Problem Set #8 Chem 471 Fall 1999

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 liter atm K^{-1} $mole^{-1}$ = 8.314 J K^{-1} $mole^{-1}$

h = 6.626 x 10^{-34} J s   c = 2.9979 x 10^{8} m s^{-1}

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

a) Simply use an expression from before:

$$\upsilon_o = \frac{k_2 E_o}{1+\frac{K_M}{S}} = \frac{(100s^{-1})(1x10^{-5}M)}{1+\frac{1x10^{-4}M}{0.10M}} = 9.99x10^{-4}\,M\,s^{-1}$$

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

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

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

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

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

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

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

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

$$K_{eq} = \frac{[ES]}{[E][S]} = \frac{k_1}{k_{-1}} = \frac{1}{K_d} = 1x10^4\,M^{-1}$$

d) From an earlier chapter:

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

$$\Delta H^\circ = -R\left[\frac{1}{\frac{1}{T_2} - \frac{1}{T_1}}\right]\ln\frac{K_2}{K_1} = -\left(8.314\,J\,mol^{-1}\,K^{-1}\right)\left[\frac{1}{\frac{1}{300K} - \frac{1}{280K}}\right]\ln\frac{1.5x10^{-4}M}{1.0x10^{-4}M}$$

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

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)

a)

$$NAD^+ + LADH \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} LADH \bullet NAD^+$$

$$LADH \bullet NAD^+ + C_2H_5OH \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} LADH \bullet NAD^+ \bullet C_2H_5OH$$

$$LADH \bullet NAD^+ \bullet C_2H_5OH \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} LADH \bullet NADH + CH_3CHO + H^+$$

$$LADH \bullet NADH \underset{k_{-4}}{\overset{k_4}{\rightleftharpoons}} LADH + NADH$$

b) Either NAD^+ is limiting or the LADH NAD^+ complex is saturated with respect to C_2H_5OH

c) $$\frac{\left(4x10^{-3}M\,hr^{-1}\right)\left(40L\right)\left(10^6\,\frac{\mu mol}{mol}\right)}{\left(3600\ s\,hr^{-1}\right)\left(3.1s^{-1}\right)} = 14\mu mol$$

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.