**Water**

≥70% of weight of most organisms
Polar molecules - hydrophilic
Nonpolar molecules - hydrophobic
Hydrogen bonds are ______ interactions compared to covalent bonds
Each water (H₂O) molecule can form H-bonds with 4 other waters

---

Hydrated Na⁺ ion
Note the orientation of the water molecules

---

Hydrated Cl⁻ ion

---

Covalent bond 0.0965 nm
Hydrogen bond 0.177 nm

---

δ⁺ δ⁺ δ⁺ δ⁺
δ⁻ δ⁻ δ⁻ δ⁻

---

δ⁺ 104.5° δ⁺
δ⁻ δ⁻
**Water**

Hydrogen bonding

- **Hydrogen acceptor**
  - C
  - O
  - H
  - O

- **Hydrogen donor**
  - N
  - O
  - H

- Between the hydroxyl group of an alcohol and water
- Between the carbonyl group of a ketone and water
- Between peptide groups in polypeptides
- Between complementary bases of DNA
Water

Amphipathic - contains regions that are polar (charged) and regions that are nonpolar
Water

Amphipathic molecules

Dispersion of lipids in $\text{H}_2\text{O}$
Each lipid molecule forces surrounding $\text{H}_2\text{O}$ molecules to become highly ordered.

Clusters of lipid molecules
Only lipid portions at the edge of the cluster force the ordering of water. Fewer $\text{H}_2\text{O}$ molecules are ordered, and entropy is increased.

Micelles
All hydrophobic groups are sequestered from water; ordered shell of $\text{H}_2\text{O}$ molecules is minimized, and entropy is further increased.
# Water

## Table 4-2

<table>
<thead>
<tr>
<th></th>
<th><img src="image" alt="Chemical Structure" /></th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Polar</strong></td>
<td></td>
</tr>
<tr>
<td>Glucose</td>
<td><img src="image" alt="Chemical Structure" /></td>
</tr>
<tr>
<td>Glycine</td>
<td><img src="image" alt="Chemical Structure" /></td>
</tr>
<tr>
<td>Aspartate</td>
<td><img src="image" alt="Chemical Structure" /></td>
</tr>
<tr>
<td>Lactate</td>
<td><img src="image" alt="Chemical Structure" /></td>
</tr>
<tr>
<td>Glycerol</td>
<td><img src="image" alt="Chemical Structure" /></td>
</tr>
<tr>
<td><strong>Nonpolar</strong></td>
<td><img src="image" alt="Chemical Structure" /></td>
</tr>
<tr>
<td>Typical wax</td>
<td><img src="image" alt="Chemical Structure" /></td>
</tr>
<tr>
<td><strong>Amphipathic</strong></td>
<td><img src="image" alt="Chemical Structure" /></td>
</tr>
<tr>
<td>Phenylalanine</td>
<td><img src="image" alt="Chemical Structure" /></td>
</tr>
<tr>
<td>Phosphatidylcholine</td>
<td><img src="image" alt="Chemical Structure" /></td>
</tr>
</tbody>
</table>
Water

Ordered water interacting with substrate and enzyme

Substrate

Enzyme

Disordered water displaced by enzyme-substrate interaction

Enzyme-substrate interaction stabilized by hydrogen-bonding, ionic, and hydrophobic interactions
## Water

### TABLE 2-5  Four Types of Noncovalent ("Weak") Interactions among Biomolecules in Aqueous Solvent

- **Hydrogen bonds**
  - Between neutral groups
    - ![Hydrogen bond between neutral groups](image)
  - Between peptide bonds
    - ![Hydrogen bond between peptide bonds](image)

- **Ionic interactions**
  - Attraction
    - ![Ionic attraction](image)
  - Repulsion
    - ![Ionic repulsion](image)

- **Hydrophobic interactions**
  - Any two atoms in close proximity

- **van der Waals interactions**
Water

(a) WATER

(b)
Water chain in cytochrome $f$
Ionization of Water

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

\( \text{H}^+ \) is a hydrogen ion  
\( \text{OH}^- \) is a hydroxyl ion

Actually

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

\( \text{H}_3\text{O}^+ \) is a hydronium ion

Hydronium ion gives up a proton

Water accepts proton and becomes a hydronium ion
**Ionization of Water**

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

\[
K_{eq} = [\text{H}^+][\text{OH}^-] / [\text{H}_2\text{O}]
\]

\[
[\text{H}_2\text{O}] \sim 55.5 \text{ mol/L} \\
K_{eq} = 1.8 \times 10^{-16}
\]

\[
K_w = (K_{eq}) [\text{H}_2\text{O}] \\
K_w = (1.8 \times 10^{-16}) (55.5)
\]

So \( K_w = [\text{H}^+][\text{OH}^-] = 10^{-14} \text{ (mol/L)}^2 \) at 25°C

In pure water, \([\text{H}^+] = [\text{OH}^-] = 10^{-7}\), a neutral solution

\[
\text{pH} = \log (1/[\text{H}^+]) = -\log[\text{H}^+]
\]

A neutral solution has a pH = 7.0
When \([\text{H}^+] > [\text{OH}^-]\), pH < 7.0 (acidic)
When \([\text{H}^+] < [\text{OH}^-]\), pH > 7.0 (basic)
**Acid/Base Pairs**

<table>
<thead>
<tr>
<th>Acid</th>
<th>Conjugate base</th>
</tr>
</thead>
<tbody>
<tr>
<td>HA⁺</td>
<td>H⁺ + A</td>
</tr>
<tr>
<td>HA</td>
<td>H⁺ + A⁻</td>
</tr>
<tr>
<td>HA⁻</td>
<td>H⁺ + A²⁻</td>
</tr>
</tbody>
</table>

For a strong acid, dissociation is complete so \([H^+] = [\text{acid}]\) and 
\[ \text{pH} = -\log [H^+] \]

For weak acid, dissociation is incomplete so 
\[ K_a = [H^+][A^-] / [HA] \]
\( K_a \) is acid dissociation constant

\[ \text{pH} \text{ is function of } [\text{acid}] \text{ and } K_a \]
\[ [H^+] = K_a [HA] / [A^-] \]

\[ -\log[H^+] = -\log K_a + \log [A^-] / [HA] \]

\[ \text{pK}_a = -\log K_a \]

\[ \text{pH} = \text{pK}_a + \log [A^-] / [HA] \]
(Henderson-Hasselbach)

The \( pK \) of an acid (base) is the pH at which the acid (base) is half dissociated
pH of aqueous fluids
Conjugate acid-base pairs

**Monoprotic acids**
- Acetic acid
  \( K_a = 1.74 \times 10^{-5} \text{ M} \)
- Ammonium ion
  \( K_a = 5.62 \times 10^{-10} \text{ M} \)

**Diprotic acids**
- Carbonic acid
  \( K_a = 1.70 \times 10^{-4} \text{ M} \);
  \( pK_a = 6.31 \times 10^{-11} \text{ M} \)
- Bicarbonate
  \( K_a = 6.31 \times 10^{-11} \text{ M} \)
- Glycine, carboxyl
  \( K_a = 4.57 \times 10^{-3} \text{ M} \);
  \( pK_a = 2.34 \text{ M} \)
- Glycine, amino
  \( K_a = 2.51 \times 10^{-10} \text{ M} \)

**Triprotic acids**
- Phosphoric acid
  \( K_a = 7.25 \times 10^{-3} \text{ M} \);
  \( pK_a = 2.14 \text{ M} \)
- Dihydrogen phosphate
  \( K_a = 1.38 \times 10^{-7} \text{ M} \);
  \( pK_a = 6.86 \text{ M} \)
- Monohydrogen phosphate
  \( K_a = 3.98 \times 10^{-13} \text{ M} \)
Titration Curve

acetic acid

\[ \text{CH}_3\text{COO}^- \]

\[ [\text{CH}_3\text{COOH}] = [\text{CH}_3\text{COO}^-] \]

pH = pK\text{a} = 4.76

Buffering region

pH 5.76

pH 3.76

OH\textsuperscript{-} added (equivalents)

Percent titrated

0 0.1 0.2 0.3 0.4 0.5 0.6 0.7 0.8 0.9 1.0
pK\textsubscript{1} = a carboxyl group
pK\textsubscript{2} = an amino group
Buffering against pH changes

Buffers: mixtures of weak acids and their conjugate bases
Resist changes in pH when small amounts of acid/base are added

Maintenance of a specific and constant pH, near 7.0 is needed by cells and organisms - small changes in pH can have a large impact on rate of cellular processes

\[ K_w = [H^+][OH^-] \]

\[ K_a = \frac{[H^+][Ac^-]}{[HAc]} \]
Buffering against pH changes
amino acid histidine - weak acid

\[
\text{protein} \quad \quad \text{protein} \\
\begin{align*}
\text{CH}_2 & \quad \text{H} \quad \text{N} \quad \text{CH} \\
\text{C} & \quad \text{N} \quad \text{C} \\
\text{H} & \quad \text{N} \\
\end{align*}
\begin{align*}
\text{CH}_2 & \quad \text{H} \quad \text{N} \quad \text{CH} + \text{H}^+ \\
\text{C} & \quad \text{N} \\
\text{H} & \quad \text{N} \\
\end{align*}
\]

\[\text{pKa} = 6.0\]
Protein enzymes have an optimum pH for activity.
**Biological buffers - bicarbonate (phosphate too)**

Exercise
lactic acid (H+) produced (pH of blood plasma lowered)
reaction pushed to produce more CO$_2$ - exhale

![Chemical reactions diagram](image)

Protein catabolism
ammonia (NH$_3$) produced and pH of blood plasma is raised
Reaction pushed to create more H+
more CO$_2$ from lungs dissolved in blood plasma

RATE OF BREATHING keeps BLOOD PH CONSTANT
Water as a reactant

**Phosphoanhydride** (a)

\[
R-O-P-O-P-O^{-} + H_{2}O \rightleftharpoons R-O-P-OH + HO-P-O^{-}
\]

**Phosphate ester** (b)

\[
R-O-P-O^{-} + H_{2}O \rightleftharpoons R-OH + HO-P-O^{-}
\]

**Carboxylate ester** (c)

\[
R^{1}-C^{\text{OR}^{2}} + H_{2}O \rightleftharpoons R^{1}-C^{\text{OH}} + HO-R^{2}
\]

**Acyl phosphate** (d)

\[
R-C-O-P-O^{-} + H_{2}O \rightleftharpoons R-C^{\text{OH}} + HO-P-O^{-}
\]