Chemistry 4010 Fall 2019 Assignment 6

Due: Nov. 26, 6:00 p.m.

Total marks: 43

In this assignment, you will be working with the Lindemann mechanism. We had previously rescaled the equations just to reduce the number of parameters. We have now seen that scaling can be used to set up a problem for singular perturbation analysis. You therefore have to start right back at the beginning with equations (2.2a) and (2.2b) from the textbook.

1. Estimate the maximum concentration of the intermediate B. **4 marks**

2. Rescale the rate equations to put the system in the standard singular perturbation form, i.e. with a small parameter multiplying the rescaled rate of formation of the intermediate. Identify the small parameter and explain why it is reasonable (physically) for this parameter to be a small quantity. Using the definition of your small parameter, give conditions under which the steady-state approximation would be expected to be valid for the Lindemann mechanism. **16 marks**

3. Obtain the outer (slow) solution of your dimensionless equations assuming that the steady-state approximation holds. **8 marks**

4. Solve one of the following two problems for 15 marks. A second solution will be marked out of a maximum of 10 bonus marks. **15 marks**

   (a) Option 1: Develop the uniform solution.

      i. Rescale time to obtain differential equations valid on the fast time scale. [2 marks]

      ii. Obtain the inner (fast) solution assuming that your small parameter is vanishingly small. [6 marks]

      iii. Obtain the uniform solution valid in the limit of a vanishingly small singular perturbation parameter for your dimensionless concentration of B. [3 marks]

iv. Use Maple to plot your dimensionless concentration of B vs time. Calculate any necessary dimensionless parameters from the following data: $k_1 = 1\,\mathrm{bar}^{-1}\mathrm{s}^{-1}$, $k_{-1} = 100\,\mathrm{bar}^{-1}\mathrm{s}^{-1}$, $k_2 = 2\,\mathrm{s}^{-1}$, $A_0 = 0.01\,\mathrm{bar}$. [4 marks]

(b) Option 2: Compute the slow manifold to first order in your small parameter.