MASSACHUSETTS INSTITUTE OF TECHNOLOGY

Chemistry 5.68J **Chemical Kinetics** Spring Term 2003
Chem. Eng. 10.652J **Kinetics of Chemical Reactions**

Problem Set #5 Due: April 24, 2003

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1. CKD Problem 4.8 (it will help to read Section 4.7 in the text first!)

2. CKD Problem 5.2 The term about two-thirds of the way through the equation in part **(c)** should read " … + $k_{-1}X_0 \times (k_3 + k_{-2}Y_0)$ + … ", not
" … + $k_{-1}X_0 + (k_3 + k_{-2}Y_0)$ + … "

3. CKD Problem 5.4 (Give at least one mechanism consistent with the data provided in the problem. The JACS references will be useful!)

4. CKD Problem 15.3

5. CHEMKIN Sensitivity and Flux Analysis Problem

Motivation: Researchers are considering combining the Water-Gas-Shift Reaction CO + H_2O with a high temperature membrane separation as a possible way to make pure H_2 at high temperatures and pressures. (Normally, the WGS reaction is run at low temperatures where the equilibrium is more towards the products H_2 + CO_2, but it is inefficient to have to cool the mixture if you want the H_2 hot anyway for the next process, e.g. producing electricity in a high temperature fuel cell.) The concept is that the CO could be made by reacting steam with coal; the pure CO_2 stream can then be sequestered much more easily than the dilute CO_2 stream made by just burning the coal.

At T = 1300 K and P = 16 atm it is easier to measure the reverse process by suddenly heating a one:one mixture of H_2 + CO_2. Construct a kinetic model for this system (you might want to just use GRI-Mech, or you could use a pared down version to try to save some CPU time, only a half-dozen reactions matter). Compute the sensitivities for the formation of CO as a function of time. What reaction has the highest sensitivity? Why does the sensitivity change with time?

Of all the reactions in your model that form two radicals, which one has the highest rate? Compute the sensitivity of CO to this reaction about halfway through the conversion. Vary this reaction's rate by a factor of 10 and run the simulation again. Did the CO concentration change by the amount predicted from the sensitivity analysis? Note: a quasi-steady-state analysis predicts the CO formation rate will depend on the square-root of this radical formation rate.

Tip: Don't compute all the sensitivities by ASEN, it takes a long time and gives tons of output you don't need. Just compute the sensitivities you care about.