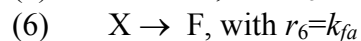
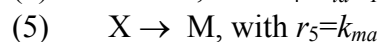
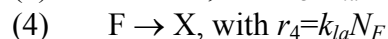
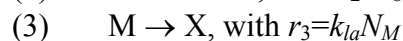
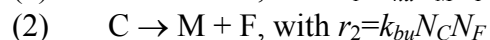


CE 561 Homework 6: (assigned 10/01/09, due 10/12/09)

- (1) Suppose we wanted to model the behavior of undergraduate students on a Saturday night at Molly's Pub in the same way we have been modeling chemical rate processes. Let N_M be the number of male undergraduates in the bar, let N_F be the number of female undergraduates in the bar, let N_C be the number of couples in the bar, let N_X be the number of individuals (male or female) that have not yet come to the bar or have left alone, and let N_{XC} be the number of couples that have left the bar together. Then the rate processes might be written in terms of the following list of "reactions"



The numerical values of the rate constants for these processes are

$$k_{hu} = 0.2 \text{ events undergraduate}^{-3} \text{ hr}^{-1}$$

$$k_{bu} = 0.1 \text{ events couple}^{-1} \text{ undergraduate}^{-1} \text{ hr}^{-1}$$

$$k_{la} = 0.3 \text{ events undergraduate}^{-1} \text{ hr}^{-1}$$

$$k_{ma} = 20 \text{ events hr}^{-1}$$

$$k_{fa} = 10 \text{ events hr}^{-1}$$

$$k_{lt} = 0.5 \text{ events couple}^{-1} \text{ hr}^{-1}$$

The "initial conditions" for this problem are that at time = 0 (when the bar opens), $N_M = N_F = N_C = N_{XC} = 0$. That is, there is nobody in the bar initially. Note that none of the rates depend on N_X , the number of people not in the bar, since there are an effectively infinite and constant number of people that are not in the bar. So, an initial condition for N_X is not needed, and we do not need to solve for N_X .

- (a) Write the rate equations for N_M , N_F , N_C , and N_{XC} . Can these differential equations be solved analytically? Comment on the physical significance of these (differential) equations and their solutions at short times (say t less than 1/2 hour).
- (b) Write a short computer program (in the language of your choice) that uses Euler's method to solve the rate equations numerically (treating N_M , N_F , N_C , and N_{XC} as continuous variables, like we usually do for chemical concentrations). The experiment ends at $t = 10$ hours (when the bar finally closes). Plot the 'concentrations' for $t = 0$ to $t = 10$ hours.
- (c) Write a short computer program that uses kinetic Monte-Carlo methods to simulate the bar's population over time, treating N_M , N_F , N_C , and N_{XC} as integer variables. Run the program several times. Plot the 'concentrations' for $t = 0$ to $t = 10$ hours.
- (d) Compare the results of parts (b) and (c), discussing similarities, differences, and the importance of statistical fluctuations for this problem.

- (2) Vasudevan *et al.* (*Int. J. Chem. Kin.*, **40**, 488-495 (2008)) conducted high-temperature gas phase kinetics experiments to determine the rate of reaction of methyl radical (CH₃) with hydroxyl radical (OH). Table I gives key parts of the reaction mechanism and rate parameters that they used to interpret their experiments and to determine rate parameters for the first reaction. I have slightly modified and simplified it.

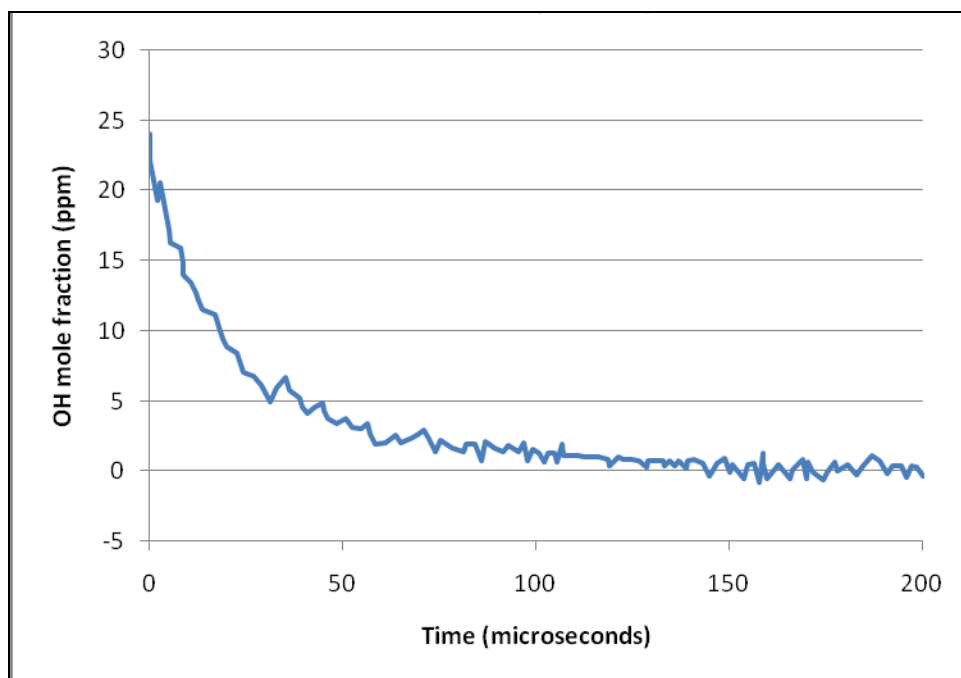
Table I. Rate Coefficients of Reactions Important in CH₃ + OH Experiments^a

| Reaction | Rate Coefficient (cm ³ mol ⁻¹ s ⁻¹) | | |
|--|---|----------|-----------------------------------|
| | <i>A</i> | <i>n</i> | <i>E</i> (cal mol ⁻¹) |
| CH ₃ + OH → Products | To be determined | | |
| (CH ₃) ₃ COOH → (CH ₃) ₃ CO + OH ^b | 2.50E+15 | 0.0 | 43,017 |
| (CH ₃) ₃ CO → (CH ₃) ₂ CO + CH ₃ ^b | 1.30E+14 | 0.0 | 15,300 |
| 2CH ₃ → C ₂ H ₆ | 3.0E+13 | 0.0 | 0 |
| OH + C ₂ H ₆ → C ₂ H ₄ + H + H ₂ O | 1.614E+06 | 2.224 | 741 |
| C ₂ H ₆ N ₂ → CH ₃ + CH ₃ + N ₂ ^b | 2.220E+39 | -7.99 | 51,505 |
| (CH ₃) ₂ CO + OH → CH ₃ COCH ₂ + H ₂ O | 2.951E+13 | 0.0 | 4,564 |
| OH + OH → O + H ₂ O | 3.57E+04 | 2.4 | -2,110 |

^a Rate constants are given by $k = A T^n \exp(-E/(RT))$

^b Rate coefficient units: s⁻¹

Data on the hydroxyl radical (OH) concentration vs. time, extracted from one of the figures in their paper, is shown in the plot below:



You can download the file containing the data shown in the plot above by clicking [here](#).

For that experiment, the initial concentrations were 21.5 ppm of $(\text{CH}_3)_3\text{COOH}$ and 75 ppm of $\text{C}_2\text{H}_6\text{N}_2$ in argon. The total pressure was 1.70 bar, and the temperature was 1245 K.

Problem:

Using the reaction mechanism presented above, apply a non-linear least squares analysis to obtain a value of the rate coefficient for the first reaction in the table above ($\text{CH}_3 + \text{OH} \rightarrow$ products). Plot the resulting model prediction along with the experimental data for the OH concentration. Compute the sensitivity of the OH concentration profile to each of the rate constants in the mechanism. How do the sensitivities of the model results to the rate coefficient being measured compare to the sensitivity of the model results to the other rate coefficients? Comment on the effect of uncertainties in the other rate constants on the fitted value of the rate constant being measured.