Chemistry 5850 Summer 2004 Assignment 6

Due: Tuesday, June 29.

Weight of this assignment: 45 marks

1. As mentioned in the notes, people rarely check the stability of the SSA in the adjoined system, although we really should. Prove that the SSA is a **globally** stable fixed point of the adjoined system for the Michaelis-Menten mechanism. [5 marks]

Hint: The adjoined system is one-dimensional in this case, so its phase space is just the real line. Sketch the flow in this trivial phase space.

2. Ozone is an important pollutant in cities where it is produced as a byproduct of burning fossil fuels. Of course, in the stratosphere, ozone also protects us from ultraviolet rays. There is therefore considerable interest in ozone chemistry. One of the ways in which ozone can decompose is by the following mechanism:

$$\begin{array}{rcl} \mathbf{X}_{(\mathrm{g})} + \mathbf{O}_{3(\mathrm{g})} & \stackrel{k_1}{\underset{k_{-1}}{\Longrightarrow}} & \mathbf{O}_{2(\mathrm{g})} + \mathbf{O}_{(\mathrm{g})} + \mathbf{X}_{(\mathrm{g})} \\ & \stackrel{k_2}{\underset{(\mathrm{g})}{\longrightarrow}} & \mathbf{2O}_{2(\mathrm{g})} \end{array}$$

In these reactions, X is an inert gas, such as nitrogen which makes up almost 80% of our atmosphere. The last reaction is shown with just a forward arrow because the reverse step has an extremely small rate constant and so is insignificant for most purposes.

- (a) In the atmosphere, this reaction normally occurs in the presence of a large excess of oxygen, such that the concentration of O_2 can be treated as constant. Develop a scaling analysis of this mechanism and obtain conditions under which the steady-state approximation for this mechanism would be valid. The use of physical intuition regarding the likely values of the rate constants is highly encouraged. [20 marks]
- (b) Based on your scaling, obtain a singular perturbation series for the slow manifold. [20 marks]