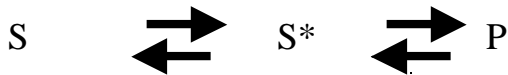


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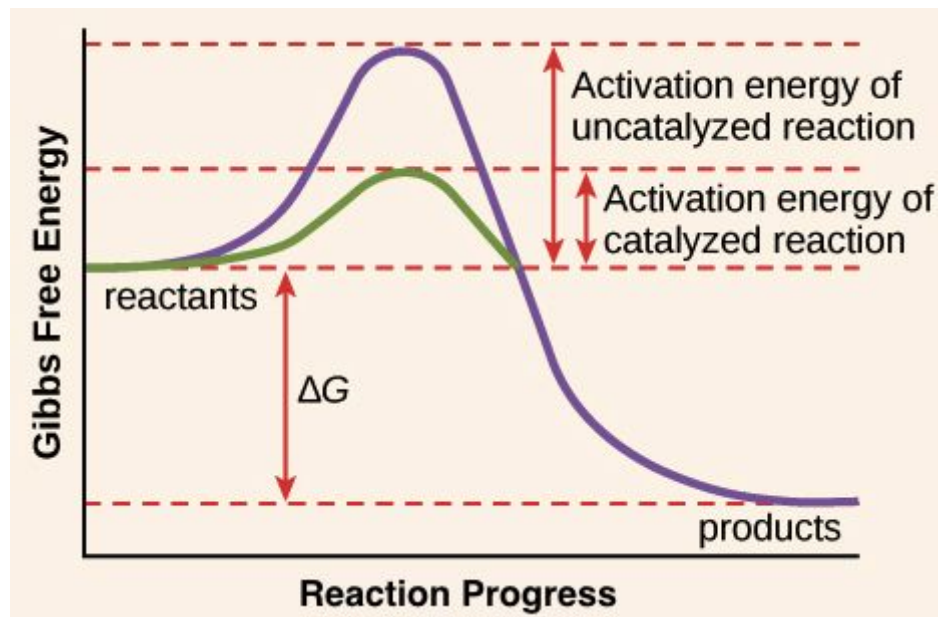
Mechanisms of Enzyme Action

Kinetics of an uncatalyzed chemical reaction:



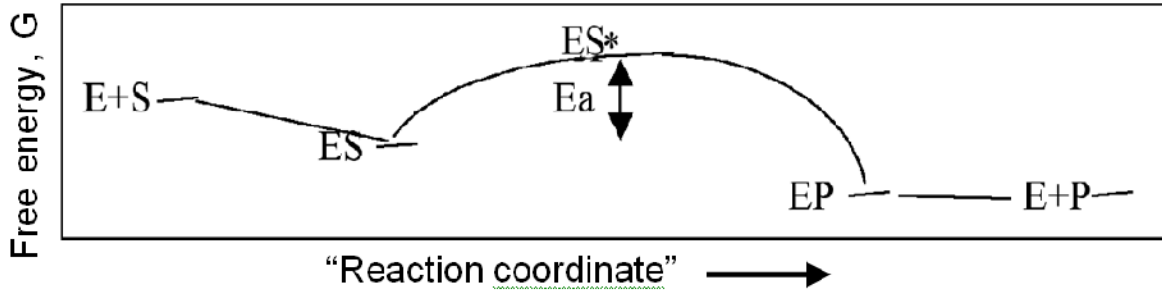
Free energy, G

Ea is “activation energy”



Kinetics of a catalyzed chemical reaction:





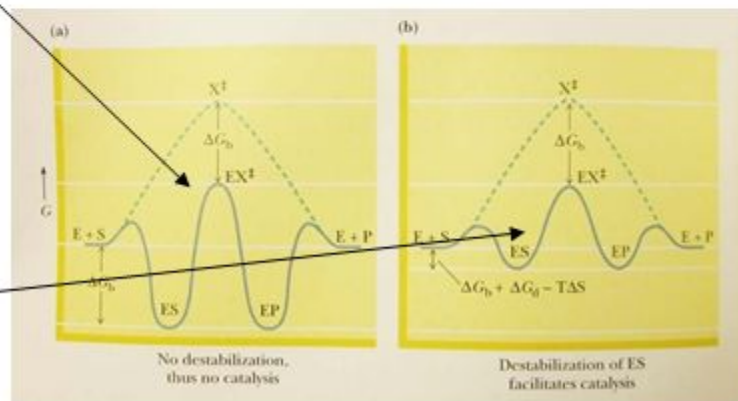
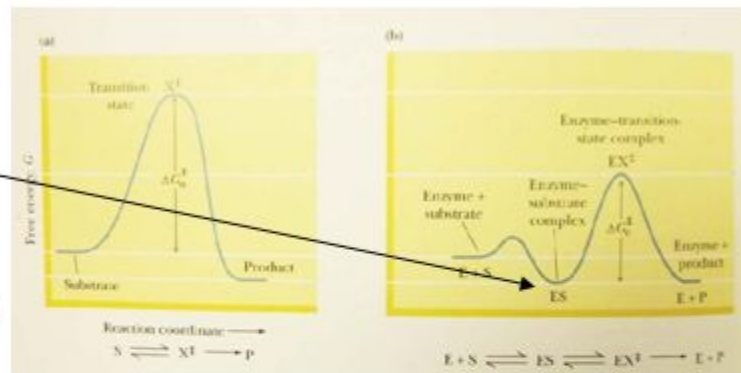
1. Enzyme does not affect ΔG or ΔG° between S and P (i.e., equilibrium)
2. Enzyme reduces E_a : E_a (catalyzed) < E_a (uncatalyzed)

A more complete way of showing the effects of enzymes:

Enzymes bind to substrates, so $G(ES) < G(E+S)$.

However, if all they did was to bind, then $E_a = \Delta G(ES^*)$ for the reaction would not be reduced.

So when they bind the substrate, they stress it in some way, raising $G(ES)$ for part of the substrate and reducing $\Delta G(ES^*) (=E_a)$.



Quantitatively, what is the effect of reducing E_a ?

For reaction A → B, $V = k[A]$

$$k = \left(\frac{\mathbf{K}}{T/h}\right) \exp(-E_a/RT)$$

\mathbf{K} = Boltzman's constant; h = Plank's constant,

So k and thus V are inversely and exponentially related to E_a and directly related to T :

A 6 kJ/mol reduction in E_a gives ca 10x increase in k and V

$$\Delta k \sim \exp(+6000/8.3 \cdot 300) \sim 11$$

(reduction in E_a is an increase from $-E_a$)

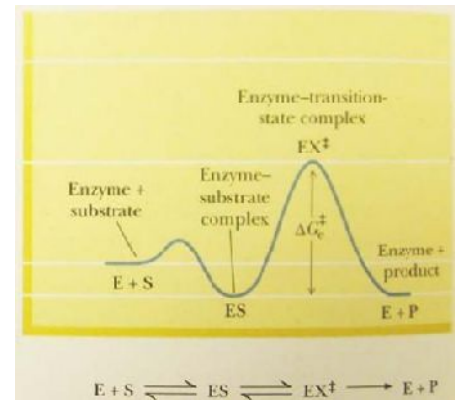
V (catalyzed)/ V (uncatalyzed) for various enzymes varies from 10^4 to 10^{21} , meaning E_a is reduced by ca 23 to 126 kJ/mol

How do enzymes reduce E_a ?

These effects raise $G(ES)$:

cage effect, orientation, steric straining of bonds (stress from H-, Vanderwaal's, ionic bonds), dislocation of bonding electrons through +/- charges

These effects reduce $G(ES^*)$: covalent bonds, acid-base catalysis, low-barrier hydrogen bonds, and metal ion catalysis



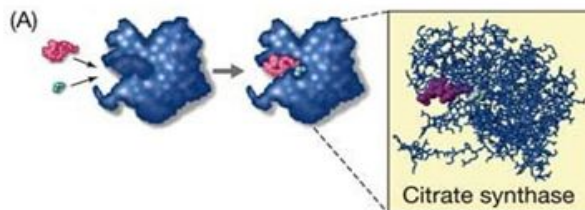
Different classes of enzymes may use

different mechanisms:

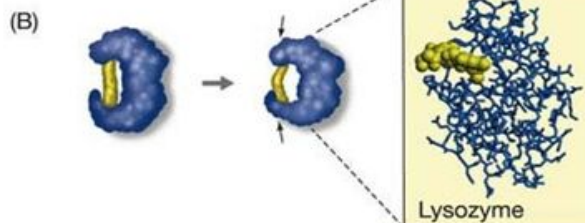
1. Oxidoreductases (oxidation-reduction reactions)
2. Transferases (transfer of functional groups)
3. Hydrolases (hydrolysis reactions)
4. Lyases (addition to double bonds)
5. Isomerases (isomerization reactions)
6. Ligases (formation of bonds with ATP cleavage)

Examples:

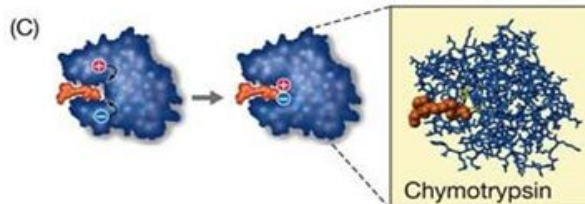
Orientation,
Cage effect



Strain



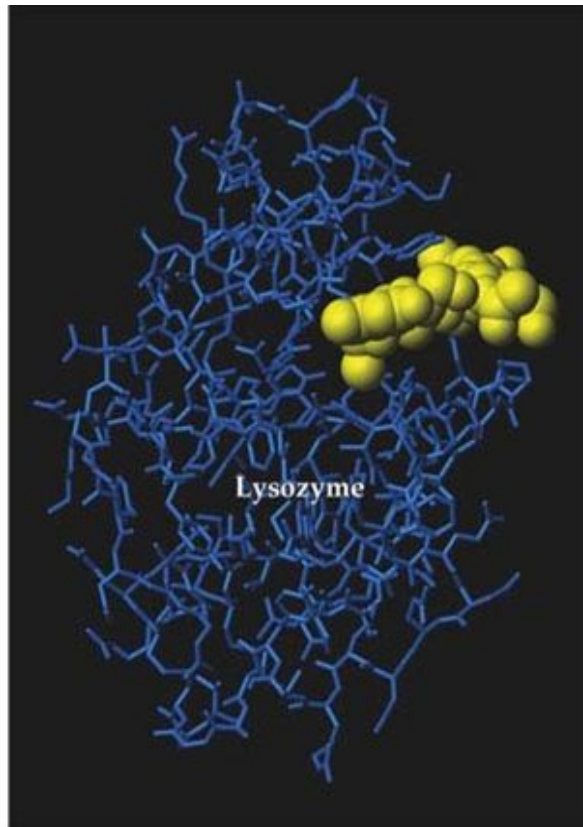
Charge effects,
Covalent bonds,
Acid-base catalysis



An example of an enzyme that sterically strains the substrate:

Lysozyme distorts the bonds of one of the sugars in the polysaccharide of a bacterial cell wall

It also places a partial charge on the substrate, making it react more easily with water (hydrolysis).



Hydrolysis breaks the polysaccharide chain and weakens the wall so that the cell lyses.

Summary

Enzymes speed reactions by reducing E_a

Enzymes reduce E_a by stressing substrate (raising $G(ES)$) and by reducing $G(ES^*)$

Lysozyme and chymotrypsin give examples of enzyme pathways for hydrolysis