Chemistry 5850 Summer 2004 Assignment 2

Due: Tuesday, May 18.

Weight of this assignment: 42 marks

1. In this question, you will be analyzing the system of ODEs obtained in example 2.1 of the lecture notes. We already know from the Liapunov analysis that the equilibrium point is globally stable. You will confirm this result using linearized stability analysis. Other skills will also be exercised.

   (a) Put the governing ODEs in a dimensionless form. [4 marks]

   (b) Carry out a linearized stability analysis of this system. Is the equilibrium point a node or a saddle? If it can be either depending on the values of the parameters, give the condition which determines which kind of fixed point we will get. [10 marks]

   (c) Try to do a phase plane analysis *without* using the information from the linearized stability analysis. Can it be done? What information, if any, is missing? [8 marks]

2. For chemical systems, functions related to the entropy or free energy are generally good Liapunov functions. The following Liapunov function, first proposed by Shear [1], can be derived from the entropy production:

   $$L = \sum_i \left[c_i \ln\left(c_i/c_i^*\right) - c_i + c_i^*\right],$$

   where c_i^* is the equilibrium concentration of species i, and the sum is taken over *all* species present in the system.

   In this problem, you will show that L is a Liapunov function for the fully reversible Lindemann mechanism.

   (a) Show that

      i. $L = 0$ at the equilibrium point, and that

      ii. L reaches a minimum at the equilibrium point.

      Conclude that L is a positive-definite function. [6 marks]

      Note: This can be done generally, or you can do this proof for the reversible Lindemann mechanism. You will need to use a bit of elementary calculus to do this.

   (b) Determine the equilibrium point in terms of the parameters, assuming that an appropriate mass-conservation equation holds. [4 marks]

   (c) Now show that L is a Liapunov function, and conclude that the equilibrium point is globally stable. [10 marks]

References

[1] D. Shear, J. Theor. Biol. **16**, 212 (1967).