Phase plane analysis problems

The first of these two problems is pretty straightforward. The second will really test your geometry. If you can handle the first problem, you should be OK in this course. If you can solve the second problem without looking at the solutions, you're heading for the top of the class! Average students may need to peek at the solutions from time to time as they are working on problem 2.

1. If we use a sufficiently large pressure of an inert gas X, collisional activation by the inert gas becomes much more efficient than the $A+A$ step in the Lindemann mechanism. The mechanism becomes

$$A + X \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} A^* + X$$
$$A^* \xrightarrow{k_2} \text{products}$$

   Sketch the trajectories generated by this mechanism in the phase plane.

2. In class, we studied the decomposition of ozone:

$$X_{(g)} + O_{3(g)} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} O_{2(g)} + O_{(g)} + X_{(g)}$$
$$O_{(g)} + O_{3(g)} \xrightarrow{k_2} 2O_{2(g)}$$

   using classical arguments. Let us now study this mechanism in the phase plane.

   In the atmosphere, oxygen molecules are in great excess so that their concentration can be treated as constant. Assume that ozone is produced at a constant rate by processes not considered directly here, i.e. include a "reaction" step

$$\xrightarrow{k_0} O_{3(g)}.$$

   (Experimentally, this can be arranged by having a constant flow of ozone into a reaction vessel.)

   (a) Write down the rate equations for ozone and for oxygen atoms. Note that since the molecular oxygen concentration is constant, these are our only two variables.

   (b) Sketch the trajectories in the phase plane. Do you expect to see a slow manifold in this mechanism?

   Notes: Don't bother calculating the equilibrium point. The equilibrium point is at the intersection of the nullclines. (Think about what the nullclines represent and how you would calculate the equilibrium point.) Figuring out what the $[O_3]$ nullcline looks like in this case is a bit more involved than some of the previous examples we have seen. If you do the analysis correctly, you will find there are two cases to consider.