Chapter 8
Acid-Base Equilibria

• 8-1 Brønsted-Lowry Acids and Bases
• 8-2 Water and the pH Scale
• 8-3 The Strengths of Acids and Bases
• 8-4 Equilibria Involving Weak Acids and Bases
• 8-5 Buffer Solutions
• 8-6 Acid-Base Titration Curves
• 8-7 Polyprotic Acids
• 8-8 Lewis Acids and Bases
Acid and Base Definitions

1) Arrhenius (Section 4.3)
   - Acids are $H^+$ donors
   - Bases are $OH^-$ donors

2) Broadened Definition (Section 4.3)
   - Acids are substances that increase $[H^+]$
   - Bases are substances that increase $[OH^-]$

3) Brønsted-Lowry (Section 8.1)
   -

4) Lewis (Section 8.8)
   -
Chapter 8
Acid-Base Equilibria

• Brønsted-Lowry
  – Acids
  – Bases
  – Conjugate Base
  – Conjugate Acid
Acid-Base Equilibria

Brønsted-Lowry Acids and Bases

A Brønsted-Lowry acid is a substance that can donate a hydrogen ion.

A Brønsted-Lowry base is a substance that can accept a hydrogen ion.

In the Brønsted-Lowry Acid and Base concept, acids and bases occur as conjugate acid-base pairs.
Conjugate means to join, unite or marry

**Conjugate Base** - subtract an H+ from the acid

**Conjugate Acid** add H+ to the base

Examples

1. is the conjugate base of H₂O
2. is the conjugated base of H₃O⁺ (called the hydronium ion)
3. is the conjugated acid of OH⁻
4. (or shown as H+) is the conjugate acid of H₂O
Conjugate Base - subtract an $H^+$ from the acid
Conjugate Acid add $H^+$ to the base

$H_2O$

- $H^+$

conjugate base of $H_2O$

conjugate acid of $H_2O$

$H^+$

Hydroxide ion

$OH^-$

$H_3O^+$

Hydronium ion

$+ H^+$

$- H^+$

Water is the conjugate acid of $OH^-$

Water is the conjugate base of $H_3O^+$
\[
\text{CH}_3\text{CO}_2\text{H} + \text{H}_2\text{O} \leftrightarrow \text{H}_3\text{O}^+ + \text{CH}_3\text{CO}_2^- \\
\text{Acetic Acid} \quad \text{Acetate Ion}
\]

<table>
<thead>
<tr>
<th>Pairs</th>
<th>1</th>
<th>2</th>
<th>2</th>
<th>1</th>
</tr>
</thead>
<tbody>
<tr>
<td>acid</td>
<td>base</td>
<td>acid</td>
<td>base</td>
<td></td>
</tr>
</tbody>
</table>

**Point of View #1**

\[
\text{CH}_3\text{CO}_2\text{H} + \text{H}_2\text{O} \leftrightarrow \text{H}_3\text{O}^+ + \text{CH}_3\text{CO}_2^- \\
\text{Acid} \quad \text{Base} \quad \text{Conjugate Acid of H}_2\text{O} \quad \text{Conjugate Base of CH}_3\text{CO}_2\text{H}
\]

**Point of View #2**

\[
\text{CH}_3\text{CO}_2\text{H} + \text{H}_2\text{O} \leftrightarrow \text{H}_3\text{O}^+ + \text{CH}_3\text{CO}_2^- \\
\text{Conjugate Acid of CH}_3\text{CO}_2^- \quad \text{Conjugate Base of H}_3\text{O}^+ \quad \text{Acid} \quad \text{Base}
\]
Autoionization of H$_2$O

H$_2$O + H$_2$O $\leftrightarrow$ H$_3$O$^+$ + OH$^-$

Pairs  1  2  2  1
acid  base acid base

Point of View #1

H$_2$O + H$_2$O $\leftrightarrow$ H$_3$O$^+$ + OH$^-$

# 1 # 2
acid base Conjugate acid of H$_2$O #2 Conjugate base of H$_2$O #1

Point of View #2

H$_2$O + H$_2$O $\leftrightarrow$ H$_3$O$^+$ + OH$^-$

Conjugate acid of OH$^-$ Conjugate base of H$_3$O$^+$ acid base
Exercise 8-1:

Trimethylamine \( (\text{C}_3\text{H}_9\text{N}) \) is a soluble weak base with a foul odor (it contributes to the smell of rotten fish). Write the formula of its conjugate acid.
Nomenclature

When $H^+$ is hydrated it is $H_3O^+$ and called a **hydronium ion**. Often $H_3O^+$ is written in a simpler notation $H^+$. 

![Diagram of OH+ ion with 111.7° angle]
Amphotericism - an ion or molecule can act as an acid or base depending upon the reaction conditions

1.) Water in NH₃ serves as an acid

\[
H₂O + NH₃ \leftrightarrow NH₄⁺ + OH⁻
\]

2.) Water in acetic acid serves as a base

\[
H₂O + CH₃CO₂H \leftrightarrow H₃O⁺ + CH₃CO₂⁻
\]
3.) Acetic Acid is also amphoteric, if in the presence of a strong acid serves as a base

\[
\text{H}_2\text{SO}_4 + \text{CH}_3\text{CO}_2\text{H} \leftrightarrow \text{CH}_3\text{CO}_2\text{H}_2^+ + \text{HSO}_4^- 
\]

**Amphoterism** - an ion or molecule can act as an acid or base depending upon the reaction conditions
Water

Autoionization of water:

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

\[
\frac{[\text{H}_3\text{O}^+][\text{OH}^-]}{[\text{H}_2\text{O}]^2} = K_W = 1.0 \times 10^{-14} \\
\text{(at 25}\degree\text{C})
\]
Strong Acids and Bases

A **strong acid** is one that reacts essentially completely with water to produce $\text{H}_3\text{O}^+(aq)$.

Hydrochloric acid (HCl) is a strong acid:

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

(reaction essentially complete)

Dissolving 0.10 mol of HCl in enough water to make 1.0 L of solution gives a final concentration of 0.10 M for $\text{H}_3\text{O}^+(aq)$.

$$[\text{H}_3\text{O}^+][\text{OH}^-] = K_W$$
A strong base is one that reacts essentially completely with water to produce OH\(^{-}(aq)\) ions.

Sodium hydroxide (NaOH) is a strong base:

Others are NH\(_2\)\(^{-}\) (amide ion) and H\(^{-}\) (Hydride ion)

\[
\text{NaOH}(s) \rightarrow \text{Na}^{+}(aq) + \text{OH}^{-}(aq) \quad \text{(reaction essentially complete)}
\]

Dissolving 0.10 mol of NaOH in enough water to make 1.0 L of solution gives a final concentration of 0.10 M for OH\(^{-}(aq)\).

\[
[H_3O^+][OH^-] = K_W
\]
The pH Function

\[ \text{pH} = -\log_{10}[\text{H}_3\text{O}^+] \]

pH < 7  acidic solution
\([\text{H}_3\text{O}^+] > [\text{OH}^-]\)

pH = 7  neutral solution
\([\text{H}_3\text{O}^+] = [\text{OH}^-]\)

pH > 7  basic solution
\([\text{H}_3\text{O}^+] < [\text{OH}^-]\)
The pH Function

EXAMPLE 8-3

Calculate the pH (at 25°C) of an aqueous solution that has an OH⁻(aq) concentration of 1.2 × 10⁻⁶ M.
If converting from pH to $[H^+]$

$$[H^+] = 10^{-pH} = 10^{-X}$$
Recall

\[ [H_3O^+][OH^-] = K_W = 10^{-14} \]

\[ \text{pH} + \text{pOH} = \text{p}K_w = 14 \]
The pH Function

Exercise page 8-4:

Calculate $[\text{H}_3\text{O}^+]$ and $[\text{OH}^-]$ in saliva that has a pH of 6.60 at 25°C.
Strengths of Acids and Bases

- **Strong acids**
  1. 
  2. 
  3. 
  4. 
  5. 
  6. 
  7. 

\[
\text{HA} + \text{H}_2\text{O} \leftrightarrow \text{H}_3\text{O}^+ + \text{A}^- \\
\text{HA} = \text{generic acid}
\]

\[
K_a = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}][\text{H}_2\text{O}]} \\
= \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}]}
\]
\[ \text{pK}_a = -\log_{10}K_a \]

**Table 8-2**

**Scale of pKa**

-11

To

+14

<table>
<thead>
<tr>
<th>Acid</th>
<th>Formula</th>
<th>Conjugate Base</th>
<th>( K_a )</th>
<th>pK(_a )</th>
</tr>
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<tbody>
<tr>
<td>Hydriodic</td>
<td>HI</td>
<td>( \Gamma )</td>
<td>( \approx 10^{11} )</td>
<td>( \approx -11 )</td>
</tr>
<tr>
<td>Hydrobromic</td>
<td>HBr</td>
<td>( Br^- )</td>
<td>( \approx 10^9 )</td>
<td>( \approx -9 )</td>
</tr>
<tr>
<td>Perchloric</td>
<td>HClO(_4)</td>
<td>ClO(_4^-)</td>
<td>( \approx 10^7 )</td>
<td>( \approx -7 )</td>
</tr>
<tr>
<td>Hydrochloric</td>
<td>HCl</td>
<td>Cl(^-)</td>
<td>( \approx 10^7 )</td>
<td>( \approx -7 )</td>
</tr>
<tr>
<td>Chloric</td>
<td>HClO(_3)</td>
<td>ClO(_3^-)</td>
<td>( \approx 10^5 )</td>
<td>( \approx -3 )</td>
</tr>
<tr>
<td>Sulfuric (1)</td>
<td>H(_2)SO(_4)</td>
<td>HSO(_4^-)</td>
<td>( \approx 10^2 )</td>
<td>( \approx -2 )</td>
</tr>
<tr>
<td>Nitric</td>
<td>HNO(_3)</td>
<td>NO(_3^-)</td>
<td>( \approx 20 )</td>
<td>( \approx -1.3 )</td>
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<tr>
<td>Hydronium ion</td>
<td>H(_2)O(^+)</td>
<td>H(_2)O</td>
<td>1</td>
<td>0.0</td>
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<tr>
<td>Urea acidium ion</td>
<td>(NH(_2))CONH(_2)</td>
<td>(NH(_2))CO (urea)</td>
<td>( 6.6 \times 10^{-1} )</td>
<td>0.18</td>
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<td>IO(_3^-)</td>
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<td>Oxalic (1)</td>
<td>H(_2)C(_2)O(_4)</td>
<td>H(_2)C(_2)O(^-)</td>
<td>( 5.9 \times 10^{-2} )</td>
<td>1.23</td>
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<td>Sulfurous (1)</td>
<td>H(_2)SO(_4)</td>
<td>HSO(_4^-)</td>
<td>( 1.5 \times 10^{-2} )</td>
<td>1.82</td>
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<td>1.96</td>
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<td>Phosphoric (1)</td>
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<td>H(_3)PO(_4^-)</td>
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<td>2.12</td>
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<td>H(_3)AsO(_4^-)</td>
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<td>Chloroacetic</td>
<td>CIC(_2)COOH</td>
<td>CIC(_2)COO(^-)</td>
<td>( 1.4 \times 10^{-3} )</td>
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<td>Hydrofluoric</td>
<td>HF</td>
<td>F(^-)</td>
<td>( 6.6 \times 10^{-4} )</td>
<td>3.18</td>
</tr>
<tr>
<td>Nitrous</td>
<td>HNO(_2)</td>
<td>NO(_2^-)</td>
<td>( 4.6 \times 10^{-4} )</td>
<td>3.34</td>
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<td>Formic</td>
<td>HCOOH</td>
<td>HCOO(^-)</td>
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<td>Benzoic</td>
<td>C(_6)H(_5)COOH</td>
<td>C(_6)H(_5)COO(^-)</td>
<td>( 6.5 \times 10^{-5} )</td>
<td>4.19</td>
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<td>H(_2)C(_2)O(_4)</td>
<td>C(_2)O(_4^-)</td>
<td>( 6.4 \times 10^{-5} )</td>
<td>4.19</td>
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<tr>
<td>Hydrazoic</td>
<td>HN(_3)</td>
<td>N(_3^-)</td>
<td>( 1.9 \times 10^{-5} )</td>
<td>4.72</td>
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<tr>
<td>Acetic</td>
<td>CH(_3)COOH</td>
<td>CH(_3)COO(^-)</td>
<td>( 1.8 \times 10^{-5} )</td>
<td>4.74</td>
</tr>
<tr>
<td>Propionic</td>
<td>CH(_3)CH(_2)COOH</td>
<td>CH(_3)CH(_2)COO(^-)</td>
<td>( 1.3 \times 10^{-5} )</td>
<td>4.89</td>
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<td>Pyridinium ion</td>
<td>HC(_2)H(_2)N(^+)</td>
<td>C(_2)H(_3)N (pyridine)</td>
<td>( 5.6 \times 10^{-6} )</td>
<td>5.25</td>
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<tr>
<td>Carbonic (1)</td>
<td>H(_2)CO(_3)</td>
<td>HCO(_3^-)</td>
<td>( 4.3 \times 10^{-7} )</td>
<td>6.37</td>
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<td>Sulfurous (2)</td>
<td>H(_2)SO(_3)</td>
<td>SO(_3^-)</td>
<td>( 1.0 \times 10^{-7} )</td>
<td>7.00</td>
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<td>H(_3)AsO(_4)</td>
<td>HAsO(_4^-)</td>
<td>( 9.3 \times 10^{-8} )</td>
<td>7.03</td>
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<td>H(_2)S</td>
<td>HS(^-)</td>
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<td>HPO(_4^-)</td>
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<td>7.21</td>
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<td>Hypochlorous</td>
<td>HClO</td>
<td>ClO(_2^-)</td>
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<td>7.52</td>
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<tr>
<td>Hydrocyanic</td>
<td>HCN</td>
<td>CN(^-)</td>
<td>( 6.2 \times 10^{-9} )</td>
<td>9.21</td>
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<td>Ammonium ion</td>
<td>NH(_4)</td>
<td>NH(_3)</td>
<td>( 5.6 \times 10^{-10} )</td>
<td>9.25</td>
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<td>Carbonic (2)</td>
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<td>HAsO(_3)</td>
<td>AsO(_3^-)</td>
<td>( 3.0 \times 10^{-12} )</td>
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<tr>
<td>Hydrogen peroxide</td>
<td>H(_2)O</td>
<td>HO(_2)</td>
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<tr>
<td>Phosphoric (3)</td>
<td>H(_3)PO(_4)</td>
<td>PO(_4^-)</td>
<td>( 2.2 \times 10^{-13} )</td>
<td>12.66</td>
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<tr>
<td>Water</td>
<td>H(_2)O</td>
<td>OH(^-)</td>
<td>( 1.0 \times 10^{-14} )</td>
<td>14.00</td>
</tr>
</tbody>
</table>

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Chapter 8
Acid-Base Equilibria

• **Base Strength**
  – strong acids have weak conjugate bases
  – weak acids have strong conjugate bases
Indicators

A soluble compound, generally an organic dye, that changes its color noticeably over a fairly short range of pH.
Typically, a weak organic acid that has a different color than its conjugate base.

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

\[
\frac{[\text{H}_3\text{O}^+][\text{In}^-]}{[\text{HIn}]} = K_a
\]
Malachite green

Thymol blue

Methyl orange

Bromocresol green

Methyl red

Bromothymol blue

Cresol red

Phenolphthalein

Thymolphthalein

Alizarin yellow

pH 0 1 2 3 4 5 6 7 8 9 10 11 12 13 14

0.2 1.8

1.2 2.8 8.0 9.6

3.2 4.4

3.8 5.4

4.8 6.0

6.0 7.6

7.0 8.8

8.2 10.0

9.4 10.6

10.1 12.0
Methyl Red

Bromothymol blue

Phenolphthalein
Indicators

Exercise 8-5:

Rainwater that has leached through a pile of building materials and puddled underneath turns bromothymol blue from yellow to blue, but it leaves phenolphthalein colorless. Estimate the pH of this water.
Equilibria Involving Weak Acids and Bases

**Weak acids** $K_a < 1$

i.e., $pK_a > 0$

$H_3O^+$ (hydronium ion)

$K_a = 1$

$pK_a = 0$

$HA + H_2O \leftrightarrow H_3O^+ + A^-$

$HA$ is a weak acid,

$K_a < 1$ or $pK_a > 1$
<table>
<thead>
<tr>
<th>Acid</th>
<th>Formula</th>
<th>Conjugate Base</th>
<th>$K_a$</th>
<th>$pK_a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydriodic</td>
<td>HI</td>
<td>$I^-$</td>
<td>$\approx 10^{11}$</td>
<td>$\approx -11$</td>
</tr>
<tr>
<td>Hydrobromic</td>
<td>HBr</td>
<td>$Br^-$</td>
<td>$\approx 10^9$</td>
<td>$\approx -9$</td>
</tr>
<tr>
<td>Perchloric</td>
<td>HClO$_4$</td>
<td>ClO$_4^-$</td>
<td>$\approx 10^7$</td>
<td>$\approx -7$</td>
</tr>
<tr>
<td>Hydrochloric</td>
<td>HCl</td>
<td>Cl$^-$</td>
<td>$\approx 10^7$</td>
<td>$\approx -7$</td>
</tr>
<tr>
<td>Chloric</td>
<td>HClO$_3$</td>
<td>ClO$_3^-$</td>
<td>$\approx 10^3$</td>
<td>$\approx -3$</td>
</tr>
<tr>
<td>Sulfuric (1)</td>
<td>H$_2$SO$_4$</td>
<td>HSO$_4^-$</td>
<td>$\approx 10^2$</td>
<td>$\approx -2$</td>
</tr>
<tr>
<td>Nitric</td>
<td>HNO$_3$</td>
<td>NO$_3^-$</td>
<td>$\approx 20$</td>
<td>$\approx -1.3$</td>
</tr>
<tr>
<td>Hydronium ion</td>
<td>H$_3$O$^+$</td>
<td>H$_2$O</td>
<td>1</td>
<td>0.0</td>
</tr>
<tr>
<td>Urea acidium ion</td>
<td>(NH$_2$)CONH$_3^+$</td>
<td>(NH$_2$)$_2$CO (urea)</td>
<td>$6.6 \times 10^{-1}$</td>
<td>0.18</td>
</tr>
<tr>
<td>Iodic</td>
<td>HIO$_3$</td>
<td>IO$_3^-$</td>
<td>$1.6 \times 10^{-1}$</td>
<td>0.80</td>
</tr>
<tr>
<td>Oxalic (1)</td>
<td>H$_2$C$_2$O$_4$</td>
<td>H$_2$C$_2$O$_4^-$</td>
<td>$5.9 \times 10^{-2}$</td>
<td>1.23</td>
</tr>
<tr>
<td>Sulfurous (1)</td>
<td>H$_2$SO$_3$</td>
<td>HSO$_3^-$</td>
<td>$1.5 \times 10^{-2}$</td>
<td>1.82</td>
</tr>
<tr>
<td>Sulfuric (2)</td>
<td>HSO$_4^-$</td>
<td>SO$_4^{2-}$</td>
<td>$1.2 \times 10^{-2}$</td>
<td>1.92</td>
</tr>
<tr>
<td>Chlorous</td>
<td>HClO$_2$</td>
<td>ClO$_2^-$</td>
<td>$1.1 \times 10^{-2}$</td>
<td>1.96</td>
</tr>
<tr>
<td>Phosphoric (1)</td>
<td>H$_3$PO$_4$</td>
<td>H$_2$PO$_4^-$</td>
<td>$7.5 \times 10^{-3}$</td>
<td>2.12</td>
</tr>
<tr>
<td>Arsenic (1)</td>
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<td>H$_2$AsO$_4^-$</td>
<td>$5.0 \times 10^{-3}$</td>
<td>2.30</td>
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<td>Chloroacetic</td>
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<td>ClCH$_2$COO$^-$</td>
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<td>2.85</td>
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<tr>
<td>Hydrofluoric</td>
<td>HF</td>
<td>F$^-$</td>
<td>$6.6 \times 10^{-4}$</td>
<td>3.18</td>
</tr>
<tr>
<td>Nitrous</td>
<td>HNO$_2$</td>
<td>NO$_2^-$</td>
<td>$4.6 \times 10^{-4}$</td>
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<td>Formic</td>
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<tr>
<td>Acid</td>
<td>Formula</td>
<td>Conjugate Base</td>
<td>$K_a$</td>
<td>$pK_a$</td>
</tr>
<tr>
<td>--------------</td>
<td>------------</td>
<td>----------------</td>
<td>-----------</td>
<td>---------</td>
</tr>
<tr>
<td>Benzoic</td>
<td>C₆H₅COOH</td>
<td>C₆H₅COO⁻</td>
<td>$6.5 \times 10^{-5}$</td>
<td>4.19</td>
</tr>
<tr>
<td>Oxalic (2)</td>
<td>HC₂O₄⁻</td>
<td>C₂O₄²⁻</td>
<td>$6.4 \times 10^{-5}$</td>
<td>4.19</td>
</tr>
<tr>
<td>Hydrazoic</td>
<td>HN₃</td>
<td>N₃⁻</td>
<td>$1.9 \times 10^{-5}$</td>
<td>4.72</td>
</tr>
<tr>
<td>Acetic</td>
<td>CH₃COOH</td>
<td>CH₃COO⁻</td>
<td>$1.8 \times 10^{-5}$</td>
<td>4.74</td>
</tr>
<tr>
<td>Propionic</td>
<td>CH₃CH₂COOH</td>
<td>CH₃CH₂COO⁻</td>
<td>$1.3 \times 10^{-5}$</td>
<td>4.89</td>
</tr>
<tr>
<td>Pyridinium ion</td>
<td>HC₅H₅N⁺</td>
<td>C₅H₅N (pyridine)</td>
<td>$5.6 \times 10^{-6}$</td>
<td>5.25</td>
</tr>
<tr>
<td>Carbonic (1)</td>
<td>H₂CO₃</td>
<td>HCO₃⁻</td>
<td>$4.3 \times 10^{-7}$</td>
<td>6.37</td>
</tr>
<tr>
<td>Sulfurous (2)</td>
<td>HSO₃⁻</td>
<td>SO₃²⁻</td>
<td>$1.0 \times 10^{-7}$</td>
<td>7.00</td>
</tr>
<tr>
<td>Arsenic (2)</td>
<td>H₅AsO₄⁻</td>
<td>HAsO₄²⁻</td>
<td>$9.3 \times 10^{-8}$</td>
<td>7.03</td>
</tr>
<tr>
<td>Hydrosulfuric</td>
<td>H₂S</td>
<td>HS⁻</td>
<td>$9.1 \times 10^{-8}$</td>
<td>7.04</td>
</tr>
<tr>
<td>Phosphoric (2)</td>
<td>H₂PO₄⁻</td>
<td>HPO₄²⁻</td>
<td>$6.2 \times 10^{-8}$</td>
<td>7.21</td>
</tr>
<tr>
<td>Hypochlorous</td>
<td>HClO</td>
<td>ClO⁻</td>
<td>$3.0 \times 10^{-8}$</td>
<td>7.52</td>
</tr>
<tr>
<td>Hydrocyanic</td>
<td>HCN</td>
<td>CN⁻</td>
<td>$6.2 \times 10^{-10}$</td>
<td>9.21</td>
</tr>
<tr>
<td>Ammonium ion</td>
<td>NH₄⁺</td>
<td>NH₃</td>
<td>$5.6 \times 10^{-10}$</td>
<td>9.25</td>
</tr>
<tr>
<td>Carbonic (2)</td>
<td>HCO₃⁻</td>
<td>CO₃²⁻</td>
<td>$4.8 \times 10^{-11}$</td>
<td>10.32</td>
</tr>
<tr>
<td>Methylammonium ion</td>
<td>CH₃NH₃⁺</td>
<td>CH₃NH₂</td>
<td>$2.3 \times 10^{-11}$</td>
<td>10.64</td>
</tr>
<tr>
<td>Arsenic (3)</td>
<td>HAsO₄²⁻</td>
<td>AsO₄³⁻</td>
<td>$3.0 \times 10^{-12}$</td>
<td>11.52</td>
</tr>
<tr>
<td>Hydrogen peroxide</td>
<td>H₂O₂</td>
<td>HO₂⁻</td>
<td>$2.4 \times 10^{-12}$</td>
<td>11.62</td>
</tr>
<tr>
<td>Phosphoric (3)</td>
<td>HPO₄⁻</td>
<td>PO₄³⁻</td>
<td>$2.2 \times 10^{-13}$</td>
<td>12.66</td>
</tr>
<tr>
<td>Water</td>
<td>H₂O</td>
<td>OH⁻</td>
<td>$1.0 \times 10^{-14}$</td>
<td>14.00</td>
</tr>
</tbody>
</table>
Problem: Calculate pH and the fraction of CH₃CO₂H ionized at equilibrium. Assume 1.0M CH₃CO₂H initially

\[\text{CH}_3\text{CO}_2\text{H} + \text{H}_2\text{O} \leftrightarrow \text{H}_3\text{O}^+ + \text{CH}_3\text{CO}_2^-\]

Init. conc.  
\[\triangle \text{conc.}\]  
Equil. conc.

\[K_a = \frac{[\text{H}_3\text{O}^+][\text{CH}_3\text{CO}_2^-]}{[\text{CH}_3\text{CO}_2\text{H}][\text{H}_2\text{O}]} = \]
A trick to solving:

Assume that $y$ is small (less than 5% of the initial conc.)

$K_a = \frac{[H_3O^+][CH_3CO_2^-]}{[CH_3CO_2H][H_2O]} = \frac{y^2}{(1.0 - y)}$

$K_a = 1.8 \times 10^{-5}$ from Table 8 - 2
Problem: Calculate pH and the fraction of CH$_3$CO$_2$H ionized at equilibrium. Assume 1.0M CH$_3$CO$_2$H initially

Fraction CH$_3$CO$_2$H ionized at equilibrium
Weak Bases

Similarly NH₃ acts as a weak base in H₂O

\[ K_b = 1.8 \times 10^{-5} \]

\[ H_2O + NH_3 \leftrightarrow NH_4^+ + OH^- \]

acidᵡ baseᵢ acidᵢ baseᵡ

\[ K_b = \frac{[NH_4^+][OH^-]}{[NH_3][H_2O]} = 1 \]
As before, you can calculate a pH at equilibrium. Assume 0.01M NH₃ initially. Calculate the pH of the resulting solution

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

Init. conc.

\[\Delta \text{ conc.}\]

Equil. conc.

\[
K_b = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3][1]} = \frac{y^2}{(0.01 - y)}
\]

\(K_b\) for \(\text{NH}_3 = 1.8 \times 10^{-5}\)
\[
K_b = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3][1]} = \frac{y^2}{0.01 - y}
\]

\[K_b = y^2 = 1.8 \times 10^{-5}\]

\[y = [\text{OH}^-] = [\text{NH}_4^+] = 4.15 \times 10^{-4}\]

\[
[\text{H}_3\text{O}^+] = \frac{K_w}{[\text{OH}^-]}
\]
• **Hydrolysis** is a term applied to reactions of aquated ions that change the pH from 7

• When NaCl is placed in water, the resulting solution is observed to be neutral (pH = 7)
• However when sodium acetate (NaC₂H₃O₂) is dissolved in water the resulting solution is basic
• Other salts behave similarly, NH₄Cl and AlCl₃ give acid solutions.
• These interactions between salts and water are called **hydrolysis**
Despite the special term, **hydrolysis**, there is no reason to treat hydrolysis in a special manner.

It is still a **Brønsted-Lowry** Acid and Base Reaction.
Example problem:

Suppose a 0.1 mole solution sodium acetate is dissolved in 1 liter of water. What is the pH of the solution?

1. Find $K_b$
2. Find $[\text{OH}^-]$
3. Find $[\text{H}^+]$
4. Find pH
Example problem:
What is the pH of the solution?

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

<table>
<thead>
<tr>
<th>Init. conc.</th>
<th>0.1M</th>
<th>0</th>
<th>~0</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \Delta ) conc.</td>
<td>-y</td>
<td>+y</td>
<td>+y</td>
</tr>
<tr>
<td>Equil. conc.</td>
<td>0.1–y</td>
<td>y</td>
<td>y</td>
</tr>
</tbody>
</table>

1. Find \( K_b \)
2. Find \([\text{OH}^-]\)
3. Find \([\text{H}^+]\)
4. Find pH

\[
K_a \times K_b = K_w
\]

\[
K_b = \frac{[\text{CH}_3\text{CO}_2\text{H}][\text{OH}^-]}{[\text{CH}_3\text{CO}_2^-][1]} = \frac{y^2}{0.1-y}
\]

\[
K_b = \frac{K_w}{K_a} = \frac{1.0 \times 10^{-14}}{1.8 \times 10^{-5}} \text{ table} = 5.6 \times 10^{-4}
\]

\[
y = [\text{OH}^-] = 7.5 \times 10^{-6}
\]

\[
[H_3O^+] = \frac{K_w}{[\text{OH}^-]} = \frac{1 \times 10^{-14}}{7.5 \times 10^{-6}} = 1.3 \times 10^{-9}
\]

\[
pH = -\log_{10}(1.39 \times 10^{-9}) = 8.89
\]
<table>
<thead>
<tr>
<th>Hydrolysis of</th>
<th>Result</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Anions</strong></td>
<td><strong>Raise pH</strong></td>
</tr>
<tr>
<td><strong>Cations</strong></td>
<td><strong>Lower pH</strong></td>
</tr>
</tbody>
</table>

**Non-Hydrolyzed Ions (a few)**

**7 Anions**, not hydrolyzed

Cl\(^-\), Br\(^-\), I\(^-\), HSO\(_4\)^-, NO\(_3\)^-, ClO\(_3\)^-, ClO\(_4\)^-

**10 Cations**, not hydrolyzed

Li\(^+\), Na\(^+\), K\(^+\), Rb\(^+\), Sc\(^+\), Mg\(^{++}\), Ca\(^{++}\), Sr\(^{++}\), Ba\(^{++}\), Ag\(^+\)
<table>
<thead>
<tr>
<th>Hydrolysis of</th>
<th>Result</th>
</tr>
</thead>
<tbody>
<tr>
<td>Anions</td>
<td>Raise pH</td>
</tr>
<tr>
<td>Cations</td>
<td>Lower pH</td>
</tr>
</tbody>
</table>

Can predict pH of some salts (relative pH)

**Na$_3$PO$_4$** is basic
(a non hydrolyzed cation and a hydrolyzed anion)

**FeCl$_3$** is acidic
(a hydrolyzed cation and a non hydrolyzed anion)
Chapter 8
Acid-Base Equilibria

• **Buffer Solutions**: important in biochemical and physiological processes

• Organisms (and humans) have built-in buffers to protect them against large changes in pH.

• **Buffers** any solutions that maintain an approximately constant pH despite small additions of acids or bases
Buffers any solutions that maintain an approximately constant pH despite small additions of acids or bases

Human blood (pH=7.4) is maintained by a combination of CO$_3$^-2, PO$_4$^-3 and protein buffers, which accept H$^+$

Death = 7.0 < pH > 7.8 = Death

How Do Buffers Work?
How Do Buffers Work?

\[
[H_3O^+] = K_a \frac{[HA]}{[A^-]}
\]

rearranged \(K_a\) formula

• \(H^+\) depends on \(K_a\) and the ratio of acid to salt.

• Thus if both conc. HA and A\(^-\) are large then small additions of acid or base don’t change the ratio much.
• $\text{H}^+$ depends on $K_a$ and the ratio of acid to salt.

• Thus if both conc. HA and $A^-$ are large then small additions of acid or base don’t change the ratio much

Try Example 8-11
8-8 Lewis Acids

• Extremely important for Organic Chemistry

• Recall from Chapter 3 that main group elements in a molecule are surrounded by 8 electrons (the Octet Rule).

• Hydrogen by 2 electrons

• Carbon is $^6$C or 1s$^2$ 2s$^2$ 2p$^2$

• Hydrogen is $^1$H or 1s$^1$
Lewis Structures

Covalent bonds

CH$_4$

methane
Lewis Structures

NH₃
ammonia

H
H
H

H
H
H

Lone pair

107.3°

H
H

H
H
H

H
H

Lone pair

104.5°

Lone pairs
Lewis Structures

Electron deficient

\[
\begin{align*}
\text{F} & \quad \text{B} \quad \text{F} \\
\text{F} & \quad \text{F} \\
\end{align*}
\]

boron trifluoride
Chapter 8
Acid-Base Equilibria

• **Lewis Acids-Bases**
  – **Lewis Acid** is any species that accepts electron pairs
    • Called **electrophiles** (electron seeking)
    • e.g., Boron, Al, Group III elements

  • **BF$_3$, Mg$^{2+}$, H+, H$_3$O$^+$**
  • **BH$_3$, SnCl$_4$, CH$_3^+$, AICl$_3$, HCl**
Chapter 8
Acid-Base Equilibria

• **Lewis Acids-Bases**
  – **Lewis Base** is any species that donates electrons through coordination to its lone pair
  • Called **Nucleophiles** (nucleus seeking)
  • e.g., Group V, VI, VII elements

• Br⁻¹, Cl⁻¹, F⁻¹, H⁻¹, HO⁻¹, :NH₃, H₂O::

![Chemical structures](image)
Lewis Acid + Lewis Base

\[
\text{acetic acid} + \text{ammonia} \rightarrow \text{acetate ion} + \text{ammonium ion}
\]
Chapter 8
Acid-Base Equilibria

• Examples/Exercises
  8-1, 8-2, 8-3, 8-4,
  8-6, 8-7, 8-8,
  8-9, 8-10, 8-11, 8-16

• Problems
  5, 9, 11, 12, 26, 31,
  42, 43, 44, 46