**Thermodynamics**

\[
\Delta E_{\text{universe}} = 0 \quad \Delta S_{\text{universe}} > 0 \quad \Delta S_{\text{system}} + \Delta S_{\text{surroundings}} = \Delta S_{\text{universe}}
\]

\[
\Delta G = \Delta H - T\Delta S \quad \text{At equilibrium } \Delta G = 0
\]

ΔH (energy required to break bonds) – (energy released during bond formation). ΔG<0 is spontaneous (exergonic); ΔG>0 is non-spontaneous (endergonic); ΔG represents the maximum possible amount of useful energy obtainable from a reaction. ΔG is totally unrelated to rate. ΔG° is relative stability of starting and ending states. ΔG depends on ΔG° and conditions.

\[
A + B \rightleftharpoons C + D \quad K_{eq} = \frac{[C][D]}{[A][B]} \quad \Delta G^\circ = -RT\ln K_{eq} \quad \Delta G = \Delta G^\circ + RT \ln \left( \frac{\text{[Products]}}{\text{[Reactants]} \right)
\]

\[\Delta G^\circ: \text{pH} = 7.0; [\text{H}_2\text{O}] \text{ is part of } \Delta G^\circ, \text{and } [\text{Mg}^{2+}] = 1 \text{ mM}.
\]

For reactions in which water and H⁺ are not reactants, \(\Delta G^\circ = \Delta G^\circ\).

Solubility in water (and other solvents) depends on ΔH and ΔS terms. The hydrophobic effect is largely due to ΔS\text{water}.

**Ionic solutes** – water is a protic solvent; it stabilizes both cations and anions.

Acid-base properties of inorganic and organic compounds: pH = pK\text{a} + \log \frac{[\text{A}^-]}{[\text{HA}]} If an acid is added to a solution, the pH will decrease. If a base is added to a solution, the pH will increase. Buffers attenuate the pH change by binding or releasing protons.

Amino acids are always ionized in aqueous solution; the charge on an amino acid or protein depends on the nature of the group(s) and the degree of protonation. The **local environment alters the pK\text{a} values for ionizable groups**.

**Primary (1°) Structure** – Covalent backbone and amino acid sequence

**Secondary (2°) Structure** – Hydrogen bonding for backbone atoms

**Tertiary (3°) Structure** – 3D structure: hydrophobic effect, H-bonds, electrostatic interactions, van der Waals interactions (favorable and unfavorable due to steric constraints, especially for peptide bond), and (relatively rare) disulfide bonds.

**Quaternary (4°) Structure** – Multichain proteins: non-covalent and (in surface/extracellular proteins) disulfide interactions between polypeptides.

Secondary structure is a way of stabilizing the polar peptide backbone; secondary structures are repeating Φ / Ψ angle pairs. Real secondary structures frequently do not have exactly the angles shown below.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>α-Helix</th>
<th>Antiparallel β-sheet</th>
<th>Parallel β-sheet</th>
<th>Collagen</th>
</tr>
</thead>
<tbody>
<tr>
<td>Φ</td>
<td>−57°</td>
<td>−139°</td>
<td>−119°</td>
<td>−51°</td>
</tr>
<tr>
<td>Ψ</td>
<td>−47°</td>
<td>135°</td>
<td>113°</td>
<td>153°</td>
</tr>
<tr>
<td>rise per residue</td>
<td>1.5 Å (3.6)</td>
<td>3.5 Å</td>
<td>3.5 Å</td>
<td>3 Å (3.3)</td>
</tr>
</tbody>
</table>

Proteins are stable because of thermodynamic and/or kinetic considerations.
Protein\textsubscript{unfolded} $\rightleftharpoons$ Protein\textsubscript{folded}

| Polar residues | $\Delta H\text{\scriptsize{chain}}$ | (+) | $\Delta S\text{\scriptsize{chain}}$ | (-) | Overall $\Delta G > 0$
| Non-polar residues | $\Delta H\text{\scriptsize{chain}}$ | small (+) | $\Delta S\text{\scriptsize{chain}}$ | (+) | Overall $\Delta G < 0$
|                     | $\Delta H\text{\scriptsize{solvent}}$ | small (-) | $\Delta S\text{\scriptsize{solvent}}$ | large | for folding

Carbohydrates are usually chiral molecules; monosaccharides have a general molecular formula $C_n(H_2O)_n$. The linear form contains a carbonyl (aldehyde or 2-ketone); monosaccharides with 5 or more carbons form cyclic hemiacetals in aqueous solution.