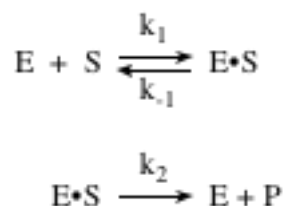


Problem Set 24: Enzyme Kinetics - the Basics

Due Dec 2, 2008

1. Consider the following set of elementary steps for an enzyme catalyzed reaction:



Using the same techniques that we applied to deriving rate laws for chemical reactions, derive an expression for $d[P]/dt$. Your answer should contain the term $\frac{k_{-1} + k_2}{k_1}$ which we will define as K_m , the Michaelis-Menten constant.

2. The equation that you derived in question 1 is not particularly useful since it (hopefully) has a term with the free enzyme concentration, $[E]$. Since enzyme concentrations are typically VERY low during steady state kinetics, it is difficult to determine what fraction of the enzyme has no substrate bound, E , and what fraction is in the $E \cdot S$ form. Fortunately, it is possible to eliminate the $[E]$ term. Use the equation $[E]_0 = [E] + [E \cdot S]$ to derive a new equation for $d[P]/dt$. $[E]_0$ is the total (initial) enzyme concentration that is added to the reaction. It is usually easy to measure $[E]_0$ experimentally. You should substitute this new equation into the expression that you wrote for $d[ES]/dt$ and then rewrite the equation for $d[P]/dt$.
3. Problem 10.5 (p. 398)
An enzyme that has a K_M value of $3.9 \times 10^{-5} \text{ M}$ is studied at an initial substrate concentration of 0.035 M . After 1 min, it is found that $6.2 \mu\text{M}$ of product has been produced. Calculate the value of V_{\max} and the amount of product formed after 4.5 min. Assume Michaelis-Menten kinetics apply.
4. The following data were obtained for an enzyme-catalyzed reaction following Michaelis-Menten kinetics as shown in question 1:

$$\begin{array}{l} k_1 \text{ and } k_{-1} \text{ are very fast (much faster than } k_2) \\ k_2 = 100 \text{ s}^{-1}, K_M = 1.0 \times 10^{-4} \text{ M at } 280 \text{ K} \\ k_2 = 200 \text{ s}^{-1}, K_M = 1.5 \times 10^{-4} \text{ M at } 300 \text{ K} \end{array}$$

- (a) For $[S] = 0.10 \text{ M}$ and $[E]_0 = 1.0 \times 10^{-5} \text{ M}$, calculate the rate of formation of product at 280 K.
- (b) Calculate the activation energy for k_2 (use the Arrhenius equation).
- (c) What is the value of the equilibrium constant at 280 K for the formation of the enzyme-substrate complex ES from E and S ?
- (d) What is the sign and magnitude of the standard thermodynamic enthalpy ΔH° for the formation of ES from E and S ?