

B. Thermodynamics

1. What is "free energy"?
2. Where is this energy stored?

We say that ΔG is a thermodynamic property, meaning that it is independent of the way that the conversion of reactants to products might proceed.

3. Based on how energy is stored in the molecules, explain why ΔG is independent of the path of the reaction.
4. If $\Delta G=0$, the reaction is at equilibrium. What then is the meaning of the magnitude of ΔG ?
5. What is a favorable reaction? What would ΔG be for a thermodynamically favorable reaction?
6. What is an unfavorable reaction? What would ΔG be for a thermodynamically unfavorable reaction?
7. Not all thermodynamically favorable reactions proceed on their own. Why?
8. Catalysts overcome this problem. How do they do it?
9. Is the equilibrium of the reaction affected by the action of a catalyst? Why or why not?
10. Is the rate of the reaction affected by the action of a catalyst? Why or why not?
11. Why can the direction in which a reaction proceeds be influenced by the relative concentration of reactants and products?

C. Kinetics

As mentioned in lecture, effect of enzymes can be quantified. The measures commonly used, K_m and V_{max} are characteristic of different aspects of enzyme's actions. To illustrate these concepts, we will break into groups of four for the following experiment.

All members of the group will try to pick up from the desk and open as many eppendorf tubes as possible in a 45 second interval. One member in each group will use the hand with taped down thumb, another with the other four fingers taped together, and the last person will use a hand in a ski glove.

1. How many eppendorf tubes was each member of the team able to pick up and open in 45 seconds?
- | | | | |
|------|--------|----------|-----------|
| hand | -thumb | -fingers | ski glove |
|------|--------|----------|-----------|

low
medium
high

2. What problems with enzyme functions does the demo represent?

Data gathered in an enzyme kinetics experiment can be represented on a graph of concentration of substrate vs. initial rate of the reaction.

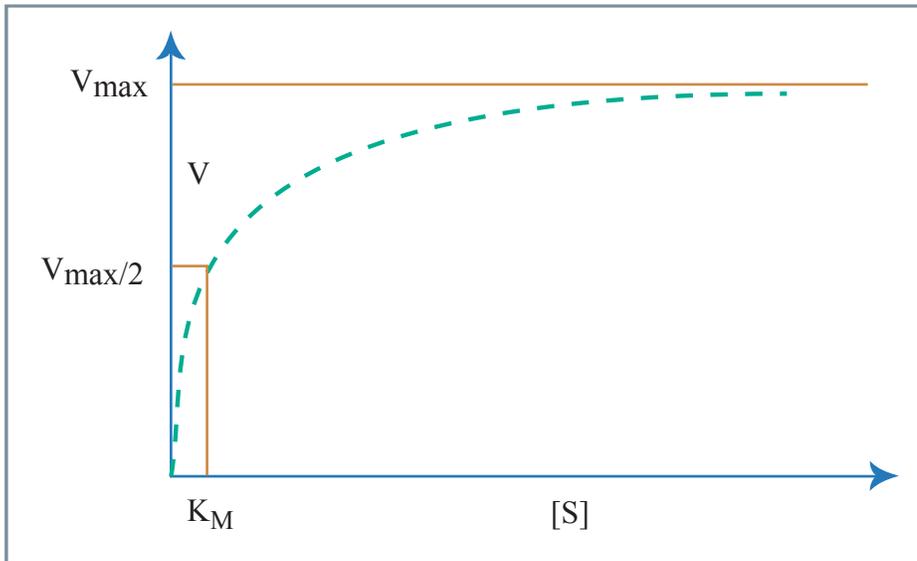


Figure by MIT OCW.

3. Why does the curve level off?

K_m is the measure of how well an enzyme binds the substrate—the less substrate it takes to achieve half maximal speed, the better is the affinity of the enzyme for the substrate.

4. How would the curve below change for the mutants described in the demo?

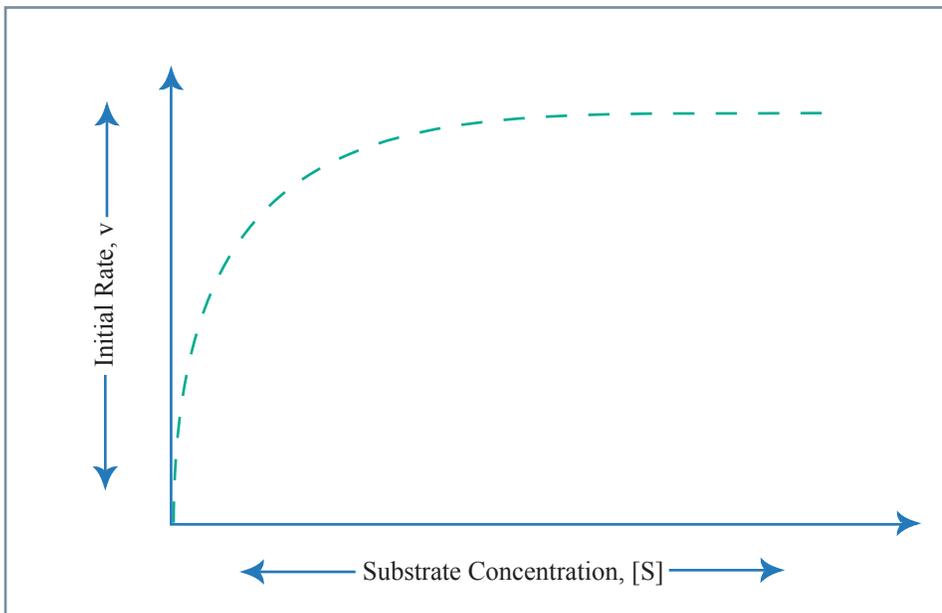


Figure by MIT OCW.

~~D. Energy currency~~

~~Enzymes can not make thermodynamically unfavorable reactions proceed. But they do lower the activation energy of a reaction in both directions.~~

B. Thermodynamics

1. What is "free energy"?

"Free energy" (defined by Gibbs, so we use the symbol G) is the total amount of energy in a system that can be used to do work. By definition,

$\Delta G = \text{the total free energy of products} - \text{the total free energy of reactants}$ "

2. Where is this energy stored?

The energy is stored in the bonds of the reactant and product molecules.

We say that ΔG is a thermodynamic property, meaning that it is independent of the way that the conversion of reactants to products might proceed.

3. Based on how energy is stored in the molecules, explain why ΔG is independent of the path of the reaction.

The energy is stored in the bonds. Regardless of how the reaction proceeds (all in one step, or in 10 steps, like glycolysis), the products will still look like the same exact molecules. Thus, the amount of energy stored in the bonds of the products will still be the same, and the difference in energy levels between reactants and products will still be the same.

4. If $\Delta G=0$, the reaction is at equilibrium. What then is the meaning of the magnitude of ΔG ?

The magnitude of ΔG is the measure of the amount of work that can be done by a chemical reaction before it reaches equilibrium.

5. What is a favorable reaction? What would ΔG be for a thermodynamically favorable reaction?

A favorable, or exergonic, reaction is one in which the energy state of reactants is higher than that of the products ($\Delta G < 0$).

6. What is an unfavorable reaction? What would ΔG be for a thermodynamically unfavorable reaction?

An unfavorable, or endergonic, reaction is the one in which the energy state of the products is higher than that of the reactants ($\Delta G > 0$).

7. Not all thermodynamically favorable reactions proceed on their own. Why?

Some reactions with negative ΔG still do not proceed at an appreciable rate. This is usually because some intermediate is in a significantly higher energy state than the reactants. The difference between the energy state of the reactants and such an intermediate is known as activation energy (E_a).

8. Catalysts overcome this problem. How do they do it?

Catalysts (most often protein enzymes) lower the activation energy of the reaction, thus allowing the reaction to proceed. They sometimes accomplish this by physically positioning reactants in a way that brings parts of the molecules that will participate in the reaction in close contact.

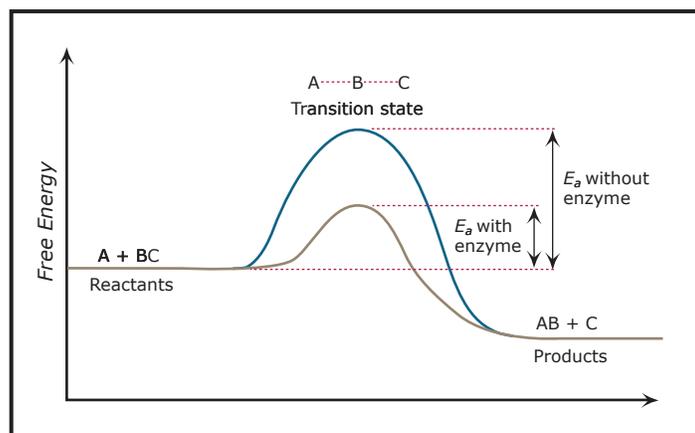
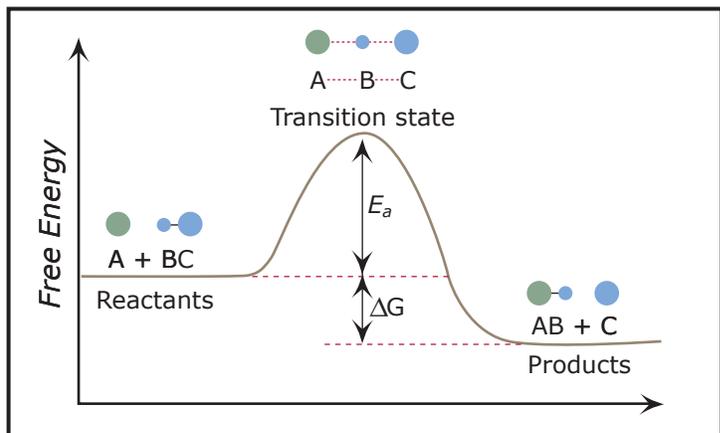


Figure by MIT OCW.

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9. Is the equilibrium of the reaction affected by the action of a catalyst? Why or why not?

The equilibrium of the reaction (relative concentrations of reactants and products) is not affected by the presence of the catalyst. This is because the equilibrium is determined by the amount of energy available to perform the work of converting reactants to products and vice versa. Since the energy is stored in the bonds, it is independent of the path the reaction takes, or the rate at which it occurs.

10. Is the rate of the reaction affected by the action of a catalyst? Why or why not?

The rate of reaction is affected. Reactants reach the transition state due to random fluctuations in energy caused by molecular motion. If E_a is lowered, much less energy is required to reach it, so more molecules will be able to do so, and the rate of the reaction will increase.

11. Why can the direction in which a reaction proceeds be influenced by the relative concentration of reactants and products?

If you have more molecules of a particular kind, it is more probable that some of them will reach the high energy state of the transition state.

C. Kinetics

As mentioned in lecture, effect of enzymes can be quantified. The measures commonly used, K_m and V_{max} are characteristic of different aspects of enzyme's actions. To illustrate these concepts, we will break into groups of four for the following experiment.

All members of the group will try to pick up from the desk and open as many eppendorf tubes as possible in a 45 second interval. One member in each group will use the hand with taped down thumb, another with the other four fingers taped together, and the last person will use a hand in a ski glove.

1. How many eppendorf tubes was each member of the team able to pick up and open in 45 seconds?
hand -thumb -fingers ski glove

low

medium

high

2. What problems with enzyme functions does the demo represent?

Problems illustrated by the demo --defective binding interactions with substrates (taped fingers), ability to catalyze the reaction (taped thumb), similar but wrong enzyme (ski glove).

Data gathered in an enzyme kinetics experiment can be represented on a graph of concentration of substrate vs. initial rate of the reaction.

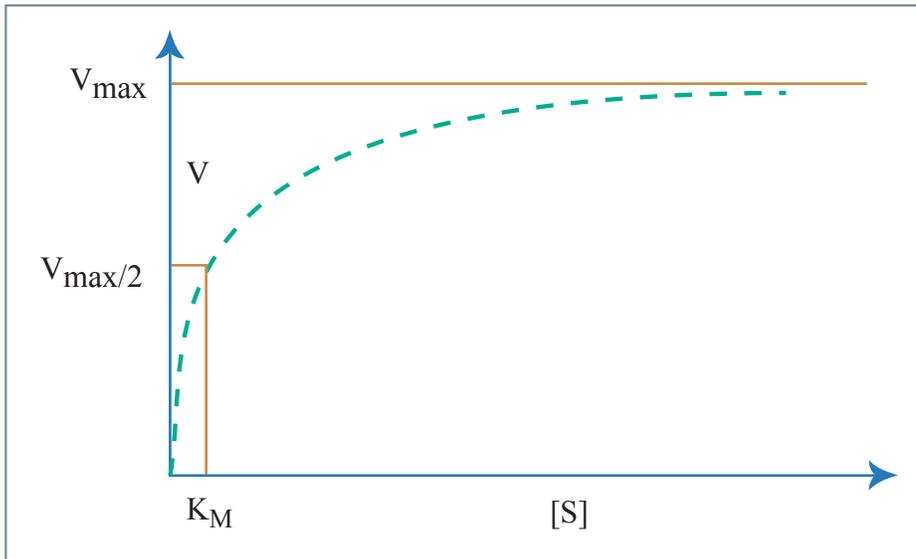


Figure by MIT OCW.

3. Why does the curve level off?

V_{max} is the property of the enzyme at a fixed concentration. The curve levels off because the enzyme is saturated. It doesn't have to go looking for substrate—there is so much of it around, that the rate-limiting step is actually the catalysis.

K_m is the measure of how well an enzyme binds the substrate—the less substrate it takes to achieve half maximal speed, the better is the affinity of the enzyme for the substrate.

4. How would the curve below change for the mutants described in the demo?

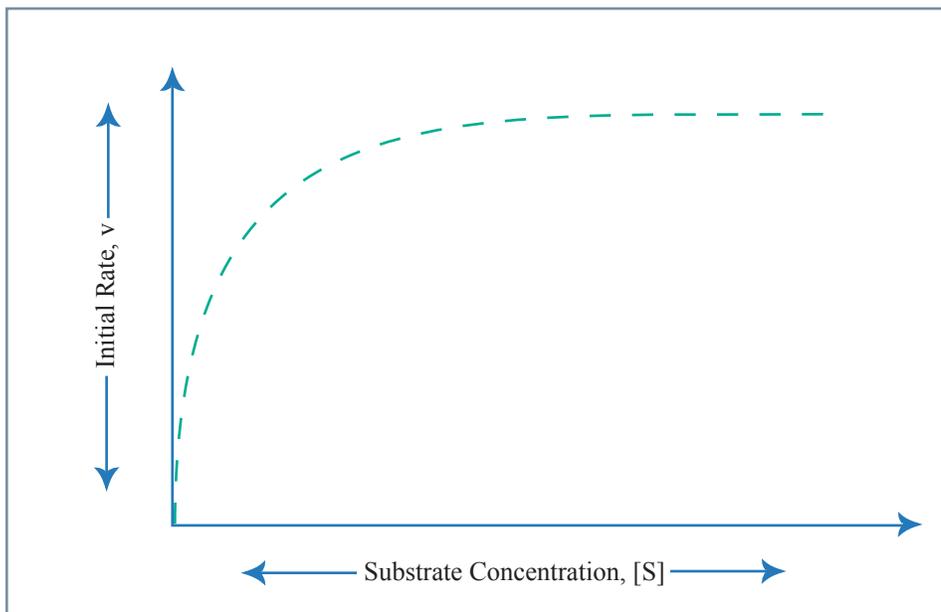


Figure by MIT OCW.

For the mutant defective in binding the substrate, K_m would be higher, but V_{max} should remain the same—if enzyme is saturated, the catalysis is the rate-limiting step.

For the mutant defective in the active site, V_{max} would decrease. K_m might actually decrease as well due to the maximal speed being lower than before, while the affinity for the substrate stays the same.

For the similar, but wrong enzyme, K_m would likely rise, while V_{max} falls—the affinity is worse, and the catalysis is slower.

~~D. Energy currency~~

~~Enzymes can not make thermodynamically unfavorable reactions proceed. But they do lower the activation energy of a reaction in both directions.~~