

**Due Monday, 12/13/99, in class
(at beginning of in-class help session).**

Show your work. Problem sets will be spot graded. Work must be shown.

$$R = 0.08206 \text{ liter atm K}^{-1} \text{ mole}^{-1} = 8.314 \text{ J K}^{-1} \text{ mole}^{-1}$$

$$h = 6.626 \times 10^{-34} \text{ J s} \quad c = 2.9979 \times 10^8 \text{ m s}^{-1}$$

1. T,S,&W Ch 8 Pb 5

a) Simply use an expression from before:

$$v_o = \frac{k_2 E_o}{1 + \frac{K_M}{S}} = \frac{(100 \text{ s}^{-1})(1 \times 10^{-5} \text{ M})}{1 + \frac{1 \times 10^{-4} \text{ M}}{0.10 \text{ M}}} = 9.99 \times 10^{-4} \text{ M s}^{-1}$$

b) We can do a "2-point fit" (in other words, solve explicitly):

$$\frac{k_2^{T=280}}{k_2^{T=300}} = A e^{\frac{-E_a}{R(280K)}} \quad \frac{k_2^{T=280}}{k_2^{T=300}} = e^{\frac{-E_a}{R(280K)}} e^{\frac{+E_a}{R(300K)}} = e^{\frac{-E_a}{R} \left(\frac{1}{280K} - \frac{1}{300K} \right)}$$

$$\ln \frac{k_2^{T=280}}{k_2^{T=300}} = \frac{-E_a}{R} \left(\frac{1}{280K} - \frac{1}{300K} \right)$$

$$E_a = -R \ln \frac{k_2^{T=280}}{k_2^{T=300}} \frac{1}{\frac{1}{280K} - \frac{1}{300K}} = -(8.314 \text{ J mol}^{-1} \text{ K}^{-1}) \ln \frac{100 \text{ s}^{-1}}{200 \text{ s}^{-1}} \frac{1}{\frac{1}{280K} - \frac{1}{300K}}$$

$$E_a = +24.4 \text{ kJ mol}^{-1}$$

c) For k_1 and k_{-1} very fast, we can ignore k_2 in the Michaelis constant.

$$K_M = \frac{k_{-1} + k_2}{k_1} \quad \frac{k_{-1}}{k_1} = K_d = \frac{[E][S]}{[ES]}$$

But the question asks for the equilibrium constant for *formation* of ES

$$K_{eq} = \frac{[ES]}{[E][S]} = \frac{k_1}{k_{-1}} = \frac{1}{K_d} = 1 \times 10^4 \text{ M}^{-1}$$

d) From an earlier chapter:

$$\ln \frac{K_2}{K_1} = -\frac{H^\circ}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$$

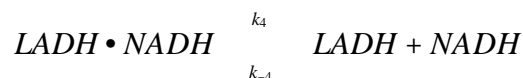
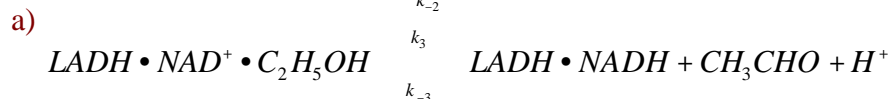
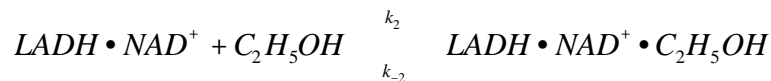
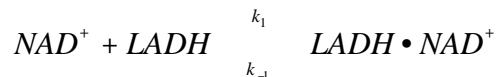
$$H^\circ = -R \frac{1}{\frac{1}{T_2} - \frac{1}{T_1}} \ln \frac{K_2}{K_1} = -(8.314 \text{ J mol}^{-1} \text{ K}^{-1}) \frac{1}{\frac{1}{300 \text{ K}} - \frac{1}{280 \text{ K}}} \ln \frac{1.5 \times 10^{-4} \text{ M}}{1.0 \times 10^{-4} \text{ M}}$$

$$H^\circ = +14.2 \text{ kJ mol}^{-1}$$

2. T,S,&W Ch 8 Pb 6

Enzymes (catalysts) act to lower the activation energy for a reaction. A high activation energy (uncatalyzed) will require a relatively high temperature for a reasonable reaction rate to be observed. The rate will depend greatly on temperature. For the catalyzed reaction, with a lower activation barrier, temperature will not be as important (in the limit that the barrier is reduced completely, the reaction will go rapidly even at very low temperatures). Hence the enzyme-catalyzed reaction should show a smaller temperature dependence. See p. 422.

3. T,S,&W Ch 8 Pb 19, parts (a), (b), (c), and (e)



b) Either NAD^+ is limiting or the $\text{LADH} \cdot \text{NAD}^+$ complex is saturated with respect to $\text{C}_2\text{H}_5\text{OH}$

c)
$$\frac{(4 \times 10^{-3} \text{ M hr}^{-1})(40 \text{ L}) 10^6 \frac{\mu\text{mol}}{\text{mol}}}{(3600 \text{ s hr}^{-1})(3.1 \text{ s}^{-1})} = 14 \mu\text{mol}$$

e) By competitive inhibition, ethanol will prevent methanol or ethylene glycol from being oxidized so rapidly. In time, other elimination processes can then remove the toxic substances from the system.