ENZYMES & KINETICS

If ΔG = negative [spontaneous reaction], why no reaction?
Activation energy required

Reaction energy versus activation energy:
Illustrate profile of chemical reaction (p 130)
metastable state: lack of stable intermediates slows reaction

catalysts stabilize intermediates, reduce activation energy, therefore speed up reactions

In biological systems, catalysis is performed by
enzymes = protein catalyst

Enzyme: apoenzyme = protein component
prosthetic groups:
if inorganic = cofactor (Mg^{++}, Ca^{++}, Fe^{++}, etc)
if organic = coenzyme (most are vitamins)
holoenzyme = entire, active enzyme

Active site substrate binding to enzyme:
Lock and key (p 132) versus induced fit (p 137)
substrate specificity high in biological systems
Steps: substrate binding, activation, chemical reaction to finish

Enzyme activity dependent on proper folding of enzyme:
Amino acid sequence, pH, temperature, osmolarity
(p 134: draw optimum curves for pH and temperature)

Allosteric site (“other place”) binds non-competitive inhibitors (for regulation)

KINETICS: (p. 137) rate = velocity = reactant consumed (or product made)/unit time.

LINEAR GRAPH: rate or velocity vs [S] shows substrate saturation Show Vmax (p. 139 & 143)
Lucy in chocolate factory: http://www.youtube.com/watch?v=8NPzLBSBzP1

Then add inhibitors: competitive & non competitive (p 145)
overcoming of competitive inhibition, but not allosteric inhibition

Examples: Competitive: pABA is displaced by sulfanilamide
Allosteric: histidine biosynthetic pathway
Isoleucine biosynthetic pathway (p 144)

Michaelis-Menten: \( v = \frac{V_{\text{max}}[S]}{K_m + [S]} \)
\( K_m \) is Michaelis Menten constant, \( = [S] \) yielding 1/2 \( V_{\text{max}} \)
Lineweaver-Burk plot, double reciprocal plot (p. 142 and 144)
\( X \) intercept = \( -1/K_m \)
\( Y \) intercept = \( 1/V_{\text{max}} \)

Note that end-product inhibition in metabolic pathways:

Regulates commitment of resources.
Example: G enzyme, first in histidine biosynthetic pathway, is inhibited by histidine,
also isoleucine inhibition of threonine deaminase (p. 147)

Glycogen phosphorylase: (p 149)
active when phosphorylated by phosphorylase kinase. Inactive if \( \text{PO}_4 \) is lacking.
Irreversible inhibition by heavy metals, halogens, alkylating agents, bind covalently to
enzyme, destroy catalytic activity.