

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).

$\Delta G < 0$ is spontaneous (**exergonic**); $\Delta G > 0$ 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.

$A + B \rightleftharpoons C + D$	$K_{eq} = \frac{[C][D]}{[A][B]}$	$\Delta G^\circ = -RT \ln K_{eq}$	$\Delta G = \Delta G^\circ + RT \ln \left(\frac{[\text{Products}]}{[\text{Reactants}]} \right)$
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ΔG° : pH = 7.0; $[H_2O]$ is part of ΔG° , and $[Mg^{2+}] = 1 \text{ mM}$.

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_{water} .

Ionic solutes – water is a protic solvent; it stabilizes both cations and anions. $F = \frac{kq_1q_2}{\epsilon r^2}$

Acid-base properties of inorganic and organic compounds: $pH = pK_a + \log \frac{[A^-]}{[HA]}$ 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_a values for ionizable groups.**

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

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

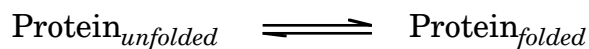
Tertiary (3°) Structure – 3D structure: hydrophobic effect, H-bonds, electrostatic interactions, van der Waals interactions (favorable and unfavorable due to steric constraints, especially for peptide bond), and (relatively rare) disulfide bonds.

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

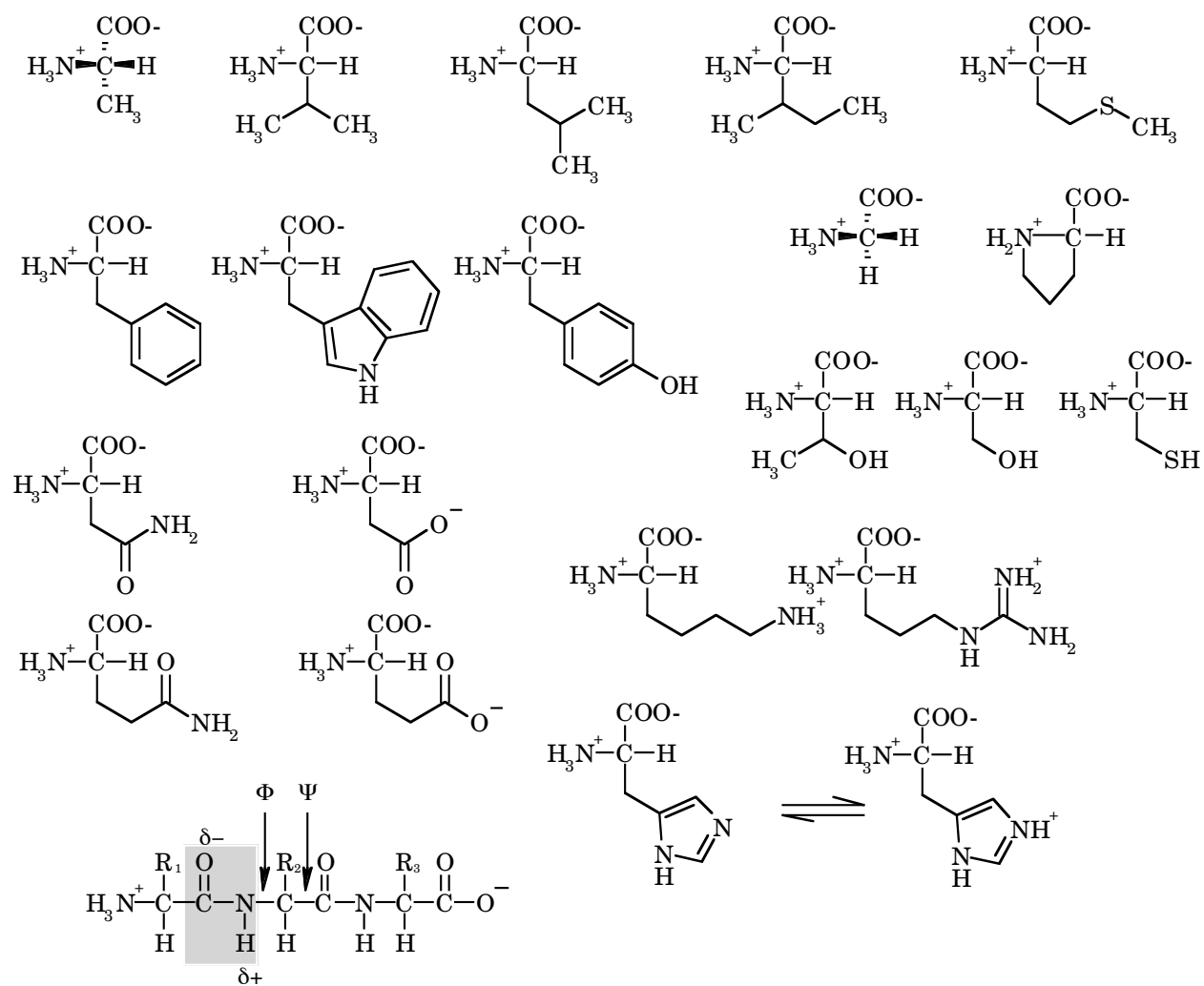
Secondary structure is a way of stabilizing the polar peptide backbone; secondary structures are repeating Φ / Ψ angle pairs. Real secondary structures frequently do not have exactly the angles shown below.

Parameter	α -Helix	Antiparallel β -sheet	Parallel β -sheet	Collagen
Φ	-57°	-139°	-119°	-51°
Ψ	-47°	135°	113°	153°
rise per residue	1.5 Å (3.6 residues/turn)	3.5 Å	3.5 Å	3 Å (3.3 residues/turn)

Proteins are stable because of thermodynamic and/or kinetic considerations.



Polar residues	ΔH_{chain}	(+)	$(-T\Delta S_{\text{chain}})$	(+)	Overall $\Delta G > 0$ for folding
	$\Delta H_{\text{solvent}}$	(-)	$(-T\Delta S_{\text{solvent}})$	(-)	
Non-polar residues	ΔH_{chain}	small (+) or small (-)	$(-T\Delta S_{\text{chain}})$	(+)	Overall $\Delta G < 0$ for folding
	$\Delta H_{\text{solvent}}$	(-) <i>significant</i>	$(-T\Delta S_{\text{solvent}})$	(-) <i>large</i>	



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.