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 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

Hydroxide ion

$\text{OH}^-$

Water is the conjugate acid of $\text{OH}^-$

H$_2$O

Hydronium ion

H$_3$O$^+$

Water is the conjugate base of H$_3$O$^+$

H$_2$O

Conjugate base of H$_2$O

Conjugate acid of H$_2$O

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

Acetic Acid \hspace{2cm} 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></td>
<td>acid</td>
<td>base</td>
<td>acid</td>
<td>base</td>
</tr>
</tbody>
</table>

**Point of View #1**

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

- **acid**
- **base**
- Conjugate acid of \( \text{H}_2\text{O} \)
- Conjugate base of \( \text{CH}_3\text{CO}_2\text{H} \)

**Point of View #2**

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

- Conjugate acid of \( \text{CH}_3\text{CO}_2^- \)
- Conjugate base of \( \text{H}_3\text{O}^+ \)
- **acid**
- **base**
Autoionization of H₂O

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

Pairs 1 2 2 1
acid base acid base

Point of View #1

\[ \text{H}_2\text{O} + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{OH}^- \]
# 1 # 2
acid base Conjugate acid of H₂O #2 Conjugate base of H₂O #1

Point of View #2

\[ \text{H}_2\text{O} + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{OH}^- \]
Conjugate acid of OH⁻ Conjugate base of H₃O⁺ acid base
Exercise 8-1:

Trimethylamine (C\textsubscript{3}H\textsubscript{9}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.

“… the formula of a conjugate acid is obtained by adding H\textsuperscript{+} to the formula of the base.”
Nomenclature

When $\text{H}^+$ is hydrated it is $\text{H}_3\text{O}^+$ and called a hydronium ion.

Often $\text{H}_3\text{O}^+$ is written in a simpler notation $\text{H}^+$
Amphoterism - an ion or molecule can act as an acid or base depending upon the reaction conditions

1.) Water in NH$_3$ serves as an acid

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

2.) Water in acetic acid serves as a base

\[ \text{H}_2\text{O} + \text{CH}_3\text{CO}_2\text{H} \leftrightarrow \text{H}_3\text{O}^+ + \text{CH}_3\text{CO}_2^- \]
3.) Acetic Acid is also amphoteric, if in the presence of a strong acid serves as a base

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

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

Autoionization of water:

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

\[
\frac{[\text{H}_3\text{O}^+][\text{OH}^-]}{[\text{H}_2\text{O}]^2} = K_W = 1.0 \times 10^{-14}
\]

(at 25°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 $\text{OH}^- (aq)$ ions.

Sodium hydroxide (NaOH) is a strong base:

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

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

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 $\text{OH}^- (aq)$.

$$[\text{H}_3\text{O}^+][\text{OH}^-] = K_W$$
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 \(\times\) 10\(^{-6}\) M.
pH = -\log_{10}[H_3O^+]\\

\text{If converting from pH to } [H^+]\\

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

\[ [\text{H}_3\text{O}^+][\text{OH}^-] = K_w = 10^{-14} \]

\[ \text{pH} + \text{pOH} = pK_w = 14 \]
Exercise page 8-4:

Calculate \([H_3O^+]\) and \([OH^-]\) in saliva that has a pH of 6.60 at 25°C.
Strengths of Acids and Bases

• Strong acids (completely ionized in water, i.e., 100%)
  1. HI
  2. HBr
  3. HClO4 (perchloric acid)
  4. HCl
  5. HClO3 (chloric acid)
  6. H2SO4
  7. HNO3

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

HA = 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

#### Known Scale of pKa

-11 To +50

E.g., Acetone = 19, methane = 48, ethane = 50
<table>
<thead>
<tr>
<th>Acid</th>
<th>Acid Strength</th>
<th>Base Strength</th>
<th>Conjugate Base</th>
</tr>
</thead>
<tbody>
<tr>
<td>HCl</td>
<td>Strong</td>
<td>Ineffective as a base</td>
<td>Cl⁻</td>
</tr>
<tr>
<td>H₂O⁺</td>
<td>Strong</td>
<td>Ineffective as a base</td>
<td>H₂O</td>
</tr>
<tr>
<td>HSO₄⁻</td>
<td>Moderately weak</td>
<td>Very weak</td>
<td>SO₄²⁻</td>
</tr>
<tr>
<td>HF</td>
<td>Moderately weak</td>
<td>Very weak</td>
<td>F⁻</td>
</tr>
<tr>
<td>HSO₅⁻</td>
<td>Very weak</td>
<td>Moderately weak</td>
<td>SO₃²⁻</td>
</tr>
<tr>
<td>NH₄⁺</td>
<td>Very weak</td>
<td>Moderately weak</td>
<td>NH₃</td>
</tr>
<tr>
<td>H₂O₂</td>
<td>Ineffective as an acid</td>
<td>Strong</td>
<td>HO₂⁻</td>
</tr>
<tr>
<td>H₂O</td>
<td>Ineffective as an acid</td>
<td>Strong</td>
<td>OH⁻</td>
</tr>
<tr>
<td>H₂</td>
<td>Ineffective as an acid</td>
<td>Strong</td>
<td>H⁺</td>
</tr>
</tbody>
</table>

© 2003 Thomson-Brooks/Cole
Strengths of Acids and Bases

B + H₂O ⇌ BH⁺ + OH⁻

B = Base

K_b = \frac{[BH^+][OH^-]}{[B][H_2O]}

pK_b = -\log_{10} K_b

K_b is the Basicity constant
\[ B + H_2O \leftrightarrow BH^+ + OH^- \]

\( B = \text{Base} \)

\[ K_b = \frac{[BH^+][OH^-]}{[B][H_2O]} \]

\[ = \frac{[BH^+][OH^-]}{[B]} \]

\[ pK_b = -\log_{10}K_b \]

\( K_b \) is the Basicity constant

\[ BH^+ + H_2O \leftrightarrow B + H_3O^+ \]

\( B = \text{Base} \)

\[ K_a = \frac{[B][H_3O^+]}{[BH^+][H_2O]} \]

\[ = \frac{[B][H_3O^+]}{[BH^+] \]}

\[ pK_a = -\log_{10}K_a \]

\( K_a \) is the Acidity constant
B + H₂O ⇌ BH⁺ + OH⁻

B = Base

BH⁺ + H₂O ⇌ B + H₃O⁺

B = Base

\[
K_b = \frac{[BH^+][OH^-]}{[B][H₂O]} = \frac{[BH^+][OH^-]}{[B]}
\]

\[
K_a = \frac{[B][H₃O^+]}{[BH^+][H₂O]} = \frac{[B][H₃O^+]}{[BH^+]}
\]

\[
K_aK_b = \left( \frac{[B][H₃O^+]}{[BH^+]} \right) \left( \frac{[BH^+][OH^-]}{[B]} \right) = \left( \frac{[B][H₃O^+]}{[BH^+]} \right) \left( \frac{[BH^+][OH^-]}{[B]} \right) = [H₃O^+][OH^-] = K_w
\]

Chapter 8
Acid-Base Equilibria

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

The strength of a base is inversely related to the strength of its conjugate acid; the weaker the acid, the stronger its conjugate base, and vice versa

\[ K_a K_b = K_w \]

\[ pK_a + pK_b = pK_w \]
Indicators (denoted by In)

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.

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

\[
\frac{[\text{H}_3\text{O}^+][\text{In}^-]}{[\text{HIn}]} = K_a
\]
Equilibria Involving Weak Acids and Bases

Weak acids $K_a < 1$

i.e., $pK_a > 0$

$H_3O^+ \text{ (hydronium ion)}$

$K_a = 1$

$pK_a = 0$

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

$HA$ is a weak acid,

$K_a < 1 \text{ or } pK_a > 1$
<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>HC$_2$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>
<td>H$_3$AsO$_4$</td>
<td>H$_2$AsO$_4^-$</td>
<td>$5.0 \times 10^{-3}$</td>
<td>2.30</td>
</tr>
<tr>
<td>Chloroacetic</td>
<td>ClCH$_2$COOH</td>
<td>ClCH$_2$COO$^-$</td>
<td>$1.4 \times 10^{-3}$</td>
<td>2.85</td>
</tr>
<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>
<td>3.34</td>
</tr>
<tr>
<td>Formic</td>
<td>HCOOH</td>
<td>HCOO$^-$</td>
<td>$1.8 \times 10^{-4}$</td>
<td>3.74</td>
</tr>
<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>H₃AsO₄⁻</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>HPO₄²⁻</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: (a) Calculate pH and (b) the fraction of $\text{CH}_3\text{CO}_2\text{H}$ ionized at equilibrium. Assume 1.0M $\text{CH}_3\text{CO}_2\text{H}$ 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.

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

Equil. conc.

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{CH}_3\text{CO}_2^-]}{[\text{CH}_3\text{CO}_2\text{H}][\text{H}_2\text{O}]}$$
\[
K_a = \frac{[H_3O^+][CH_3CO_2^-]}{[CH_3CO_2H][H_2O]} = \frac{y^2}{(1.0 - y)}
\]

\[K_a = 1.8 \times 10^{-5}\] from Table 8 - 2

A trick to solving:

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

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

\[y = 4.24 \times 10^{-3} = [H_3O^+]\]

\[pH = -\log (4.24 \times 10^{-3}) = 2.37\]
Problem: (a) Calculate pH and (b) the fraction of CH$_3$CO$_2$H ionized at equilibrium. Assume 1.0M CH$_3$CO$_2$H initially

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

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

Similarly NH$_3$ acts as a weak base in H$_2$O

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

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

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

\[ K_b = \frac{[NH_4^+][OH^-]}{[NH_3][H_2O]} = 1 \]
As before, you can calculate a pH at equilibrium. Assume 0.01M NH$_3$ initially. Calculate the pH of the resulting solution

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

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

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

\[ K_b \text{ for NH}_3 = 1.8 \times 10^{-5} \]
As before, you can calculate a pH at equilibrium. Assume 0.01M NH₃ initially. Calculate the pH of the resulting solution

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

\[
K_b = \frac{y^2}{0.01} \approx 0.01 = 1.8 \times 10^{-5}
\]

\[
y = [\text{OH}^-] = [\text{NH}_4^+] = 4.2 \times 10^{-4}
\]

\[
[\text{H}_3\text{O}^+] = \frac{\text{Kw}}{[\text{OH}^-]} = \frac{1 \times 10^{-14}}{4.2 \times 10^{-4}} = 2.4 \times 10^{-11}
\]

\[
\text{pH} = -\log_{10}(2.4 \times 10^{-11}) = 10.62
\]
• **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?

Init. conc.

$\Delta$ conc.

Equil. conc.

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

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

<table>
<thead>
<tr>
<th>Initial concentration</th>
<th>0.1M</th>
<th>0</th>
<th>~0</th>
</tr>
</thead>
<tbody>
<tr>
<td>Change in concentration</td>
<td>-y</td>
<td>+y</td>
<td>+y</td>
</tr>
<tr>
<td>Equilibrium concentration</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>Raise pH</td>
</tr>
<tr>
<td><strong>Cations</strong></td>
<td>Lower pH</td>
</tr>
</tbody>
</table>

**Non-Hyrolyzed 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 $\text{CO}_3^{-2}$, $\text{PO}_4^{-3}$ and protein buffers, which accept $\text{H}^+$

Death = $7.0 < \text{pH} > 7.8 = \text{Death}$

How Do Buffers Work?
How Do Buffers Work?

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

HA = generic acid

\[ K_a = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}]} \]

rearranged \( K_a \) formula

\[ [\text{H}_3\text{O}^+] = K_a \frac{[\text{HA}]}{[\text{A}^-]} \]

• \([H^+]\) 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
\[ \text{HA} + \text{H}_2\text{O} \leftrightarrow \text{H}_3\text{O}^+ + \text{A}^- \]

- \( \text{H}^+ \) depends on \( K_a \) and the ratio of acid to salt.

- Thus if both conc. HA and \( \text{A}^- \) are large then small additions of acid or base don’t change the ratio much

Try Example 8-11

© 2003 Thomson-Brooks/Cole
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

[Diagram of the Lewis structure of methane, \( \text{CH}_4 \), with covalent bonds indicated.]
Lewis Structures

NH₃ ammonia

Water

Lone pair

Lone pairs
Lewis Structures

Electron deficient

\[ \text{boron trifluoride} \]

\[ \text{F} - \text{B} - \text{F} \]

\[ \text{F} - \text{B} - \text{F} \]
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
  
• **BF₃, Mg²⁺, H⁺, H₃O⁺, BH₃, SnCl₄, CH₃⁺, AlCl₃, 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::**
Lewis Acid + Lewis Base

Acetic acid + Ammonia → Acetate ion + Ammonium ion

Lewis Acid + Lewis Base + Lewis Base + Lewis Acid
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