

Chemistry 545  
Spring 2004  
Problem Set 2  
Due Monday, February 9

Reading assignment: SFH Chapters 2.1-2.3, 3, and 4.

1. Write and execute a Mathematica program to solve the kinetic equations for the following network:

$x \xrightarrow{k_1} y \xrightarrow{k_2} z$  with the following sets of rate constants:

A.  $k_1 = 5 \text{ s}^{-1}$ ,  $k_2 = 2 \text{ s}^{-1}$

B.  $k_1 = 0.5 \text{ s}^{-1}$ ,  $k_2 = 2 \text{ s}^{-1}$

for  $t$  between 0 and 10 seconds, using NDSolve. Have the program plot  $x(t)$ ,  $y(t)$  and  $z(t)$ . The example on page 101 of Wolfram is helpful.

2. In the previous problem, derive the differential equations for all the sensitivity coefficients of  $x(t)$  and  $y(t)$ . Solve and plot these coefficients using Mathematica. Explain your results.

3. Use Mathematica to solve the rate equations for the reaction  $\text{H}_2 + \text{Cl}_2 \rightarrow 2\text{HCl}$  (See SFH, page 42, equations 2-138 to 2-141). Assume the following rate constants:

$$k_2 = 3.5 \times 10^{-11} e^{-2290/T} \text{ cm}^3/\text{molecule/s}$$

$$k_3 = 7.8 \times 10^{-12} e^{-1600/T} \text{ cm}^3/\text{molecule/s}$$

$$k_4 = 1.46 \times 10^{-10} e^{-593/T} \text{ cm}^3/\text{molecule/s}$$

$$k_5 = 6.3 \times 10^{-34} e^{900/T} \text{ cm}^6/\text{molecule}^2/\text{s} \text{ for } M=\text{Ar}$$

For reaction (2-138), assume an absorption coefficient of  $\text{Cl}_2$  at 330 nm is 65 liters/mol/cm (base e), and a laser intensity of 1 mW/cm<sup>2</sup>. Also assume initial conditions of 1 Torr of  $\text{H}_2$ , 1 Torr of  $\text{Cl}_2$ , and one atmosphere of Ar. Assume a constant temperature of 300 K.

Use Mathematica to calculate the concentrations of  $\text{H}_2$ ,  $\text{Cl}_2$ , H, Cl, and HCl as functions of time. Plot your results on several time scales in order to reveal the different time scales for various processes. Compare all of your answers with the steady state solutions.

4. Prove that in a linear least squares fit of the function  $y = a + bx$ , the fitted function passes through the mean values of  $x$  and  $y$ .