Notes 10/26

Friday, October 26, 2007
10:00 AM

Notes 1026

Audio recording started: 10:01 AM Friday, October 26, 2007

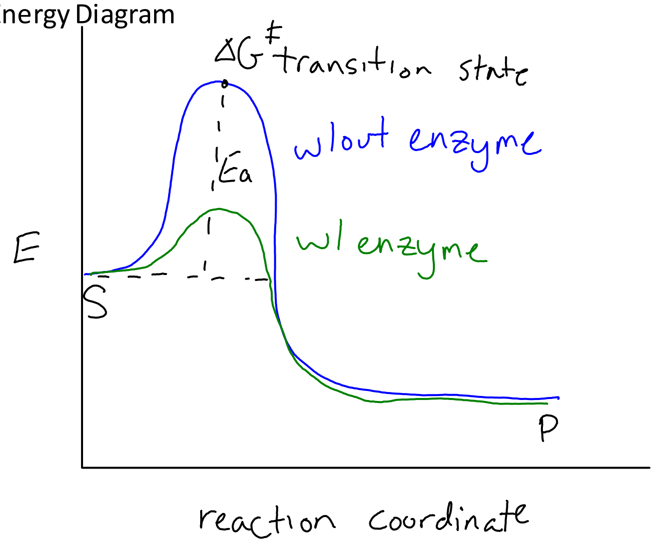
Quiz Expectation:

- Lipid linked vs lipid proteins
- Classify enzyme reactions
- Energy diagrams
- Kinetics

- Life depends on enzymes
- Enzymes effect reaction rates, not equilibrium
- STC, 298K, 1atm, pH 7
- $\Delta G'^0$ biochemical standard free E change
- $E + S \rightleftharpoons ES \rightleftharpoons EP \rightleftharpoons EP$

  $S \rightleftharpoons P$

- Energy Diagram



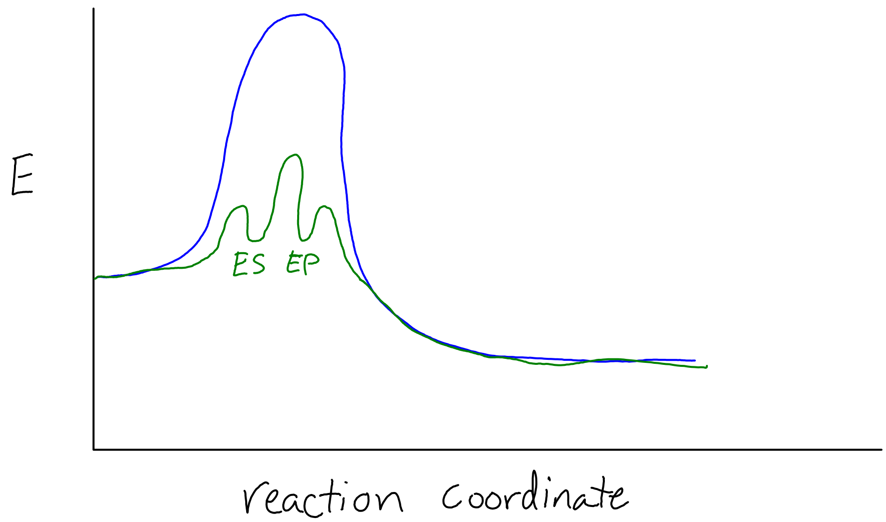
- E barrier
  - Alignment of reacting group
  - Formation of translent unstable charge
  - Bond rearrangements
  - Other transformation
- For a reaction to go, the molecule must overcome this $\Delta G^{\ddagger}$

- What is the source of E?
  - Chemical reaction taking place substrate + E's functional groups (specific amino acids side chains,

metal ion, coenzyme)

- Binding E = ΔG_B
- Binding E (ΔG_B) is a major source of free enzyme used by the enzyme to lower the Ea ($\Delta G^{\ddagger}$) of the reaction.
- This same ΔG_B gives enzyme specificity
- A higher Ea means that the reaction is slower
- Energy can come from heat; however, this can denature enzymes
- Enzyme accelerates interconversion of Substrate to Product
- Equilibrium point is unchanged.
- $E + S \rightleftharpoons ES \rightleftharpoons EP \rightleftharpoons EP$

  reaction intermediates



- Overall reaction rate is determined by rate limiting step
- Rate Limiting Step = the step with highest Ea

- Reaction Rates + Equilibria have precise thermodynamic definitions.
- $S \rightleftharpoons P$

- Equilibrium constant K_{eq} or K
- $K'_{eq} = \dfrac{[P]}{[S]}$

- From thermodynamics we can relate K'eq + $\Delta G'^0$
  - $\Delta G'^0 = -RT\ln K'_{eq}$
    - R=8.315 J/molK
    - T=298K (25^0C)
    - K'_{eq} is directly related to the overall standard free E change for the reaction
  - Large $\Delta G'^0$ = favorable reaction equilibrium

- $S \rightleftharpoons P$

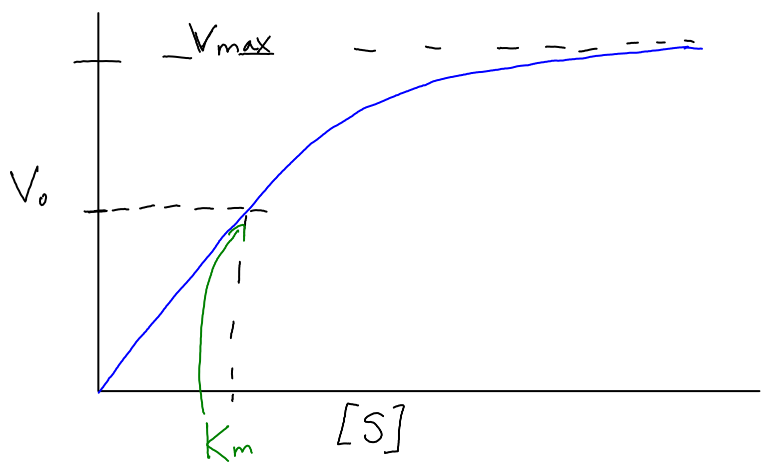
  $V = k[S]$ 1st order reaction
  - K value is defined under standard state conditions
  - The units of k = s^{-1}

- Example:
  - $V = 0.03 s^{-1}[S]$
    - This means 3% of available substrate will be converted to P in 1 second.
  - When k=2,000
    - This means all of the substrate becomes product in less than a second
- 2nd order reaction:
  - K is a 2nd order rate constant, units are $M^{-1}s^{-1}$ (M=molarity, s=seconds)
  - $V=k[S_1][S_2]$

- Transition State Theory allows us to relate the rate constant to $\Delta G^{\ddagger}$
  - $k = \frac{KT}{h} e^{-\Delta G^{\ddagger}/RT}$
    - K=bollzmann constant
    - h=Plank's constant
  - A lower $\Delta G^{\ddagger}$ means a higher k + vice versa.
- Enzyme kinetics
  - The central approach to understanding enzyme catalyzed is to study the rate of the reaction + how it changes in response to changes in experimental parameters.

- Substrate concentration effects the rate of enzyme catalyzed reactions

- [S] changes during the course of a reaction
- Initial rate (initial V): [S]>>[E]



Michaelis constant (K_m) The [S] where $V_0 = 1/2V_{max}$

- Michalis - Menten in 1913
  - Postulated the enzyme 1st combines reversibiliy with a substrate to form ES

$$E + S \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} ES$$

$$ES \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} EP$$ } Rate limiting Step slower

Michalis Menten equation

Michalis - Menten equation

- $V_0 = \frac{V_{max} - [S]}{K_m + [S]}$