above pH 7.8.
- *Phenolphthalein* is colorless below pH 8.2 but red above pH 10;
- A mixture of indicators known as *universal indicator* gives approximate pH measurements in the range 2-10 pH.
- For more accurate pH measurements, an electronic pH meter can be used.
**Buffer Solutions**

**Buffer**: A combination of substances that act together to prevent a drastic change in pH. Usually mixture of a weak acid and its conjugate base is used to prepare a buffer solution.

For example, a solution that contains 0.10 M acetic acid and 0.10 M acetate ion can be utilized as a buffer, Fig 10.6.

If a small amount of OH⁻ is added to the above buffer solution, the pH will increase, but not very much because acetic acid of the buffer mixture will neutralize the added OH⁻.
If small amount of $\text{H}_3\text{O}^+$ is added to the buffer, the pH will decrease, but again not very much since acetate ion of the buffer mixture will neutralize the added $\text{H}_3\text{O}^+$.

Fig 10.6 pH changes in pure water and a buffer solution

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Buffers should meet the following requirements to be the most effective:

- The ration of [HA] to [A⁻] should be close to 1.
- The amounts of [HA] and [A⁻] in the buffer should be approximately 10 times greater than either the amount of acid or base you expect to add.
10. 13 Buffers in the Body

The pH of body fluid is maintained by the following three major buffer systems:

- Carbonic acid – bicarbonate system
- Dihydrogen phosphate – hydrogen phosphate system
- Proteins acting as either proton acceptor or proton donors at different pH values.

Relationships of the bicarbonate buffer system to the lungs and kidneys shown in the following figure 10.7.
Fig 10.7 Lungs and kidneys relation with the bicarbonate buffer system
One equivalent of acid is equal to the molar mass of the acid divided by the number of H\(^+\) ion produced per formula unit. Similarly, one equivalent of a base is the weight in grams that can produced one mole of OH\(^-\) ions. For example;

One equivalent of the monoprotic acid HCl is 36.5 g, which comes from the molar mass of the acid (36.5 g) divided by 1 (the number of H\(^+\) ion HCl can produced).
One equivalent of diprotic acid $\text{H}_2\text{SO}_4$ is 49.9 g. Molar mass of $\text{H}_2\text{SO}_4$ (98.0 g) divided by 2 (number of $\text{H}^+$ sulfuric acid can produced)

$$\text{One equivalent of } \text{H}_2\text{SO}_4 = \frac{\text{Molar mass of } \text{H}_2\text{SO}_4}{2} = \frac{98.0 \text{ g}}{2} = 49.0 \text{ g}$$

Divide by 2 because $\text{H}_2\text{SO}_4$ is diprotic.