

The computer program CKS (Chemical Kinetics Simulator) developed by Frances Houle and Bill Ginsberg at the IBM Almaden Research Center, is available as a free download: see the course website for the link. CKS has been installed on the computers in the Chemistry computer lab, 613 Altschul.

CKS solves complicated kinetic mechanisms using a stochastic approach to solve the kinetic equations (first-order differential equations). It can be used for gas or solution phase reactions. To run it you need a file (*.rxn) with a reaction mechanism and corresponding rate constants. The rate constants may be supplied as constants for a particular temperature, or as temperature dependent in the form $k = A T^n \exp(-E_a/RT)$. ($n=0$ reduces to the Arrhenius equation). You may select concentrations and time to be in a number of different units. You then specify the particular conditions for a simulation run: initial concentrations and temperature. After running the simulation, you can view a plot of the resulting concentrations as a function of time.

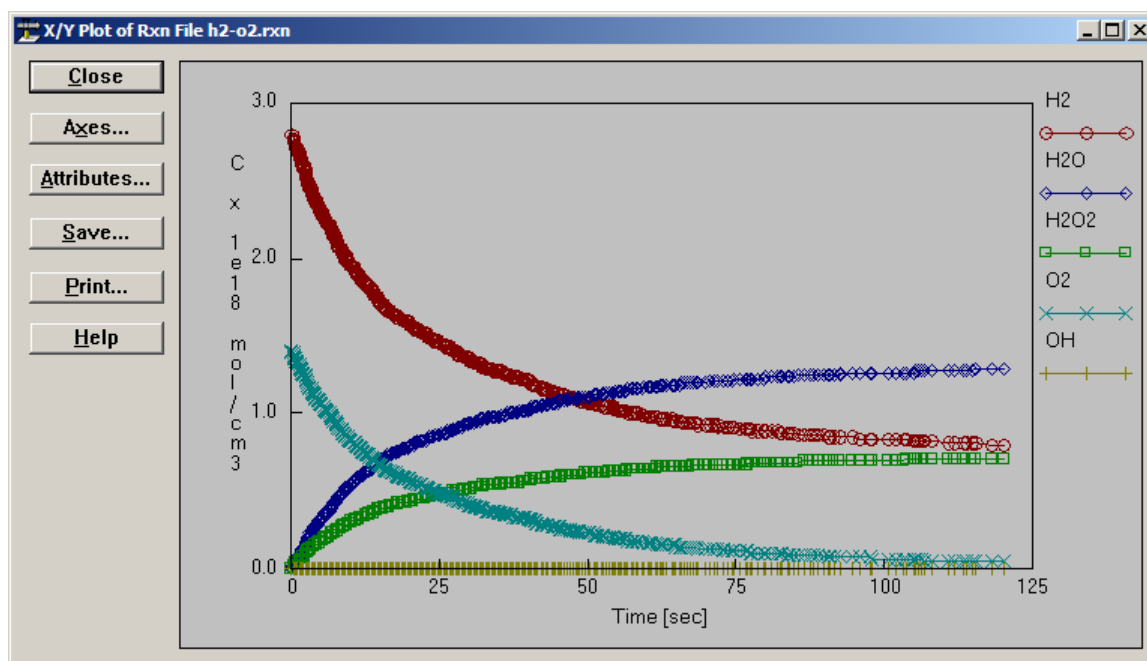
The program comes with a number of mechanisms with sample simulations in the folder **demos**. I have created a few more. "h2-o2" and "ch4-o2" are combustion mechanisms for hydrogen and methane, taken from M.J. Pilling and P.W. Seakins, *Reaction Kinetics* (Oxford U. Press, 1995). "EK-MM" and "EK-2" are two variants of enzyme kinetics mechanisms. If you wish to create a mechanism, a useful compendium of gas phase rate constants is <http://kinetics.nist.gov/index.jsp>

To run the program, click on the file **cks.exe** in the folder **CKS** (a shortcut may be on the desktop). Under files, select open. If the folder **new** is not shown, click on the **CKS** file in the folders box, and then click on **new**. Highlight your reaction scheme: *.rxn, and press **ok**. If using your own computer, first create the folder **new**, and copy the file you need to it. The new files **h2-o2.rxn**, **ch4-o2.rxn** etc. are available from "files" on the course web page.

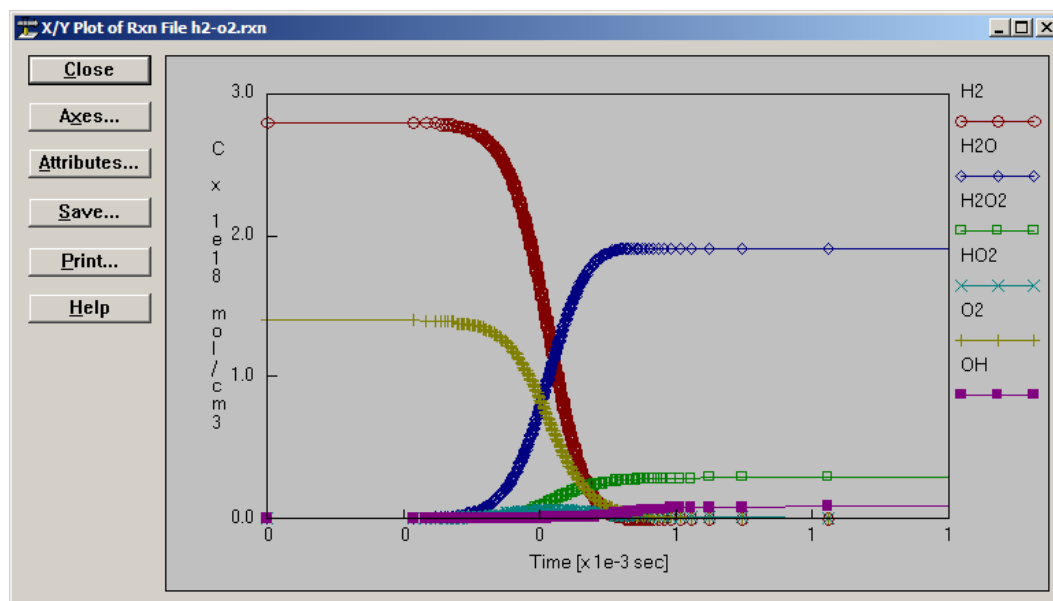
Suggestions: For simplicity, run all simulations at fixed temperature, and look at plots of concentrations vs. time. Print the graphs immediately; I do not have a way to view saved plot files! (You may be able to print them to a pdf file.)

Explosions. The hallmark for explosive behavior is a sudden change in both the timescale of the reaction and the shapes of the curves. Compare carefully the figures below:

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Exploding



Choose one of the projects below. You may work in groups of two or three. Sign for your choice: no more than three groups on any project. When looking at effects of concentration, make real but modest changes, perhaps a factor of 2 at a time. Some choices of concentrations may lead to impractical (nonsensical) timescales: reactions complete in 10^{-30} sec or 10^{30} sec.

Use the ideal gas law to convert between molecules/cc and mmHg or atmospheres. A species M that appears in a mechanism is a non-reactive collider (moderator) that can exchange energy. Its concentration will not vary, but it still can have an effect on the rate.

1) Work with the mechanism **h2-o2** (Pilling and Seakins, page 252). Concentrations are in molecules/cm³. Take as initial concentrations $[H_2] = 2.8E18$ ($= 2.8 \times 10^{18}$), $[O_2] = 1.4E18$, and $[M] = 5.2E18$. (What are these in mmHg?) Start with (fixed) $T = 750$ K. What are the major combustion products? For this combination of concentrations, find the explosion limit (to within 10°): the temperature at which the reaction suddenly goes much faster (finishing in milliseconds instead of minutes). Then, investigate one or more of the following questions:

- How does $[M]$ influence the reaction, both its rate, and the ultimate outcome?
- With the reaction conditions above, H_2O and H_2O_2 are both major products. Does the ratio $[H_2]_0/[O_2]_0$ influence the relative amounts? $[H_2]_0 = [H_2]$ at time $t = 0$.
- Investigate how the explosion limit for this reaction depends on p . Change p by changing all the concentrations by a common factor. (You might start by doubling them all).
- OH , H , OOH , and O are all reactive intermediates. Do the concentrations of all three remain very small? Is this true if you change the initial concentrations? What does this imply about using the steady state hypothesis for this mechanism? *Please note:* the program simulates reactions of discrete molecules. Since the numbers are much less than molar, steady state for a substance with a very small concentration may appear as an oscillation between two values, representing zero and one molecule. This is an artifact, not an oscillating reaction!

2) Work with the mechanism **ch4-o2** (Pilling and Seakins, page 192), a partial (but still quite complex) mechanism for the combustion of methane. Concentrations are in molecules/cm³. Take as initial concentrations $[CH_4] = 1E18$, $[O_2] = 2E18$, $[M] = 1E18$, and $T = 600$ K. (What

are these in mmHg?) What is the fate of carbon for these conditions: which carbon containing species are present at equilibrium, and what are their approximate amounts? (You can look at no more than seven at a time.) Adjust the scale on the time axis so you can observe the different processes. Approximately how long does it take for $\frac{1}{2}$ the initial methane to disappear? Describe in words how this reaction proceeds. ["Initially the methane reacts, forming ____; this reaction is $\frac{1}{2}$ complete in about ____ seconds. Then..."]. Then investigate one or more of the following questions:

- How does $[M]$ influence the reaction, both its rate, and the ultimate outcome?
- In combustion, flames are adjusted to alter the relative amounts of fuel (hydrocarbon) to oxygen. Depending on this ratio, flames are characterized as *lean* or *rich*. How does variation of $[CH_4]_0/[O_2]_0$ alter the range of products?
- Save the results of the early part of the simulation (from the plot) as a .txt file, and import this into Excel. Make first and second order plots for the disappearance of CH_4 . Which is the empirical rate law, and what is its rate constant? Relate this to k 's in the actual mechanism.
- Investigate some other aspect of this mechanism.

3) Study the mechanism EK-MM for classical Michealis-Menton kinetics, with the possible inclusion of a competitive inhibitor, I (setting $[I]_0 = 0$ omits this). The values of the temperature-independent rate constants and concentrations are arbitrary. First, run with $[E]_0 = 0.1$, $[S]_0 = 1$, with no inhibitor. What is the initial rate v : the initial slope of $[P]$ vs. t ? Does this agree with the prediction of MM analysis? (Look at the reaction scheme to determine K_M and k_2). Record the time it takes for the reaction to go halfway: the time when the $[S]$ and $[P]$ curves cross. Next, set $[I]_0 = 1$. Compare both the initial rate and the time for the reaction to go halfway with that for the uninhibited reaction. Then do one or more of the following:

- Vary $[S]_0$ so that it is larger than K_M . How does the reaction differ?
- Look at other systematic changes in the rate constants or concentrations.
- Substitute parameters (rate constants and concentrations) for a real enzyme system, and run.
- Mechanism EK-2 adds an intermediate step before product is formed. How does this step influence the observed kinetics? How does this depend on the rate constants?

4) Work with the demo mechanism **orgnator**. This model oscillating reaction was named the Oregonator by its inventor, Prof. R. Noyes, at the University of Oregon. (The mechanism has been modified slightly from that originally published.)

- What is the mechanism? Is there a slow step?
- What is the net reaction? What are reactants, products? What species are catalysts?
- Which is the autocatalytic step or steps?

5) Study another of the demo mechanisms. Describe what it does. Vary reaction conditions and see what happens. [Feel free to come discuss this as you proceed.]

6) Create your own mechanism and study it. [Feel free to come discuss this as you proceed.]

The results of these should be written up in a brief summary, submitted by your group. Answer all questions. Describe what you varied and what you learned. Include annotated plots: be sure to specify completely the reaction conditions for any simulation. Selected projects will be presented orally.