Thermodynamics

a small digression before talking about Enzymes

2nd Law of Thermodynamics -- for any spontaneous process, the **Entropy** (disorder) of the universe, $\Delta S_{universe}$, must increase. This is very difficult to measure, however ===> we need a criterion of spontaneity which applies to our system (organism).

At constant Temperature and Pressure (conditions under which we exist, more or less) the criterion is the change in

Gibbs Free Energy = ΔG

It is determined by the **Entropy** change of the system, ΔS, and by the change in **Enthalpy**, ΔH, or heat content of the system (the energy exchanged with the surroundings) if

$\Delta H < 0$ --> the reaction is exothermic and heat is given off

$\Delta H > 0$ --> the reaction is endothermic and heat is absorbed

$$\Delta G = \Delta H - T\Delta S$$

What does ΔG Depend Upon?

Given the Following Chemical Reaction

$$aA + bB \rightleftharpoons cC + dD$$

The Free Energy Change is:

$$\Delta G = \Delta H - T\Delta S$$

and

$$\Delta G = \Delta G^o + RT\ln\frac{[C]^c[D]^d}{[A]^a[B]^b}$$

A reaction can be spontaneous even if:

- $\Delta G^o > 0$ -- ΔG can still be < 0 if [C] and [D] are small or [A] and [B] are large
- $\Delta S < 0$ --if ΔH is << 0
- $\Delta H > 0$ --if ΔS is >> 0

Equilibrium

At Equilibrium there is no net change in free energy

==> $\Delta G = 0$

$$0 = \Delta G^{o} + RT \ln \frac{[C]^{c}[D]^{d}}{[A]^{a}[B]^{b}}$$

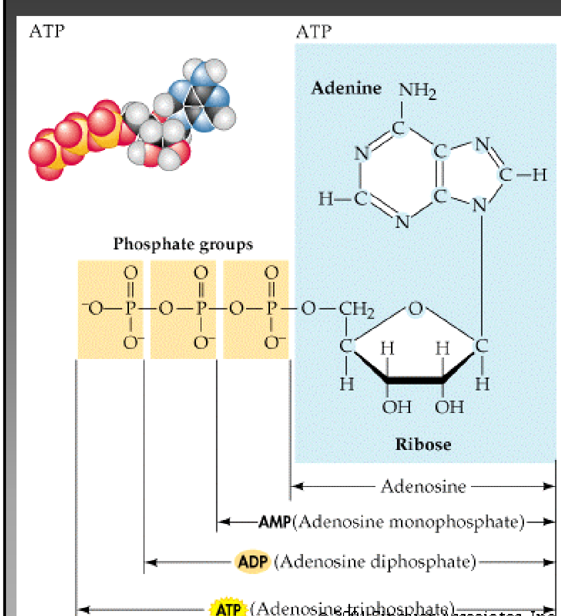
and

$$\frac{[C]^{c}[D]^{d}}{[A]^{a}[B]^{b}} = K_{eq}$$

Therefore...

$$\Delta G^{o} = -RT \ln K_{eq}$$

Figure 6.8: ATP and Hydrolysis of ATP



Consider the reaction...

$$ATP + H_2O \rightleftharpoons ADP + Pi$$

ATP has more free energy than ADP and Pi

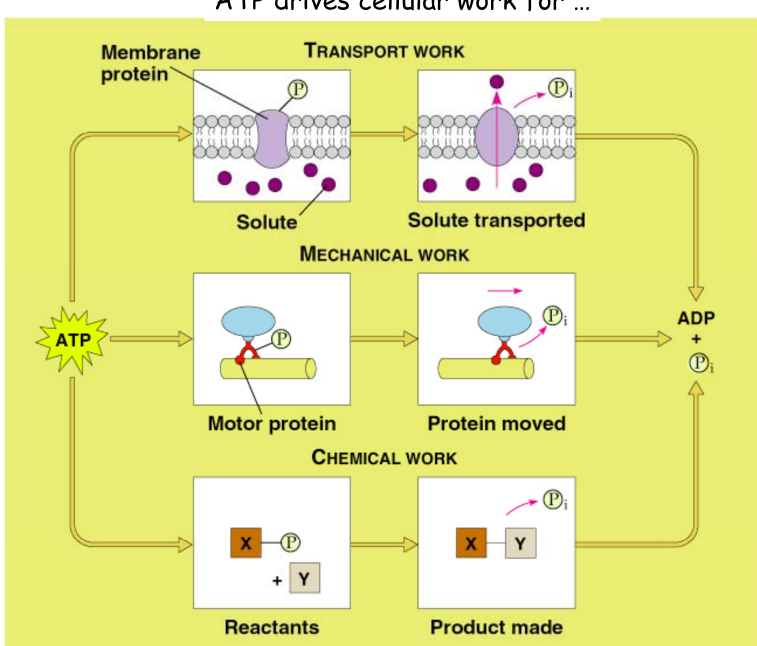
➔The free energy change for this reaction, ΔG, is less than 0 and the reaction is favorable, i.e. it is **Exergonic**.

Note: Pi is an abbreviation for phosphate ions.

ATP Provides Energy for:

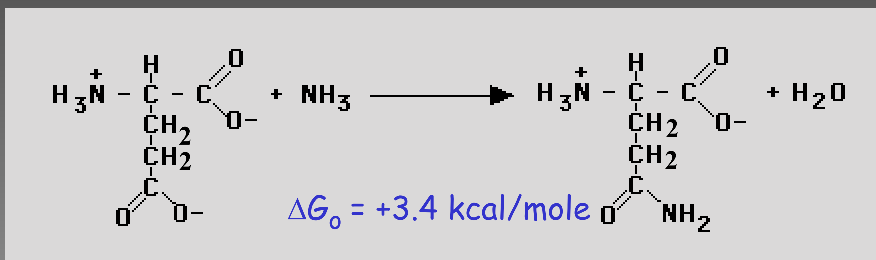
- **Mechanical Work:** Muscle contraction, flagella and cilia movement etc.
- **Transport Work:** Pumping ions and molecules across membranes against a concentration gradient
- **Chemical Work:** Coupling energy from ATP to Endergonic reactions to make them go

ATP drives cellular work for …

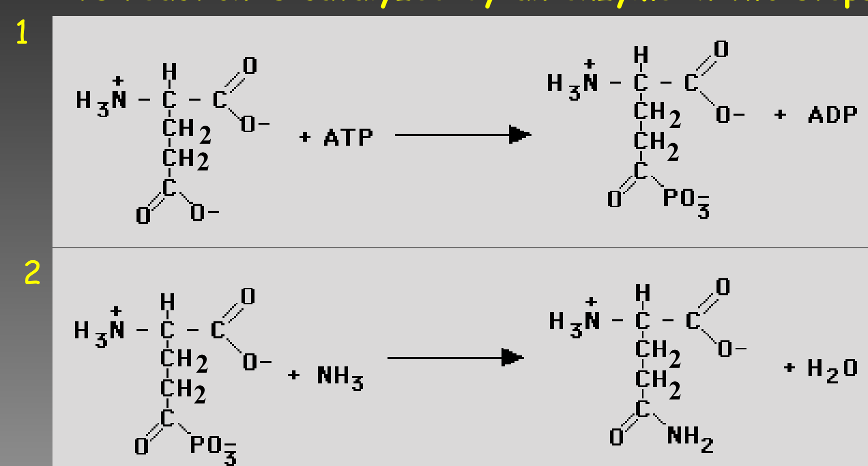


See Figure 6.7: Energy coupling by phosphate transfer

Glutamate + Ammonia Glutamine



This reaction is catalyzed by an enzyme in two steps



Energetically, this can be described as the sum of the following two reactions

Glu + NH_3 ----> Glu-NH_2 + H_2O ΔG_o = +3.4 kcal/mole

ATP + H_2O ----> ADP + Pi ΔG_o = -7.3 kcal/mole

Glu + NH_3 + ATP ----> Glu-NH_2 + ADP + Pi ΔG_o = - 3.9 kcal/mole

Figure 6.9: **The ATP Cycle**

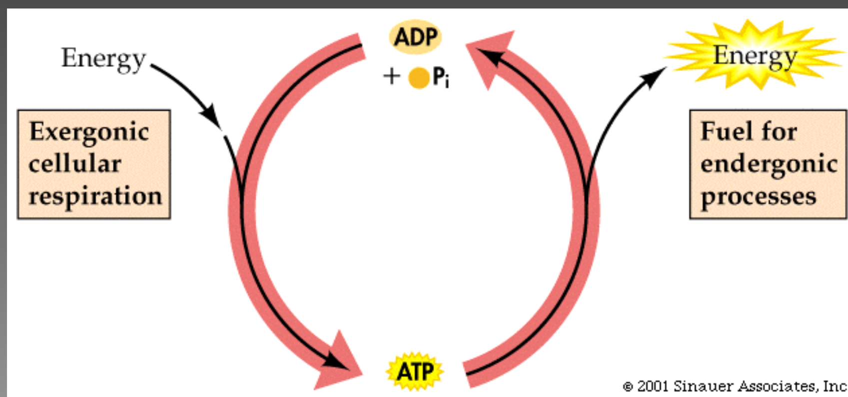


Figure 6.11: ***Activation Energy*** Initiates Reactions

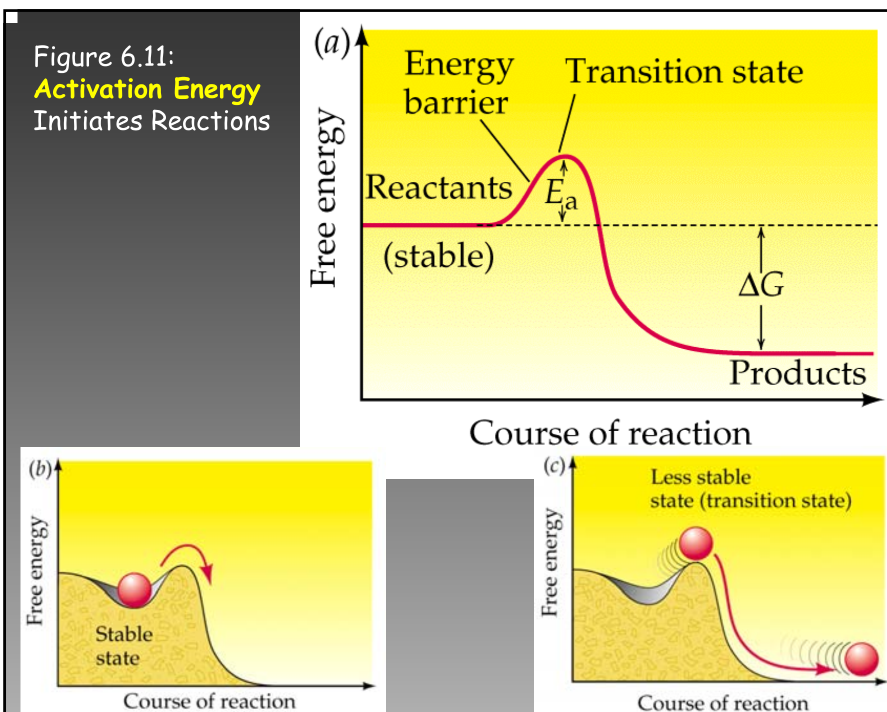
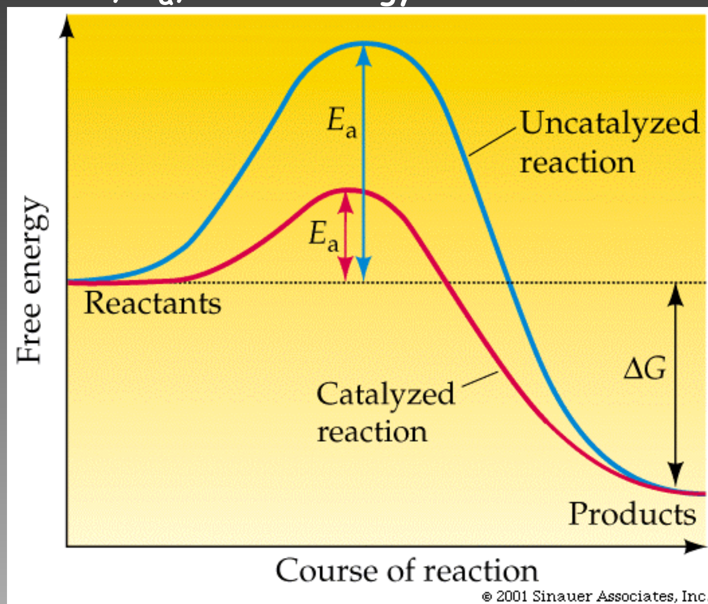


Figure 6.14: Enzymes reduce the energy of activation, E_a, or the energy barrier of a reaction.



Characteristics of Enzymes

Increase rates (alter kinetics) -- Increase the rate of approach to equilibrium but don't change ΔG

Specificity--Enzymes bind specific molecules and not others

Induced Fit--Enzyme adapts to bind Substrate and bend it into the transition state whose structure is intermediate between the structures of the substrate and the product.

pH Optimum--since enzymes are composed of aa's, their structures and therefore activity (rate at which they catalyze reactions) depend upon the pH which can drastically alter their structures.

Temperature--rates of enzyme catalyzed reactions increase with temperature (as do all reactions) up the the point where the enzyme's tertiary structure is destroyed (denatured) by heat energy.

The rate of an enzyme catalyzed reaction is described the the **Michaelis-Menton Equation** which is a model for enzyme action in which each enzyme molecule binds to one substrate, S, molecule at a time converting it to a product, P. At high [S] the enzyme becomes **Saturated**. See **Figure 6.16**

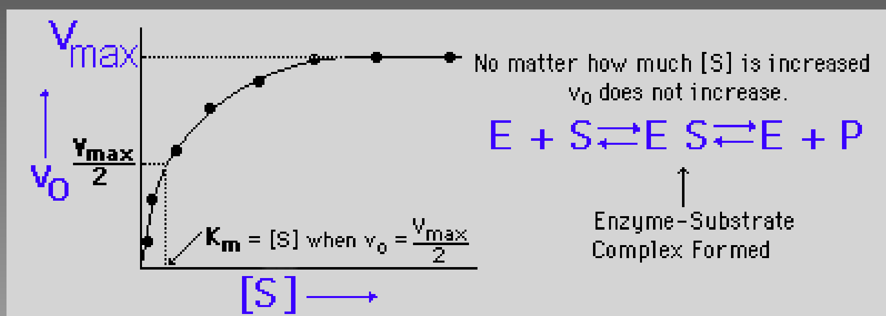


Figure 6.13: **The catalytic cycle of an enzyme**

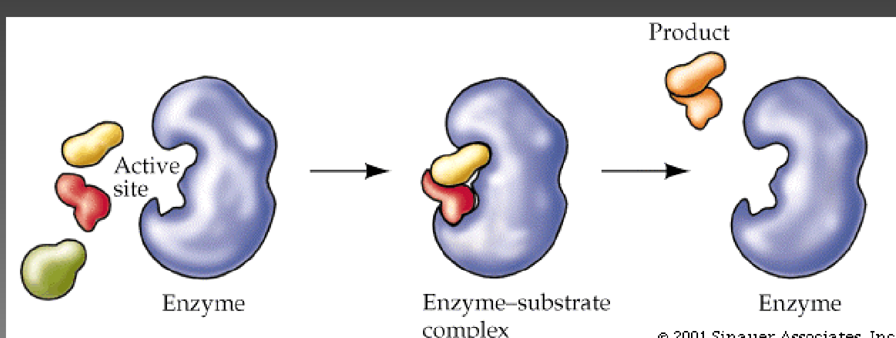
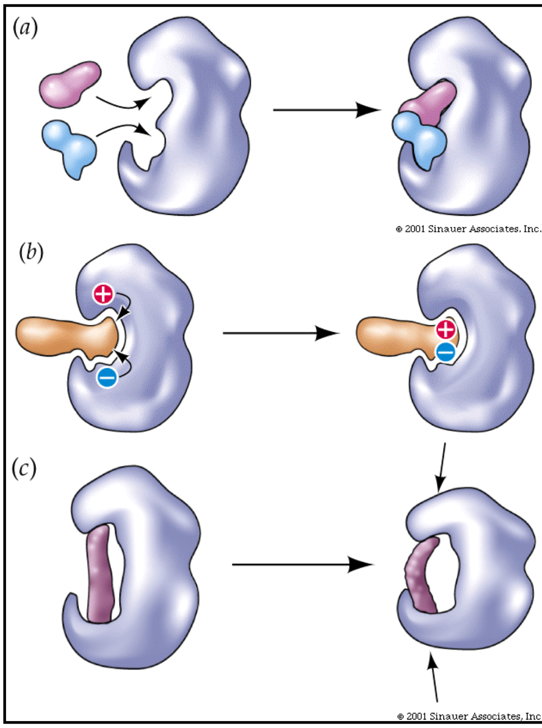


Figure 6.15: Enzymes catalyze reactions by…



Orienting molecules

Charge interactions

Deforming the substrate

Figure 6.25: **pH affects enzyme activities**

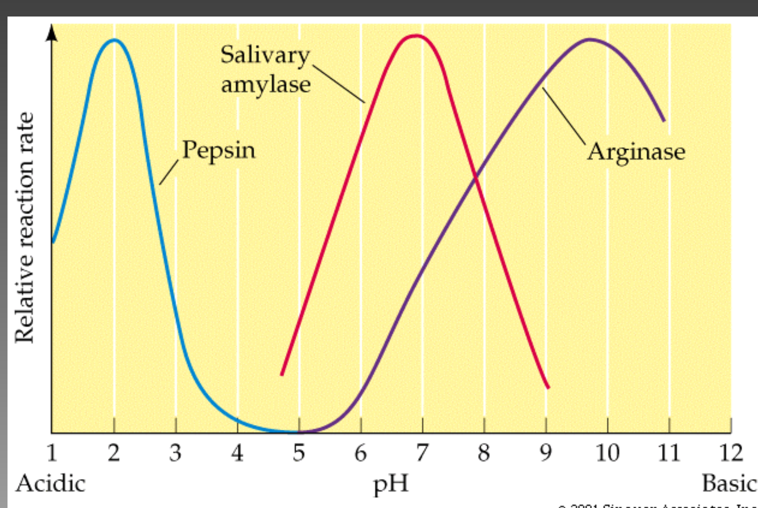


Figure 6.26: Enzymes are sensitive to temperature

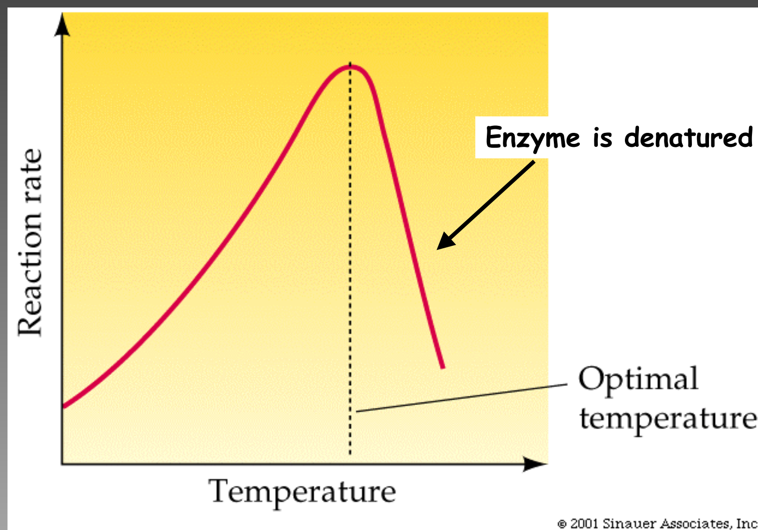


Figure 6.21: Enzyme Inhibition

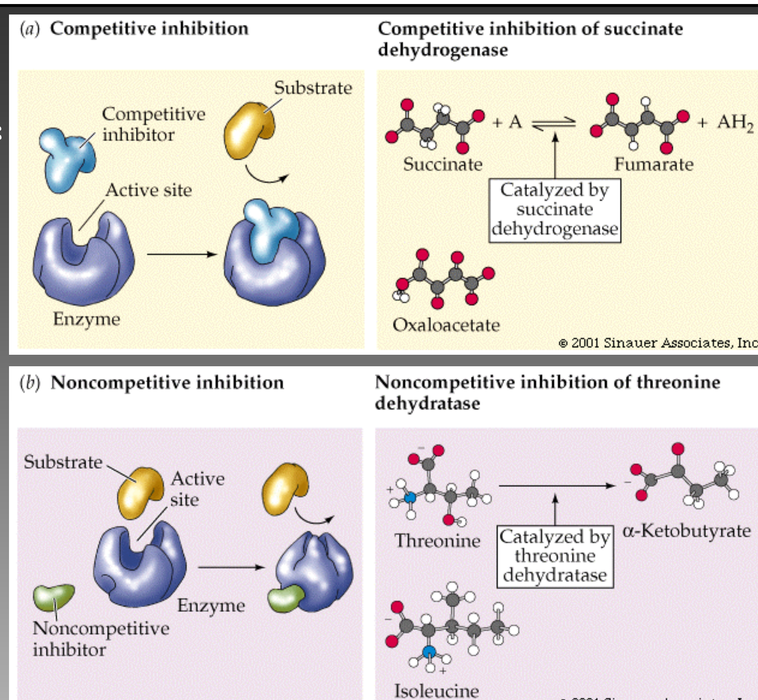


Figure 6.24: Feedback Inhibition

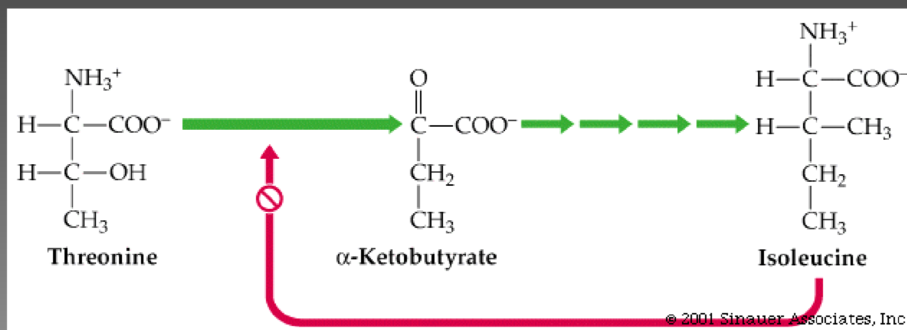


Figure 6.23: Allosteric Regulation Of Enzymes