AME 598i
Prof. J. M. Powers
Homework 3
Due: Friday, 7 February 2003

Consider the ozone reaction mechanism given by Powers, Singh, and Paolucci, 2002, *Journal of Chemical Physics*, Vol. 117, p. 1482-1496. This is available in the documents section of the course website under the link "JCP slow manifold paper." Take the system to be isothermal with $T = 3000\ K$ and isochoric. At $t = 0\ s$, we have $Y_O = 0.25$, $Y_{O_2} = 0.25$, $Y_{O_3} = 0.5$ and $p = 100\ kPa$. You may find it useful to copy all files in the directory $/afs/nd.edu/users/powers/Public/chemkin/$ into a directory in your home space.

1. Show that this mechanism is identical to that given by Margolis, 1978, *Journal of Computational Physics*, Vol. 27, p. 410. This will essentially require proper unit conversions and interpretations of nomenclature.

2. Find the density ρ and molar concentrations c_i at $t = 0\ s$.

3. Write a system of three ordinary differential equations in three unknowns to describe the evolution of each species concentration. Include appropriate initial conditions.

4. Find conserved quantities, and give the physical significance of each.

5. Reduce the system to two ordinary differential equations in two unknowns, where the unknowns are $[O]$ and $[O_3]$.

6. Find all equilibrium states, and identify which are physical.

7. Perform a local linear analysis around each physical equilibrium, and identify the time scales of reaction.

8. Write two Fortran 77 (or equivalent) codes to integrate the full equations from the initial state to the equilibrium state. Include a copy of your codes (leaving out the dlsode subroutine) as an appendix to your solution.

   (a) In the first code, write your own algorithms to calculate the reaction rate and thermodynamics properties.

   (b) In the second code, use the Chemkin software package to calculate the reaction rates and thermodynamic properties.

9. Plot all species concentrations versus t, being careful to elucidate all the time scales in the system.

10. Use standard software packages, such as those available in the IMSL subroutines or available on http://www.netlib.org, to calculate the Jacobian at each point in the calculation, use standard packages to evaluate the eigenvalues of the Jacobian, and then plot the evolution of the system's time scales from the beginning of the calculation up to equilibrium.

11. Plot $[O]$ versus $[O_3]$.

12. Plot $p(t)$.

13. Using the thermochemical calculator (http://blue.caltech.edu/tcc) to estimate the enthalpies at the end states, calculate the total heat transfer in kJ in the process.