

4.7 Projects

Project 4.17. Chemical oscillations

The kinetics of chemical reactions can be modeled by a system of coupled first-order differential equations. As an example, consider the following reaction:



where A, B , and C represent the concentrations of three different types of molecules. The corresponding rate equations for this reaction are

$$\frac{dA}{dt} = -kAB^2 \quad (4.27a)$$

$$\frac{dB}{dt} = kAB^2 \quad (4.27b)$$

$$\frac{dC}{dt} = kAB^2. \quad (4.27c)$$

The rate at which the reaction proceeds is determined by the reaction constant k . The terms on the right-hand side of (4.27) are positive if the concentration of the molecule increases in (4.26) as it does for B and C , and negative if the concentration decreases as it does for A . Note that the term $2B$ in the reaction (4.26) appears as B^2 in the rate equation (4.27). In (4.27) we have assumed that the reactants are well stirred so that there are no spatial inhomogeneities. In Section 7.8 we will discuss the effects of spatial inhomogeneities due to molecular diffusion.

Most chemical reactions proceed to equilibrium, where the mean concentrations of all molecules are constant. However, if the concentrations of some molecules are replenished, it is possible to observe oscillations and chaotic behavior (see Chapter 6). To obtain oscillations, it

is essential to have a series of chemical reactions such that the products of some reactions are the reactants of others. In the following, we consider a simple set of reactions that can lead to oscillations under certain conditions (see Lefever and Nicolis):



If we assume that the reverse reactions are negligible and A and B are held constant by an external source, the corresponding rate equations are

$$\frac{dX}{dt} = A - (B + 1)X + X^2Y \quad (4.29a)$$

$$\frac{dY}{dt} = BX - X^2Y. \quad (4.29b)$$

For simplicity, we have chosen the rate constants to be unity.

- The steady state solution of (4.29) can be found by setting dX/dt and dY/dt equal to zero. Show that the steady state values for (X, Y) are $(A, B/A)$.
- Write a program to solve numerically the rate equations given by (4.29). Your program should input the initial values of X and Y and the fixed concentrations A and B , and plot X versus Y as the reactions evolve.
- Systematically vary the initial values of X and Y for given values of A and B . Are their steady state behaviors independent of the initial conditions?
- Let the initial value of (X, Y) equal $(A + 0.001, B/A)$ for several different values of A and B , that is, choose initial values close to the steady state values. Classify which initial values result in steady state behavior (stable) and which ones show periodic behavior (unstable). Find the relation between A and B that separates the two types of behavior. \square

Project Description / Goals: While most chemical reactions converge to equilibrium, chaotic oscillatory behavior can be observed under certain circumstances. A system of reactions where the products of some reactions are the reactants to others can lead to this oscillatory property. Given reverse reactions are negligible and A / B are held constant by an external source, the steady state solutions of the following rate equations:

$$\frac{dX}{dt} = A - (B + 1)X + X^2 Y$$

$$\frac{dY}{dt} = BX - X^2 Y.$$

can be derived by setting dX / dt and dY / dt to zero:

a) Steady state solutions of by setting dx/dt and dy/dt to 0

(1) $\frac{dX}{dt} = A - (B+1)X + X^2 Y$

(2) $\frac{dY}{dt} = BX - X^2 Y$

- $\frac{dY}{dt} = 0$ * solve for Y

$$0 = BX - X^2 Y$$

$$0 = X(B - XY)$$

$$0 = B - XY$$

$$Y = B/X$$

* for solution $X \neq 0$

- Sub $Y = B/X$ into $\frac{dX}{dt} = 0$

$$0 = A - (B+1)X + X^2 (B/X)$$

$$0 = A - (B+1)X + BX$$

$$0 = A - BX - X + BX$$

$$0 = A - X$$

$$X = A$$

- Since $Y = B/X$, $Y = B/A$

- Therefore, proved that steady state values are: $(X, Y) = (A, B/A)$

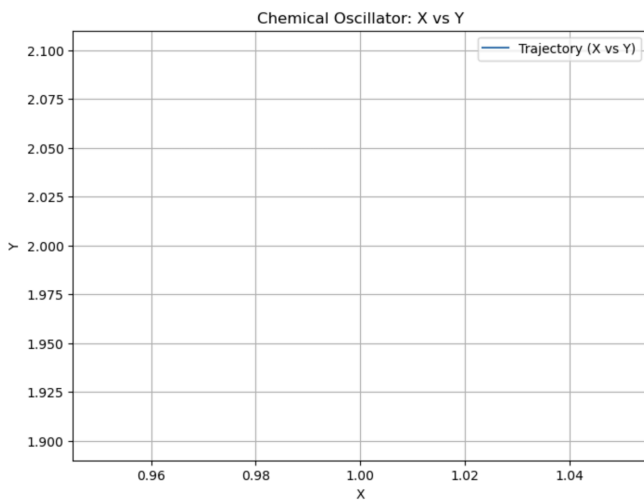
$$(X, Y) = (A, B/A)$$

Goals:

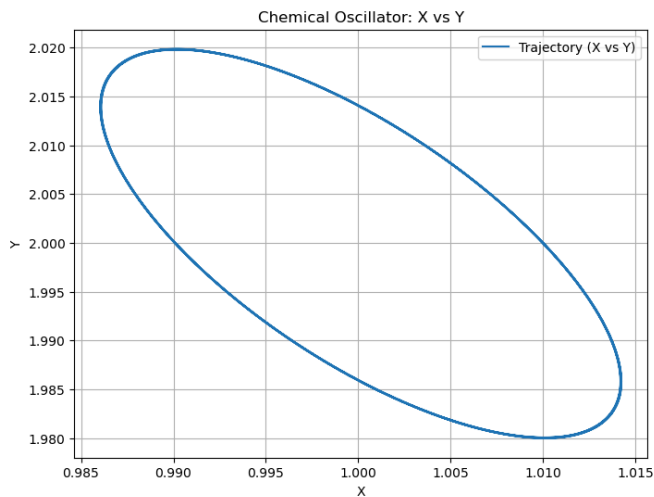
1. Develop a program that numerically solves the rate equations above
2. Methodically vary the initial conditions (X and Y) for certain concentrations (A and B values). Observe if the initial conditions influence the steady state behavior. Does the system always reach the same steady state, regardless of the starting conditions?
3. Classify the system's behavior for initial conditions close to the steady state ($A + 0.01, B / A$). Determine the relation between A and B that differentiates stable steady-state behavior from unstable periodic behavior.

I also explored Lotka - Volterra like rate equations with this model, but I will get into that later.

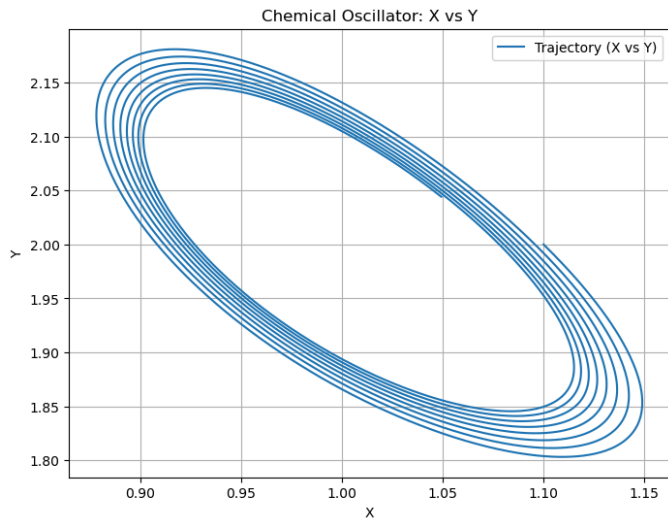
Using cpODEmodel and stepping algorithm RK4, I created a program that solves the rate equations. Below are graphs I generated showing X vs Y as a means to show how the reactions evolve.



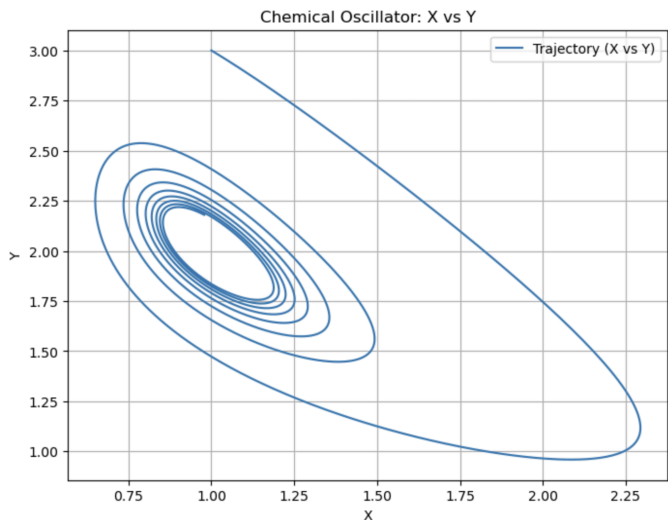
Conditions: $A = 1, B = 2, s_0 = [A, B/A]$
The system is in equilibrium because $[X, Y]$ is the steady state solution calculated above. No matter what the values of A and B, the system is in a steady state.



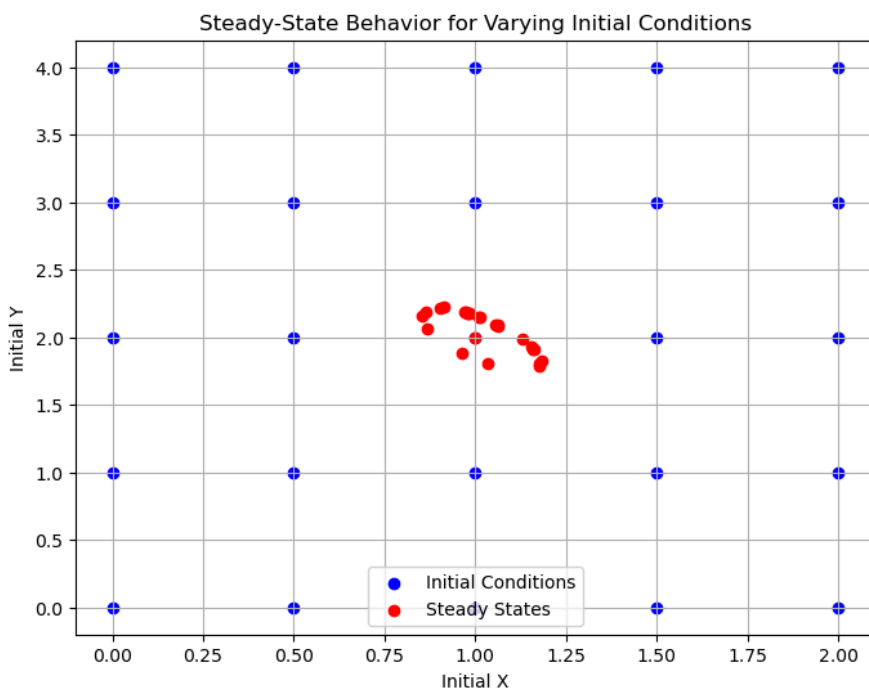
Conditions: $A = 1, B = 2, s_0 = [A + 0.01, B/A]$
The system is perturbed from its steady state and enters a periodic cycle about a stable limit



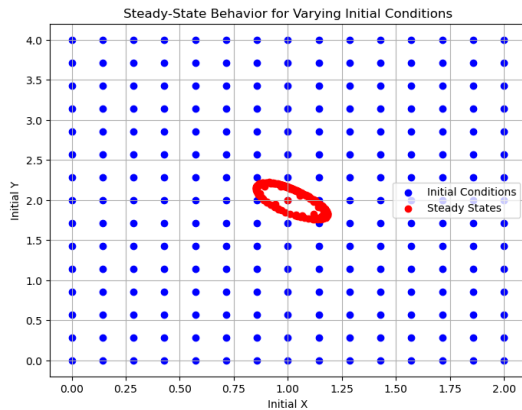
Conditions: $A = 1$, $B = 2$, $s_0 = [A + 0.1, B/A]$
 The system is perturbed even more out of its steady state. It remains in a periodic / orbit state for a while, and is very close to being stable, but stops at a certain point.



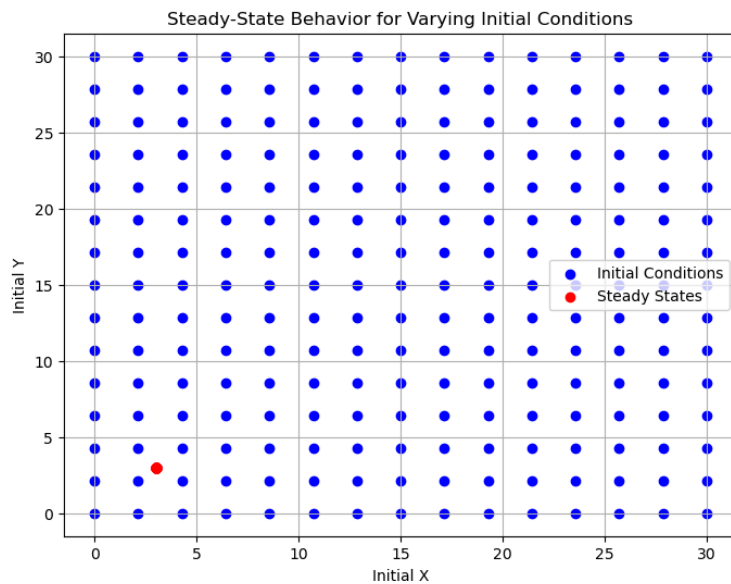
Conditions: $A = 1$, $B = 2$, $s_0 = [A + 1, B/A]$
 Clearly now the system is unstable, as it has deviated from the steady state too much to remain stable.



Next I created a function to get the final x and y steady state positions of a reaction. I fed it a range of X and Y values, and plotted the results. While the X and Y initial values are evenly spaced, the steady states congregate around the point (1,2), which were my fixed A and B concentration values. It appears that the steady state values depend on the A and B parameters, **not** the initial conditions.



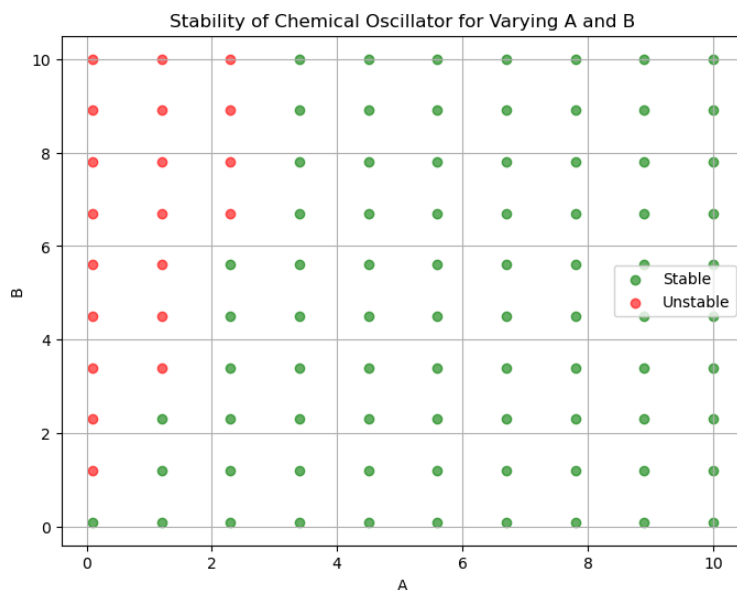
I repeated this but for more X and Y values and the pattern is reinforced.



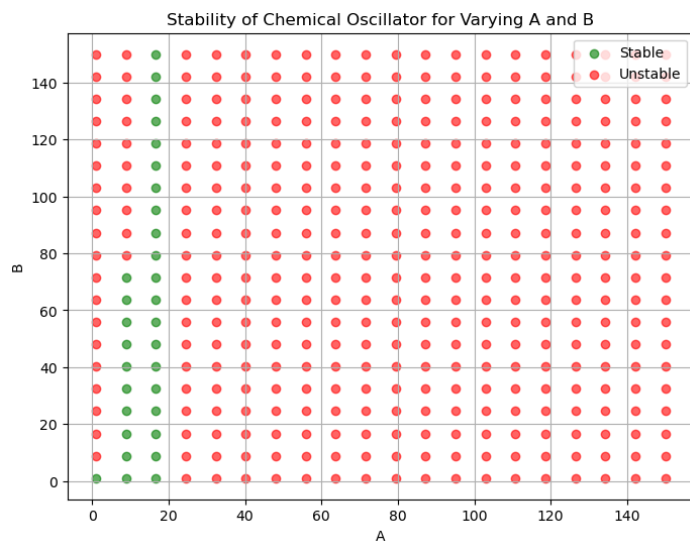
$A = 3, B = 9$

Steady state convergence to point (3,3). It seems that reactions can converge to (A,B) or some ratio of (A,B). Again, initial conditions having no effect if they're not the steady state condition

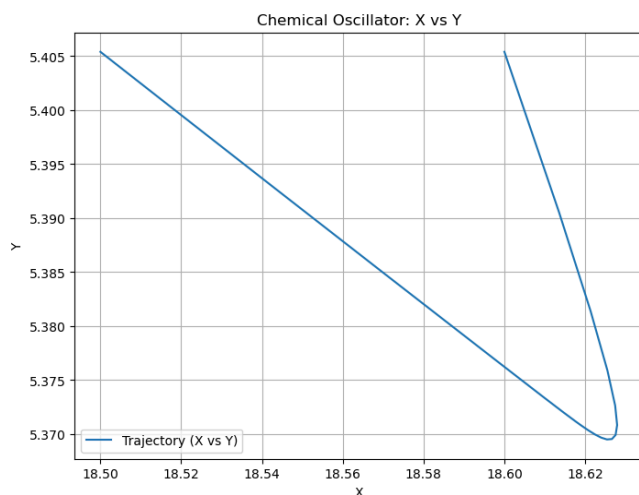
I created another function called `classify_behavior` that checks if a system has reached steady state by computing the difference between successive values and comparing it against a threshold value. Using this function to evaluate reactions for varying A and B concentrations, the following graph is produced:



Green dots represent stable states and red unstable. There appear to be distinct regions. To clarify / deduce any other patterns, I'm going to expand the x and y axes to account for even more A and B concentration combinations.

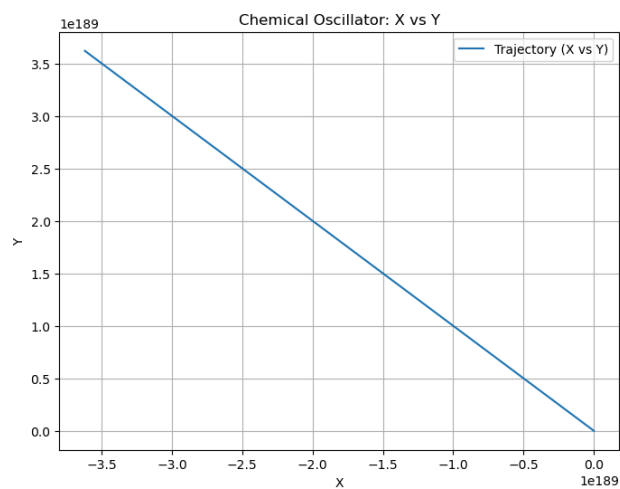


Axes expanded to 150 for A and B. This proved vitally important, as one might have concluded by just looking at the top chart that stable A,B parameters outnumber the unstable ones. However, this chart shows a column from 0 to 18 that gradually tapers off that accounts for the stable configurations, with every other region yielding chaos.



$A = 18.5$, $B = 140$, $s_0 = [A+0.1, B/A]$

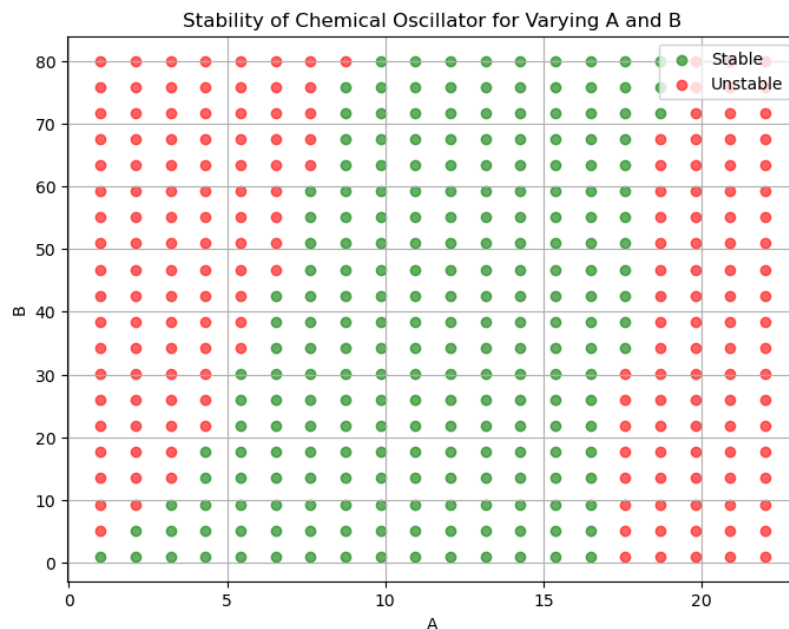
A reaction taken from the zone of stability to confirm



$A = 80$, $B = 80$, $s_0 = [A+0.1, B/A]$

A reaction taken from deep in the zone of instability. This doesn't look unstable, but likely oscillates indefinitely between the two ends of the line.

Find the relation between A and B that separates the two types of behavior:



By honing in on the patch of stable conditions, a slope can be used to compute a ratio between A and B (within a range) that approximates if a stable solution can be predicted from just knowing the concentrations beforehand.

$$\text{Slope} = (80 - 0) / (12 - 0) = 6.67$$

Approximate: for A = [0,18] if $(B / A) < 6.67$, the reaction is likely stable.

Conclusions:

- Initial conditions close to the steady-state values ($X=A$, $Y=B/A$) tend to result in steady-state behavior, until a large enough “push” can break the reaction out of equilibrium. If the push is not big enough, the reaction may enter an indefinite periodic cycle.
- Steady state behavior is independent from initial conditions, and dependent on the A and B concentration parameter. No matter the initial values for X and Y, the states converge to some point that is proportional to the values of A and B or just A and B themselves.
- There are distinct patterns in the values for A and B that produce unstable and stable reactions. Instability appears to be the norm, with a relatively small sliver of stability that can be analyzed and computed to generate predictions.

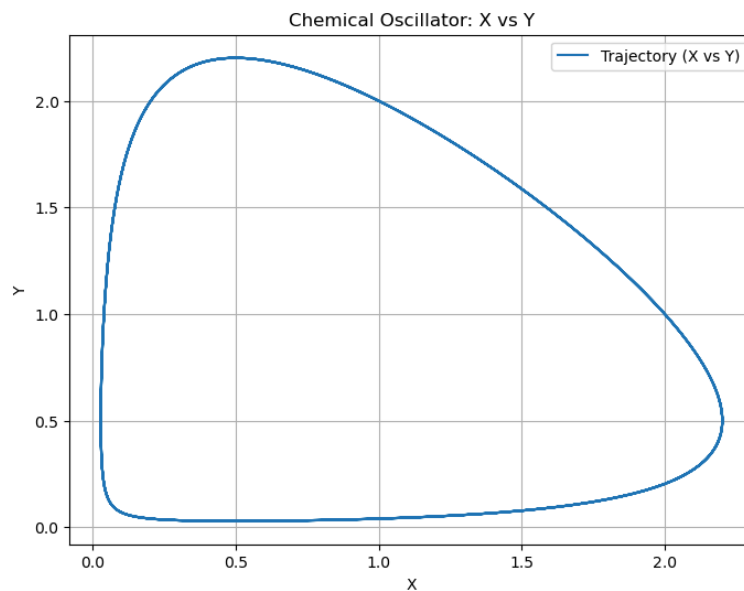
Future Work

- Use regression / curve fitting to identify the critical threshold between A and B mathematically
- Analyze properties of oscillation like period or amplitude and try to deduce if they are influenced by A, B, or initial conditions
- Use statistical / machine learning models for classification of points as steady state or periodic.
- Compare this model to other models of oscillatory behavior to learn and apply new concepts.

Lotka - Volterra Equations (or Predator-Prey equations)

- A type of oscillatory equation used to describe predator-prey dynamics in biology modeling
- As predator numbers rise, prey are hunted to a diminished size, which in turn causes a food shortage for the predators, decreasing their population size, etc.

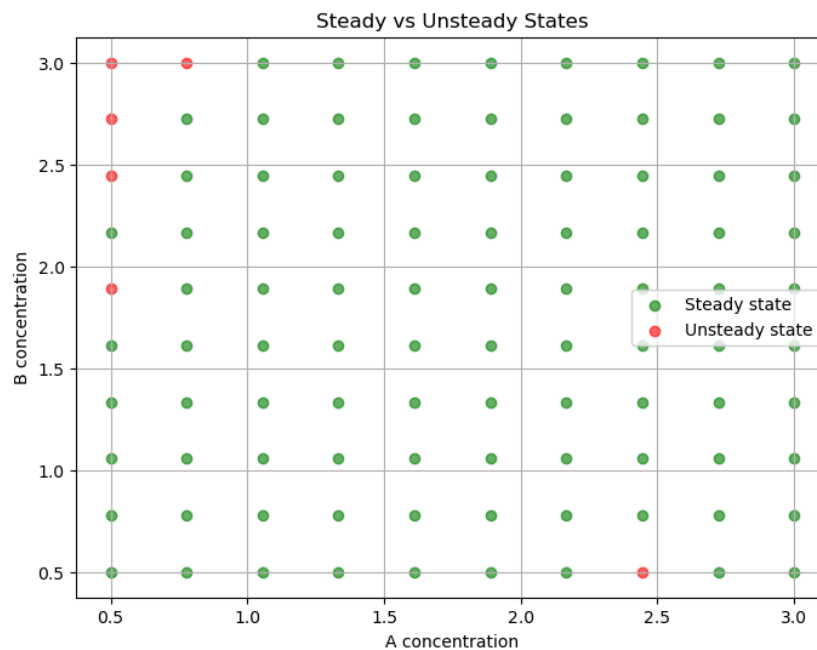
Implemented in cpODEmodel similar to ChemicalOscillatorModel



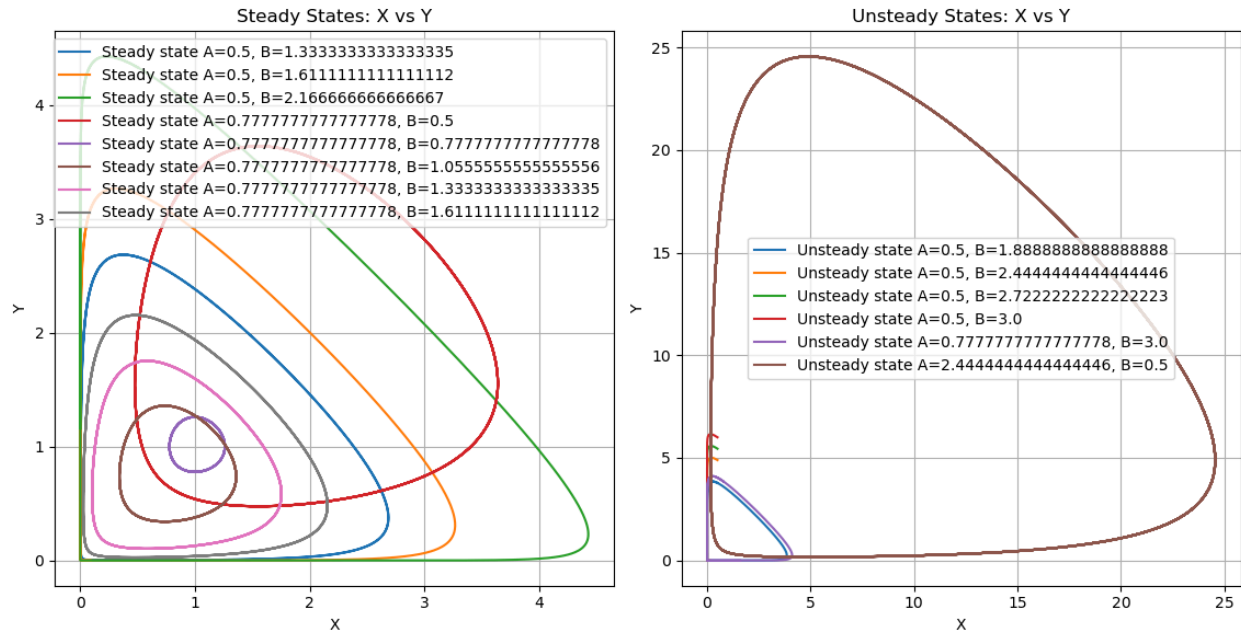
Generated oscillations with the same equations as the other models, and noticed an interesting feature.

$\max(x) = \max(y)$ and $\min(x) = \min(y)$

Can be used to classify these oscillations as Lotka Volterra-like



Attempted to find patterns in A and B concentrations but turned out to be more difficult to delineate patterns and relationships between A and B.



Plotted the steady vs unsteady oscillations - not immediately clear what differentiates some of them.

Steady / Unsteady not a very useful label, as the steady state solution was not optimized for this problem. It would be more accurate to say: how well did it match with the property $\max(x) = \max(y)$ and $\min(x) = \min(y)$.

Did not go nearly as in depth with this model but found it interesting to implement and generate plots with.