Homework #5 Due 3/4/25

Consider the decomposition of NF_3, which is a toxic etchant gas used in the microelectronics industry. When heated this gas decomposes to products. Though this is a simple and fundamental system, few studies have been performed on it. We'll look at this system in a bit more depth using our thermodynamics and kinetics tools.

Several papers are provided on the website in two parts: primary references and secondary ones. Read the primary references in depth, and you can look over the secondary references for supplemental information. These references all consider the kinetics of decomposition of NF_3 at elevated temperatures.

1) For a mixture of 1 part NF_3 and 10 parts helium (by moles), run the Gordon McBride code to get equilibrium composition (fixed T & P) at 1 atm for temperatures of 1200 and 1500 K. These conditions are very similar to those studied in the papers. Look at the species the code considers. You'll need to make a chemical and thermodynamic input file (zero.inp) for this system. Consider elements N, F, Ar, and He.

a) List all the possible species that could be present in this system.

b) Eliminate ionic species, and N_3, N_2F_4 and N_2F_2 (all of which will be negligible at high temperatures). For all the remaining species, assemble a thermodynamic data file in the chemkin format for all species for which you can find data. Use the same format as in the gri30.inp file.

2) Assemble a one-reaction (forward and reverse) mechanism for this system based on Doroshchenko et al. and Evans and Tschuikow works. Plot the forward rate constant versus temperature over the 1200 to 1500 K range for each of those works. Complete the input file with this one reaction. Start with the Evans and Tschuikow recommended constants. Note that the units for the ZeroD code are mol & cm^3 on A, the format for the n constant is T^n, and the E_a is in calories per mole, and run the simulation under the conditions of Evans and Tschuikow's Figure 3. Note that the pressure, P_2, is 1.07 atm. Run at constant P and T. Compare the relative X_{NF2} mole faction with the data from the Figure 3 plot (digitized in the Plot Data.xlsx file).

3) Now switch to the rate data and conditions from Doroshchenko et al. We'll try to replicate their Figure 1. Unfortunately, they don't say what the temperature and pressure are. Assume the pressure is 1 atm. Use your simulation results to estimate the temperature of the run in Figure 1?

4) For the conditions of Doroshchendo et al. that you calculated in 3), compare the predictions using the rate constants from Evans and Tschuikow and Dorkoshchenko et al. Is there a big difference? Based on the papers, what are some possible sources of this discrepancy?

5) Now, using data from NIST Chemical Kinetics Database, and the Meeks et al. paper, assemble a larger mechanism including many more reactions that you think might be relevant, sticking to the set of species you obtained in part 1b). Re-run the simulations in 4). Plot mole fractions versus time of all species. What differences do you see in the simulation results and the plots between the single reaction case and the full mechanism? Other than the primary reaction, which reactions do you think are particularly important to include in more detailed simulations?