Aqueous Solutions

Pratt & Cornely
Chapter 2

Water

- Electrostatic forces
- \( \approx 2.3 \) H-bonds/water molecule
- Liquid vs. solid water
Intermolecular Forces

- Relative strength of IMF
- Permanent dipole
- London dispersion forces

Solvation

- Dielectric constant
- Solvation shell
- Ionic, polar, and nonpolar compounds
Hydrophobic Effect

- The exclusion of nonpolar substances from aqueous solution
- \( \Delta G = \Delta H - T\Delta S \)
- Cage-like structure of water molecules minimized upon aggregation
- Powerful structural determination

Amphipathic Compounds

- Structures determined by hydrophobic effect
  - Micelles
  - Bilayer
  - Vesicle
Compartmentalization

- Formation of cells and organelles
- Limits diffusion of molecules unless small and nonpolar (O$_2$, CO$_2$)
- Essential for life: don’t reach equilibrium!

Problem 27

- Which of these substances might be able to cross a bilayer? Explain.
Autoionization of Water

Proton jumping: faster than diffusion limit

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

\[ K_w, \quad The \quad Ion \quad Product \quad of \quad Water \]

\[ K_{eq} = \frac{[H^+][OH^-]}{H_2O} \quad K_{eq}[H_2O] = [H^+][OH^-] \]

\[ (1.8 \times 10^{-16} \text{ M})(55.5 \text{ M}) = 1.0 \times 10^{-14} \text{ M}^2 = [H^+][OH^-] \]

\[ K_w = [H^+][OH^-] = 1.0 \times 10^{-14} \text{ M}^2 \]
Reciprocal Relationship

<table>
<thead>
<tr>
<th>pH</th>
<th>$[H^+]$ (M)</th>
<th>$[OH^-]$ (M)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1</td>
<td>$10^{-14}$</td>
</tr>
<tr>
<td>1</td>
<td>$10^{-1}$</td>
<td>$10^{-13}$</td>
</tr>
<tr>
<td>2</td>
<td>$10^{-2}$</td>
<td>$10^{-12}$</td>
</tr>
<tr>
<td>3</td>
<td>$10^{-3}$</td>
<td>$10^{-11}$</td>
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<tr>
<td>4</td>
<td>$10^{-4}$</td>
<td>$10^{-10}$</td>
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<td>5</td>
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<td>8</td>
<td>$10^{-8}$</td>
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<td>9</td>
<td>$10^{-9}$</td>
<td>$10^{-5}$</td>
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<td>10</td>
<td>$10^{-10}$</td>
<td>$10^{-4}$</td>
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<td>11</td>
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<td>$10^{-12}$</td>
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<td>$10^{-13}$</td>
<td>$10^{-1}$</td>
</tr>
<tr>
<td>14</td>
<td>$10^{-14}$</td>
<td>1</td>
</tr>
</tbody>
</table>

pH of Neutral Water

$$K_w = [H^+][OH^-] = 1.0 \times 10^{-14} \text{ M}^2$$

$$K_w = [H^+]^2 = 1.0 \times 10^{-14} \text{ M}^2$$

$$[H^+] = 1.0 \times 10^{-7} \text{ M}$$

$$\text{pH} = -\log[H^+] = \log \frac{1}{[H^+]}$$
Problem 34

Like all equilibrium constants, the value of $K_w$ is temperature dependent. What is the pH of a neutral solution at 30 °C, where $K_w = 1.47 \times 10^{-14}$?

pH of Solutions

- If acid is added to water, the concentration of hydronium increases and pH decreases
- If base is added to water, the concentration of hydronium decreases (ion product of water) and the pH increases
- Addition of MORE acid vs. addition of a STRONGER acid
Strong Acid

- Complete dissociation
- What is the pH of a 0.01 M HCl solution?
- You add a drop of HCl to make a 1 x 10^{-8} M solution. What is the pH?
- What is your assumption?

Weak Acids

Strong

Before Ionization

HCl

At Equilibrium

H^+ Cl^-

Weak

Before Ionization

HF

At Equilibrium

H^+ F^-
Weak Acid Dissociation Constants

- Weak acids have low [pdts], therefore low $K_a$
- Low $K_a$ = high $pK_a$
- Weaker acids have __________ $K_a$ values and __________ $pK_a$s

\[ \text{CH}_2\text{COOH} \xrightarrow{K_a} \text{H}^+ + \text{CH}_3\text{COO}^- \]

\[ K_a = \frac{[\text{H}^+][\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]} \]

---

**TABLE 2.4 pK Values of Some Acids**

<table>
<thead>
<tr>
<th>Name</th>
<th>Formula*</th>
<th>pK</th>
</tr>
</thead>
<tbody>
<tr>
<td>Trifluoroacetic acid</td>
<td>CF$_2$COOH</td>
<td>0.18</td>
</tr>
<tr>
<td>Phosphoric acid</td>
<td>H$_3$PO$_4$</td>
<td>2.10$^a$</td>
</tr>
<tr>
<td>Formic acid</td>
<td>HCOOH</td>
<td>3.75</td>
</tr>
<tr>
<td>Succinic acid</td>
<td>HOOCCH$_2$CH$_2$COOH</td>
<td>4.2$^a$</td>
</tr>
<tr>
<td>Acetic acid</td>
<td>CH$_3$COOH</td>
<td>4.76</td>
</tr>
<tr>
<td>Succinate</td>
<td>HOOCCH$_2$CH$_3$COO$^-$</td>
<td>5.64$^a$</td>
</tr>
<tr>
<td>Thiophenol</td>
<td>C$_7$H$_5$SH</td>
<td>6.60</td>
</tr>
<tr>
<td>Phosphate</td>
<td>H$_3$PO$_4$</td>
<td>6.82</td>
</tr>
<tr>
<td>N-(2-acetamido)-2-aminoo-ethanesulfonic acid (ACES)</td>
<td>H$_3$NCOCH$_2$CH$_2$CH$_3$SO$_3$</td>
<td>6.90</td>
</tr>
<tr>
<td>Imidazole</td>
<td></td>
<td>7.00</td>
</tr>
<tr>
<td>$p$-Nitrophenol</td>
<td>HO(\vdash)NO$_2$</td>
<td>7.24</td>
</tr>
<tr>
<td>N-2-hydroxyethylpiperazine-N' 2-ethanesulfonic acid (HEPES)</td>
<td>HOCH$_2$CH$_2$NH(\vdash)NCH$_2$CH$_3$SO$_3$</td>
<td>7.55</td>
</tr>
<tr>
<td>Glycinate</td>
<td>$^1$H$_2$NCH$_2$CONH$_2$</td>
<td>8.20</td>
</tr>
<tr>
<td>Tris(hydroxymethyl)-aminomethane (Tris)</td>
<td>(HOCH$_2$)$_2$CH$_2$NH</td>
<td>8.30</td>
</tr>
<tr>
<td>Boric acid</td>
<td>H$_3$BO$_3$</td>
<td>9.24</td>
</tr>
<tr>
<td>Ammonium ion</td>
<td>NH$_4^+$</td>
<td>9.25</td>
</tr>
<tr>
<td>Phenol</td>
<td>C$_7$H$_5$OH</td>
<td>9.90</td>
</tr>
<tr>
<td>Methylammonium ion</td>
<td>CH$_3$NH$_3^+$</td>
<td>10.60</td>
</tr>
<tr>
<td>Phosphate</td>
<td>HPO$_4^{2-}$</td>
<td>12.38$^a$</td>
</tr>
</tbody>
</table>

*The acidic hydrogen is highlighted in red: "pK$_a" = \text{pK}_{H^+} - \text{pK}_a" \text{pK}_a".

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Henderson-Hasselbalch

$$
HA \rightleftharpoons H^+ + A^- \quad \log K_a = \log \frac{[H^+][A^-]}{[HA]}
$$

$$
\log K_a = \log[H^+] + \log \frac{[A^-]}{[HA]}
$$

$$
-\log[H^+] = -\log K_a + \log \frac{[A^-]}{[HA]}
$$

$$
pH = pK_a + \log \frac{[A^-]}{[HA]}
$$

Qualitative Understanding

- Relationship of
  - Solution pH
  - Strength of acid
  - Ratio of CB to CA
- Solve quantitatively, but understand qualitatively
• What is/are the major ionization state(s) for succinic acid at pH 3.2, 4.2, 5.2, and 6.2?

\[
pH = pK_a + \log \frac{[A^-]}{[HA]}\]

Understand Figures

Be able to explain what is happening as you trace the line from left to right in this figure.

**Key Tool in biochemistry:** Buffer
Buffers

Buffer action:

\[
\begin{align*}
\ce{OH- + H^+ &<=> H2O} \\
\ce{HA &<=> A^- + H^+}
\end{align*}
\]

Buffers

\[
\begin{align*}
\text{H}^+ &\quad \text{H}^+ \\
\text{Cl}^- &\quad \text{Cl}^-
\end{align*}
\]

Buffers

\[
\begin{align*}
\text{H}^+ &\quad \text{H}^+ \\
\text{Cl}^- &\quad \text{Cl}^-
\end{align*}
\]
Buffer Capacity

• Depends on pKa of CA/CB mix
• Depends on concentration of CA/CB

Making a Buffer

• **Problem 63**: An experiment requires a HEPES buffer, pH 8.0. Write an equation for dissociation of HEPES. What is its effective buffer range? Describe how you would make 1.0 L of 0.10 M HEPES buffer (MW = 260.3 g/mol) using 6.0 M HCl.
Polyprotic Acids

- Must be able to match the pKa with the appropriate proton
- Assumptions are legitimate if the pKa values are more than ~3 units from each other

Blood Buffer

- Physiologic pH 7.4
- Closed vs. Open systems
- Acidosis
Kidney Function

- Kidneys fight acidosis caused by common metabolic processes
- Reclaims excreted bicarbonate by excreting acid
- Forms new bicarb by CO₂ producing metabolism