Problem Set #7   Chem 471   Fall 1999

Due Monday, 11/29/99, in class.

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

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

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

1. T,S,&W Ch 7 Pb 7

   a) Steady state of B tells us that:

   $$\frac{dB}{dt} = 0 = k_1 A - k_2 B - k_3 BC = k_1 A - \left(k_2 + k_3 C\right)B$$

   $$B = \frac{k_1}{k_2 + k_3 C}A$$

   $$\frac{dD}{dt} = k_3 BC = \frac{k_1 k_3}{k_2 + k_3 C}AC$$

   b) Fast (or "pre-") equilibrium dictates:

   $$K = \frac{[AB]}{[A][B]} \qquad [AB] = K[A][B]$$

   $$\frac{d[D]}{dt} = k[AB][C] = kK[A][B][C]$$

   Note that in this case, it was important not to drop the bracket [X] notation, in order to avoid confusion.

2. T,S,&W Ch 7 Pb 9

a) As discussed on p. 371, we plot the data for k_1, as shown at right. From this plot, we obtain a slope of -12711 K
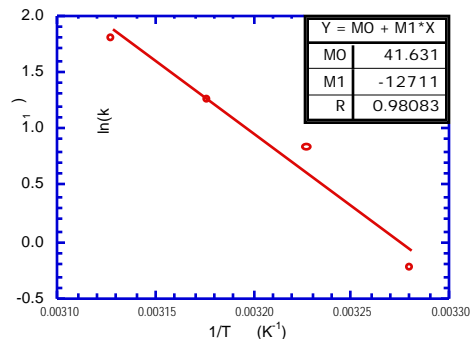
$$slope = -12711 \quad \frac{-E_a}{R}$$

$$E_a = (-12711\ K)(8.314\ J\,K^{-1}mol^{-1}) = 106\ kJ\,mol^{-1}$$

$$H^{\ddagger} = E_a - RT$$

$$H^{\ddagger} = 106\ kJ\,mol^{-1} - (8.314\ J\,K^{-1}mol^{-1})(312K)$$

$$H^{\ddagger} = 103\ kJ\,mol^{-1}$$

From the Arrhenius plot, we have

$$int\,ercept = 41.6 = \ln A$$

Then from equation 7.54 (using the average temperature for T)

$$S = R\ \ln\frac{Ah}{k_B T} - 1\ = R\ \ln A + \ln\frac{h}{k_B T} - 1$$

$$= (8.314\ J\,K^{-1}mol^{-1})\ (41.6) + \ln\frac{6.626\ x\ 10^{-34}\ J\,s}{(1.3807x10^{-23}\ J\,K^{-1})(312K)} - 1$$

$$= (8.314\ J\,K^{-1}mol^{-1})((41.6) + (-29.5) - 1) = 92.3\ J\,K^{-1}mol^{-1}$$

If you used the approximation, you would get 101 J K^{-1} mol^{-1}, not far off.

Similarly for k_{-1}, we plot the data for k_{-1}. From this plot, we obtain a slope of -29295 K

$$slope = -29295 \quad \frac{-E_a}{R}$$

$$E_a = (-29295\ K)(8.314\ J\,K^{-1}mol^{-1}) = 244\ kJ\,mol^{-1}$$

$$H^{\ddagger} = E_a - RT$$

$$H^{\ddagger} = 244\ kJ\,mol^{-1} - (8.314\ J\,K^{-1}mol^{-1})(312K)$$

$$H^{\ddagger} = 241\ kJ\,mol^{-1}$$

From the Arrhenius plot, we have

$$int\,ercept = 95.9 = \ln A$$

Then from equation 7.54
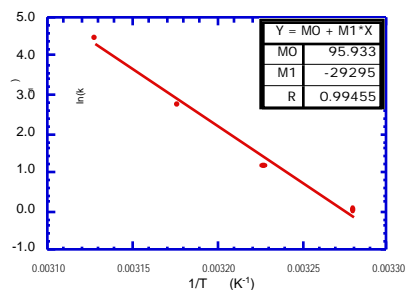
$$S^{\ddagger} = R\left[\ln\frac{Ah}{k_B T} - 1\right] = R\left[\ln A + \ln\frac{h}{k_B T} - 1\right]$$

$$S^{\ddagger} = \left(8.314\ J\ K^{-1}mol^{-1}\right)\left[(95.9) + \ln\frac{6.626\ x\ 10^{-34}\ J\ s}{\left(1.3807 x10^{-23}\ J\ K^{-1}\right)(312K)} - 1\right]$$

$$S^{\ddagger} = \left(8.314\ J\ K^{-1}mol^{-1}\right)\left((95.9) + (-29.5) - 1\right) = 544\ J\ K^{-1}mol^{-1}$$

If you used the approximation, you would get 552 J K^{-1} mol^{-1}, not far off.

In reality, if the data are fit directly to the equation for k and a more complete statistical analysis is carried out, one finds that over the temperature range studied, $H^{\ddagger}$ and $S^{\ddagger}$ are interdependent, that is, they cannot be determined independently.

b) For this we return to the temperature dependence of the equilibrium constant, which is simply the ratio of the two rate constants, at each temperature.

From Chapter 3, we have:

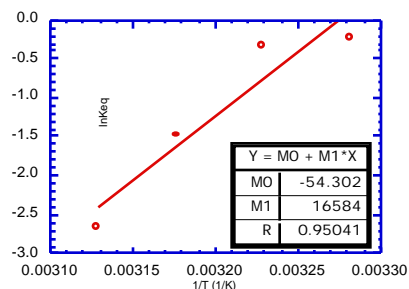$$\ln K = \frac{S^0}{R} - \frac{H^0}{RT}$$

The plot at right provides:

$$slope = 16584 K = -\frac{H^0}{R}$$

Y = M0 + M1*X	
M0	-54.302
M1	16584
R	0.95041

$$H^0 = -(16584 K)\left(8.314\ J\ K^{-1}mol^{-1}\right)$$

$$H^0 = -138\ kJ\ mol^{-1}$$

$$int\,ercept = -54.30 = \frac{S^0}{R}$$

$$S^0 = (-54.30)\left(8.314\ J\ K^{-1}mol^{-1}\right) = -451\ J\ K^{-1}mol^{-1}$$

c) Remembering that the base pair donors and acceptors are H-bonded with water in the single stranded form, one more Watson-Crick pair would mean one more (base-water) bond to break in forming the transition state. Therefore, $H^{\ddagger}$ may actually **increase** slightly (become more positive). If the H-bonds in the duplex are slightly more favorable than the H-bonds to water, then adding one more WC pair, will **decrease** somewhat the overall H for the reaction.

3. T,S,&W Ch 7 Pb 10

a) 1st order in A, 0th order in B

$$\frac{A_t}{A_0} = e^{-kt} \qquad \ln \frac{A_t}{A_0} = -kt \qquad k = -\frac{1}{t} \ln \frac{A_t}{A_0}$$

$$k = -\frac{1}{1hr} \ln 0.9 = 0.105 hr^{-1}$$

$$\frac{A_{t=2hr}}{A_0} = e^{-\left(0.105 hr^{-1}\right)2 hr} = 0.81 \qquad (81\%)$$

b) 1st order in A, 1st order in B, but with equimolar starting conc's of A and B

$$\frac{1}{C_A^t} - \frac{1}{C_A^0} = kt \qquad k = \frac{1}{t} \left[\frac{1}{C_A^t} - \frac{1}{C_A^0} \right] = \frac{1}{t} \left[\frac{1}{C_A^t / C_A^0} - \frac{1}{1} \right] \frac{1}{C_A^0}$$

$$k = \frac{1}{1hr} \left[\frac{1}{0.9} - \frac{1}{1} \right] \frac{1}{C_A^0} = \left(0.111 hr^{-1}\right) \frac{1}{C_A^0}$$

$$C_A^t = \left[\frac{1}{C_A^0} + kt \right]^{-1}$$

$$C_A^{t=2hr} = \left[\frac{1}{C_A^0} + \left(0.111 hr^{-1}\right) \frac{1}{C_A^0} (2hr) \right]^{-1} = \left(1 + 0.222\right)^{-1} C_A^0$$

$$\frac{C_A^{t=2 hr}}{C_A^0} = 0.82 \qquad (82\%)$$

c) 0th order in A, 0th order in B

$$A_t - A_0 = -kt \qquad k = -\frac{1}{t}\left(A_t - A_0\right) = -\frac{1}{t}\left[\frac{A_t}{A_0} - 1\right] A_0$$

$$k = -\frac{1}{1hr}(0.9 - 1)A_0 = \left(0.10 hr^{-1}\right) A_0$$

$$A_{t=2 hr} = A_0 - \left(0.10 hr^{-1}\right) A_0 (2 hr) = A_0 - 0.2 A_0$$

$$\frac{A_{t=2hr}}{A_0} = 0.80 \qquad (80\%)$$

d) 1st order in A, 1/2 order in B, but again, equimolar starting concentrations

Looks like: $v = kA^{1.5}$

$$\frac{1}{n-1}\left[\frac{1}{A_t^{n-1}} - \frac{1}{A_0^{n-1}}\right] = kt \qquad \frac{1}{0.5}\left[\frac{1}{A_t^{0.5}} - \frac{1}{A_0^{0.5}}\right] = kt$$

$$k = \frac{1}{t}\frac{1}{0.5}\left[\frac{1}{A_t^{0.5}} - \frac{1}{A_0^{0.5}}\right] = \frac{1}{t}\frac{1}{0.5}\left[\frac{A_0^{0.5}}{A_t^{0.5}} - 1\right]\frac{1}{A_0^{0.5}}$$

$$k = \frac{1}{t}\frac{1}{0.5}\left[\left(\frac{A_t}{A_0}\right)^{-0.5} - 1\right]A_0^{-0.5} = \frac{1}{1hr}\frac{1}{0.5}\left[(0.9)^{-0.5} - 1\right]A_0^{-0.5} = \left(0.108hr^{-1}\right)A_0^{-0.5}$$

$$\frac{1}{A_t^{0.5}} = \frac{1}{A_0^{0.5}} + 0.5kt$$

$$\frac{A_0^{0.5}}{A_t^{0.5}} = 1 + A_0^{0.5}0.5kt \qquad \left(\frac{A_t}{A_0}\right)^{0.5} = \left(1 + A_0^{0.5}0.5kt\right)^{-1} \qquad \frac{A_t}{A_0} = \left(1 + A_0^{0.5}0.5kt\right)^{-2}$$

$$\frac{A_{t=2hr}}{A_0} = \left(1 + A_0^{0.5}0.5\left(\left(0.108hr^{-1}\right)A_0^{-0.5}\right)(2hr)\right)^{-2} = \left(1 + 0.5\left(\left(0.108hr^{-1}\right)\right)(2hr)\right)^{-2}$$

$$= \left(1 + 0.108\right)^{-2} = 0.81 \quad (81\%)$$

4. T,S,&W Ch 7 Pb 15

a) $\dfrac{dB}{dt} = k_1A - k_4B - k_{-1}B + k_2C - k_{-2}B$

b) Fast equilibrium:

$$\frac{B}{A} = K_1 \qquad \frac{C}{A} = K_3 \qquad \frac{B}{C} = K_2$$

$$B = K_1A \qquad C = K_3A$$

This problem appears more complicated than it is. First, K1, K2, and K3 are not all independent (only 2 are). Second, we really only need the first expression above. The reaction is then just like other fast equilibrium reactions dealt with in the text.

$$\frac{dP}{dt} = k_4B = k_4K_1A$$

c) At time equals zero, we allow equilibrium to be set up. Let's redefine the book's nomenclature: AT is the total, starting concentration of A. A0 is the concentration of A at time close to 0, but after equilibrium is established.

Now, with time, P is formed and:

$$B = K_1A \qquad C = K_3A \qquad A_T = A + B + C + P$$

$$A_T = A + K_1A + K_3A + P = (1 + K_1 + K_3)A + P$$

$$A = \frac{A_T - P}{1 + K_1 + K_3} \qquad B = \frac{K_1(A_T - P)}{1 + K_1 + K_3}$$

$$\frac{dP}{dt} = k_4B = k_4 \frac{K_1(A_T - P)}{1 + K_1 + K_3}$$

$$\frac{dP}{(A_T - P)} = \frac{k_4 K_1 dt}{1 + K_1 + K_3}$$

$$(A_T - P)^{-1}dP = \frac{k_4 K_1}{1 + K_1 + K_3} \ dt$$

To do this integral, we brush off our calculus texts and find that we simply set:

$$Q = A_T - P \qquad dQ = -dP$$

$$- \ Q^{-1}dQ = \frac{k_4 K_1}{1 + K_1 + K_3} \ dt$$

$$- \ln Q = -\ln(A_T - P) = \ln \frac{1}{(A_T - P)} = \frac{k_4 K_1}{1 + K_1 + K_3}t + C$$

At time=0, we have:

$$\ln \frac{1}{(A_T - 0)} = \frac{k_4 K_1}{1 + K_1 + K_3}(0) + C$$

$$C = \ln \frac{1}{A_T}$$

Therefore:

$$\ln \frac{1}{(A_T - P)} = \frac{k_4 K_1}{1 + K_1 + K_3}t + \ln \frac{1}{A_T}$$

$$\ln \frac{A_T}{(A_T - P)} = \frac{k_4 K_1}{1 + K_1 + K_3}t$$

This would be sufficient, but let's take it further:

$$\frac{A_T}{(A_T - P)} = e^{\frac{k_4 K_1}{1 + K_1 + K_3}t}$$

$$A_T - P = A_T e^{\frac{-k_4 K_1}{1 + K_1 + K_3}t}$$

$$P = A_T - A_T e^{\frac{-k_4 K_1}{1 + K_1 + K_3}t} = A_T \left(1 - e^{\frac{-k_4 K_1}{1 + K_1 + K_3}t}\right)$$

5. T,S,&W Ch 7 Pb 18

a) The reaction is first order in A. A two-fold drop from 40 to 20 nM takes 311 s, while a two-fold drop from 20 to 10 nM takes 310 s. The data and a direct fit to first order kinetics are shown at right. The best fit rate constant (k_1) is 0.00223 s^{-1}. (You can also do this by linearization).

$Y = MO*e^{M1*X}$	
MO	50.011
M1	-0.0022319
R	1

$Y = MO + M1*X$	
MO	3.9123
M1	-0.0022319
R	1
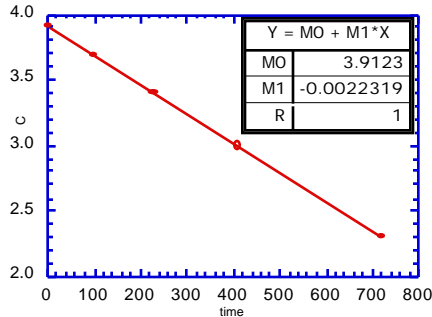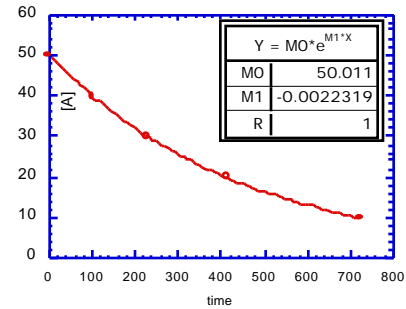
ernatively, we could plot the linearized form:

and we get a slope of -0.002232 s^{-1}

b)
$$A \quad \xrightarrow{k_1} \quad A^*$$
$$A^* + P \quad \xrightarrow{k_2} \quad AP$$
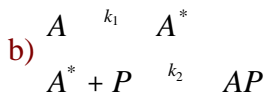
where the 2nd step is much faster than the first. The first step is an activation of the reactant A.

The measured k would be k_1 above. $\dfrac{dP}{dt} = k_1 A$

To show this mathematically, at steady state: $\dfrac{dA^*}{dt} = 0 = k_1 A - k_2 A^* P$

So that $\dfrac{dP}{dt} = k_2 A^* P = k_2 \dfrac{k_1 A}{k_2} = k_1 A$

c)

$$k_{283} = Ae^{-E_a/R(283K)}$$

$$k_{273} = Ae^{-E_a/R(273K)}$$

$$2 = \frac{k_{283}}{k_{273}} = \frac{Ae^{-E_a/R(283K)}}{Ae^{-E_a/R(273K)}} = e^{-\frac{E_a}{R}\left[\frac{1}{283K} - \frac{1}{273K}\right]}$$

$$\ln 2 = -\frac{E_a}{R}\left[\frac{1}{283K} - \frac{1}{273K}\right] = -\frac{E_a}{8.314\ J\,K^{-1}mol^{-1}}\left(-1.294x10^{-4}\ K^{-1}\right) = E_a\left(1.557x10^{-5}\ J^{-1}\ mol\right)$$

$$E_a = \frac{\ln 2}{\left(1.557x10^{-5}\ J^{-1}\ mol\right)} = 44.5\ kJ\,mol^{-1}$$

6. T,S,&W Ch 7 Pb 20

$$k_{298} = Ae^{-E_a/R(298K)}$$

$$k_{308} = 2k_{298} = Ae^{-E_a/R(308K)}$$

$$2Ae^{-E_a/R(298K)} = Ae^{-E_a/R(308K)}$$

$$2e^{-E_a/R(298K)} = e^{-E_a/R(308K)}$$

$$\ln 2 - \frac{E_a}{R(298K)} = -\frac{E_a}{R(308K)}$$

$$\ln 2 = \frac{E_a}{R(298K)} - \frac{E_a}{R(308K)} = \frac{E_a}{R}\left(\frac{1}{298K} - \frac{1}{308K}\right) = \frac{E_a}{R}\left(3.247x10^{-3}K^{-1}\right)$$

$$E_a = \frac{R(\ln 2)}{\left(3.247x10^{-3}K^{-1}\right)} = \frac{\left(8.314\ J\ K^{-1}mol^{-1}\right)(\ln 2)}{\left(3.247x10^{-3}K^{-1}\right)} = 1.77\ kJ\ mol^{-1}$$

7. T,S,&W Ch 7 Pb 22

a) Given that $-\dfrac{dA}{dt} = k_1AB$

However, B remains constant, so that we could write $-\dfrac{dA}{dt} = k_1AB = k_1'A$

(where $k_1' = k_1B$)

The solution is then that of a first order reaction:

$$-\frac{dA}{dt} = k_1'A \qquad A = A_0e^{-k_1't} = A_0e^{-k_1Bt}$$

b) This part recognizes that B is essentially constant.

$$-\frac{dA}{dt} = k_2AB$$

$$-\frac{dA}{A} = k_2Bdt \qquad \text{but B is constant}$$

$$-\frac{dA}{A} = k_2B\ dt$$

$$A_o - A = k_2Bt$$

c)

$$\upsilon_o = \left.-\frac{dA}{dt}\right|_o$$

$$-\frac{dA}{A} = \frac{k_1AB}{1 + \dfrac{k_1A}{k_2}}$$

For low [A],

$$\frac{k_1 A}{k_2} << 1$$

$$-\frac{dA}{A} = \frac{k_1 A\text{B}}{1 + \dfrac{k_1 A}{k_2}} \qquad \frac{k_1 A\text{B}}{1 + 0} = k_1 A\text{B}$$

For high [A],

$$\frac{k_1 A}{k_2} >> 1$$

$$-\frac{dA}{A} = \frac{k_1 A\text{B}}{1 + \dfrac{k_1 A}{k_2}} \qquad \frac{k_1 A\text{B}}{0 + \dfrac{k_1 A}{k_2}} = k_2\text{B}$$