Chemistry 4010 Fall 2019 Assignment 5

Due: Oct. 29, 6:00 p.m.

Total marks: 53

In this assignment, you will be analyzing the mechanism for the gas-phase reaction

$$2\,NO + O_2 \longrightarrow 2\,NO_2.$$

The mechanism is

$$2\,NO \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} N_2O_2,$$

$$N_2O_2 + O_2 \xrightarrow{k_2} 2\,NO_2.$$

The analysis is more complex than anything we have done thus far, so I have tried to break it down into steps, each of which should be within your abilities. I am hoping that the complexity of this problem will demonstrate the power of the methods we are developing. You can actually tackle some fairly difficult problems at this point. You will also get to practice several foundational skills we have been working on throughout the term.

1. Write down the rate equations for all species in this mechanism. **4 marks**

2. There are two element conservation relations: one for the oxygen atoms, and one for the nitrogen atoms. Write down these conservation relations. **2 marks**

   Note: You can write these down directly from the stoichiometry of the reactants and products, or you can derive them from the rate equations by looking for combinations that add to zero.

3. Eliminate the product $[NO_2]$ from the latter two equations. Write the resulting equation with all the concentrations on one side and the constants on the other. For simplicity in what will follow, call the combination of constants on one side of the equation c. **2 marks**

4. Specialize the relationship obtained above to $t = 0$, when the reactants have just been mixed and there is no intermediate. The sign of the constant c tells us whether there is an excess of NO or of O_2. Which sign corresponds to NO being in excess? Which sign corresponds to excess O_2? **2 marks**

5. Use the equation obtained in question 3 to eliminate $[N_2O_2]$ from your rate equations. **2 marks**

6. Find the equilibrium points of the resulting two-dimensional system. **4 marks**

7. You will have found three equilibrium points. One is always negative and can be neglected. The other two can be positive or negative depending on the value of c, but only one of the two is positive and therefore a physical equilibrium for any given value of c. At what value of c does the physical equilibrium point change? Which equilibrium point is physically realizable in each range of c values? **3 marks**

8. Carry out a linear stability analysis of the two physically relevant equilibria. What can be said from the linear stability analysis about how the stability of each equililbrium point depends on c? **10 marks**

   Hint: One of the two equilibria has an equilibrium value of [NO] that is the solution of a quadratic equation. For this equilibrium, just leave [NO] in the Jacobian matrix, i.e. do not substitute in its equilibrium value. You will find that you can determine the stability of this equilibrium without explicitly substituting in the value of [NO]. This may require a bit of thought about the signs of various quantities appearing in the equations for the eigenvalues.

9. One of the two equilibria satisfies the conditions of the centre-manifold theorem provided c is not too large. **22 marks**

   (a) Compute the eigenvector associated with the zero eigenvalue. [4 marks]

   (b) Assume that the centre manifold can be developed in a Taylor series, say

   $$[\mathrm{O}_2]_{\mathrm{CM}}([\mathrm{NO}]) = a_0 + a_1[\mathrm{NO}] + a_2[\mathrm{NO}]^2 + O([\mathrm{NO}]^3).$$

   Using the information you have so far, determine a_0 and a_1. [4 marks]

(c) Write down the invariance equation that the centre-manifold must satisfy. [1 mark]

(d) Substitute your expression for the centre manifold into the invariance equation. Determine a_2. [5 marks]

(e) Now substitute your equation for the centre manifold into $d[\mathrm{NO}]/dt$. Keep only the leading-order term. [4 marks]

(f) Use the latter result to determine the stability of the equilibrium point. [4 marks]

10. Now combine your linear stability results with your centre-manifold analysis to give a complete characterization of the stability of the two equilibria as a function of c. **2 marks**