

## 5.68J/10.652J Fall 2020

### Homework #1: Using CHEMKIN (or similar software e.g. CANTERA or RMS)

Due 9:30 a.m. Tuesday Sept. 8. Use the reaction mechanism provided; later in the semester we'll discuss how to make and improve mechanisms like this. Dr. Chas McGill ([cjmcgill@mit.edu](mailto:cjmcgill@mit.edu)) will give CHEMKIN tutorials and is available to help with CHEMKIN. Most senior members of Green and West groups are experienced with this type of modeling and may be willing to give you some help.

#### Problem 1. H atom reaction with ethane

- (a) Use CHEMKIN or similar software to study the reaction of 1 ppmv of Hydrogen atoms in ethane ( $C_2H_6$ ) at  $T=1000$  Kelvin,  $P=1$  atmosphere (isothermal, isobaric). On what timescale does the mole fraction of H atoms drop (i.e. what is the half-life of an H atom in this system at these conditions)? (Hint, it is very fast). Does the mole fraction of ethane change much on this short timescale? What product species are being formed rapidly as the H atoms react, formed by what reaction? Plot the logarithm of H atom mole fraction versus time; is the plot linear at short times as expected if the H atom decay is exponential in time? (If the plot is linear, we call this a pseudo-first-order process; pseudo because the H atoms are actually participating in bimolecular reactions not decaying unimolecularly.). What happens at slightly longer times?
- (b) Use ROP analysis during the very early times to confirm that the expected reaction is indeed responsible for most of the loss of H atom. If only this reaction matters, then one should be able to determine the rate coefficient  $k(T)$  of this key reaction from the half-life of the H atom (for example, if you measured the half-life for decay of H atoms experimentally.) Give the algebraic expression for  $k$  in terms of the half-life and the initial mole fractions and pressure. If you plug in the value of the half-life from the plots of H vs. time, do you get a value for  $k(1000\text{ K})$  that is consistent with the Arrhenius parameters for the key reaction given in the chem.inp file?
- (c) Use sensitivity analysis on this short time scale to confirm that the mole fraction of H atom at the  $t^*=t_{\text{half-life}}$  you are using is only sensitive to the  $k$  for the one key reaction, i.e. that your analysis in part (b) is sensible. In reality, the values of the Arrhenius parameters used in the chem.inp file has some uncertainty. If the  $A$  factor in chem.inp was a factor of two larger than its true value, how much larger than the model prediction would the true mole fraction of H atoms at  $t^*$  be?
- (d) What happens at slightly longer times when the H atom mole fraction is no longer dropping rapidly? Use ROP analysis to see what reactions are turning on at these slightly longer times that stop the H atom concentration from continuing to drop. Is the H atom concentration stabilizing towards a value set by an equilibrium or by a steady-state, or is something else happening? Does sensitivity analysis at this somewhat longer time identify the same important reactions as the ROP analysis?

### Problem 2. Pyrolysis of Ethane

- (a) Now simulate a system of pure ethane (no initial H atoms) at 1000 K and 1 atm. This is one of the most important and largest-volume commercial chemical reactions; ethane is a major component in natural gas, and the desired product ethene ( $C_2H_4$ ) is the key ingredient used for making many man-made materials. Run the simulation until the mole fraction of ethane has dropped approximately in half – what is its half-life in this system? Plot the log of the  $C_2H_6$  mole fraction versus time – is it a straight line, or not? Is  $C_2H_6$  decay a pseudo-first-order process?
- (b) Make a Flux Diagram at that time-point and from it and ROP analyses write down the main sequence of balanced reactions that is converting  $C_2H_6$  into  $C_2H_4$ . What is the main reaction consuming  $C_2H_6$  at that time point?
- (c) Do a sensitivity analysis at that time-point to see which rate coefficients affect the predicted mole-fraction of  $C_2H_6$ . Is the conversion of  $C_2H_6$  very sensitive to the main reaction you identified in part (b)? Is the conversion of  $C_2H_6$  more sensitive to other reaction(s) in the main sequence? Does the sensitivity analysis identify any reactions as being important that do not show up at all in Part (b)? What are these extra reactions doing?
- (d) If you run this reaction at  $P=2$  atm, pure ethane, is the half-life of ethane longer or shorter than at  $P=1$  atm? Why?
- (e) If you run this reaction at  $P=2$  atm, but the initial composition is 50% ethane and 50% He, is the ethane half-life longer or shorter or the same as the case with pure ethane at  $P=1$  atm? Note that in these two cases the initial concentration of ethane is identical. Also note that the He is completely inert. Speculate about what is causing any difference between the two cases.
- (f) One expects the reaction kinetics to lead to chemical equilibrium. What is the equilibrium distribution of the species in the model, if one starts from pure ethane, and holds the system at 1000 K and 1 atm?
- (g) If you switch from an isothermal to an adiabatic reactor, what happens to the ethene production? Why?

### Problem 3. Pyrolysis of Propane in a Plug Flow Reactor

- (a) As in Problem 1, consider what happens at short times if a small amount of H atom is introduced into pure propane. In this case, there are two competing reactions, what are they? How is the half-life of the H atom related to the  $k$ 's of these two reactions? How is the product distribution related to these two  $k$ 's?
- (b) Simulate the pyrolysis of pure propane at 850 K and 1000 K, for  $P=1$  atm, in an isothermal plug flow reactor with an inlet flow velocity of 1 cm/second. Note that a much longer reactor is needed at the lower temperature.
- (c) What is the ratio of propene/ethene produced at short times? What is the ratio at the point where the propene mole fraction reaches its peak? Are these answers different at the two temperatures? If so, why?
- (d) Why doesn't the propene mole fraction keep climbing rapidly like the ethene mole fraction does?

**Note:** The purpose of this program is to gain experience actually running kinetic simulations and interpreting the output, it does not matter exactly how accurate the kinetic model is. You may see some strange-looking results, just note the oddities, we can discuss in class.

**Hints about tolerances:**

Often it helps to set the atol in the CHEMKIN or CANTERA ODE solvers very small (perhaps  $1e-23$ ). The default value is too large to properly handle situations with extremely low concentrations of reactive intermediates. rtol in the range  $1e-6$  to  $1e-8$  usually works OK with stiff ODE solvers.