M350: Ordinary Differential Equations
Lawrence University
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Exploration 10.7 : Chemical Oscillating Reactions

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Yes, Chemical Reactions can oscillate

The discovery of the Belousov-Zhabotinsky reaction in the 1950s, which displayed oscillatory behavior before reaching equilibrium, revolutionized the understanding of chemical reactions. This finding led to the recognition that chemical systems can exhibit complex behaviors, including oscillations and chaos.
A simpler example of such dynamic behavior is seen in the chlorine dioxide-iodine-malonic acid reaction. Though the exact differential equations for this reaction are complex, they can be effectively approximated by a planar nonlinear system:

$$x' = a - x - \frac{4xy}{1+x^2}$$
$$y' = bx\left(1 - \frac{y}{1+x^2}\right)$$

Here, x and y represent the concentrations of iodine ion (I^-) and chlorine dioxide (ClO_2^-), respectively. The parameters a and b are constants that influence the reaction's dynamics, illustrating the intricate and non-monotonic behaviors possible in chemical reactions.
1. Begin the exploration by investigating these reaction equations numerically. What qualitatively different types of phase portraits do you find?
Given our differential equations that vary on the parameters a, b, we vary the parameter values to find phase portraits of different natures.
In our numerical experimentation of varying the parameter values, we can find real and spiral sinks/sources. We can also see saddles. Inevitably, we see the necessity to understand the $a - b$ plane more thoroughly to understand how the nature of phase portraits change based on their values.
We use Fieldplay and Sagemath to visualize the phase portraits in the next page.

Table 1: Summary of Phase Portraits

a,b Values	**Nature of Phase Portraits**
(2,2)	Real Sink
(4,4)	Spiral Sink
(11,1)	Spiral Source
(21,1)	Real Source
(-10,10)	Saddle

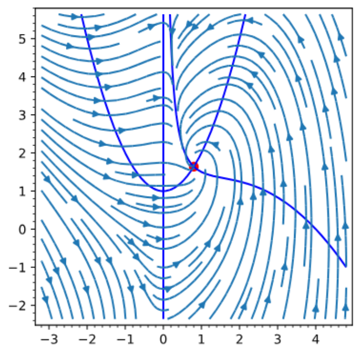

Figure 1: Spiral Sink

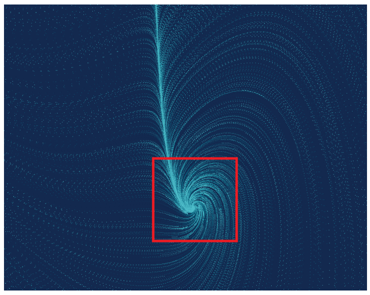

Figure 2: Spiral Sink in Fieldplay

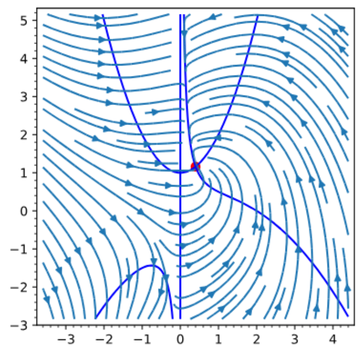

Figure 3: Real Sink

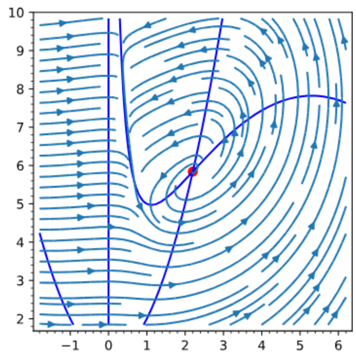

Figure 4: Spiral Source

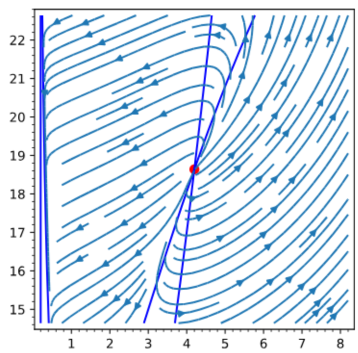

Figure 5: Real Source

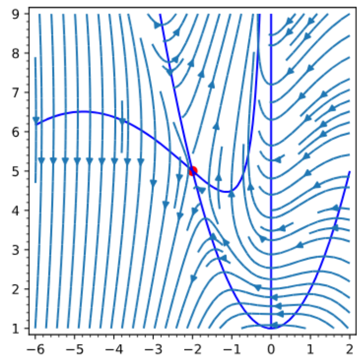

Figure 6: Saddle

2. Find all equilibrium points for this system.
We are given the system of differential equations : $x' = a - x - \frac{4xy}{1+x^2}$ and $y' = bx(1 - \frac{y}{1+x^2})$
At equilibrium, we have $x' = y' = 0$
Plugging in $y' = 0$, we get two solutions $x = 0, a = 0, y = k; k \in R$ and $x = \frac{a}{5}, y = 1 + \frac{a^2}{25}$. But problem is we know that a is nonzero. So the valid solution we are left with is $x = \frac{a}{5}, y = 1 + \frac{a^2}{25}$.

3. Linearize the system at your equilibria and determine the type of each equilibrium.
So our system of differential equations looks like this: $\left(a - x - \frac{4xy}{x^2+1}, -bx\left(\frac{y}{x^2+1} - 1\right)\right)$
To linearize, we compute the Jacobian with respect to (x,y) and evaluating at equilibrium $(\frac{a}{5}, 1 + \frac{a^2}{25})$ we get: $J_{eq} = \begin{pmatrix} \frac{8a^2}{a^2+25} - 5 & -\frac{20a}{a^2+25} \\ \frac{2a^2b}{a^2+25} & -\frac{5ab}{a^2+25} \end{pmatrix}$. This computation is done via our best friend Sagemath.

4. In the ab-plane, sketch the regions where you find asymptotically stable or unstable equilibria.

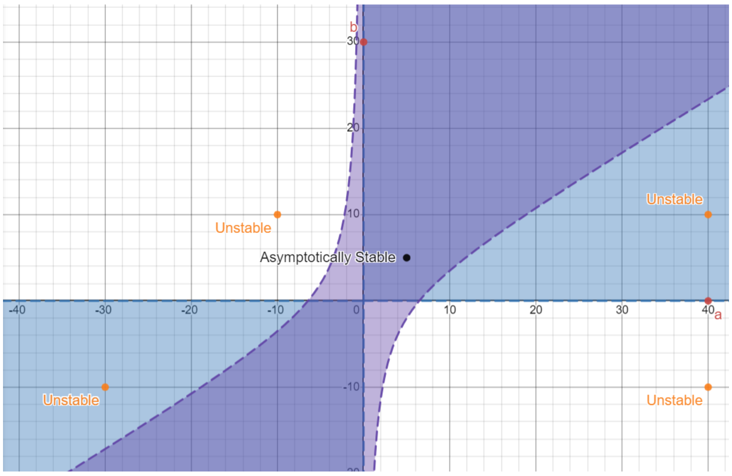

Figure 7: ab-plane visualization

To construct the ab-plane we first realize that it's helpful to determine the Trace and determinants of our Jacobian matrix.
From our computed Jacobian J_{eq}, we can easily compute the trace(T) to be $T = \frac{8a^2}{a^2+25} - 5 - \frac{5ab}{a^2+25}$ and determinant $D = \frac{40a^3b}{(a^2+25)^2} - 5 \cdot a \cdot \frac{\left(\frac{8a^2}{a^2+25}-5\right)b}{a^2+25}$
We know that we are looking for real sinks or spiral sinks as they are the only asymptotically stable regions. Centers will be the stable not asymptotically stable regions and everything else (sources, saddles) will be unstable regions.
The dark blue region of our ab-plane is the asymptotically stable region- this is where our T is negative and D is positive. This region only corresponds to sinks.
5. Identify the ab-values where the system undergoes bifurcations
So we can get the ab-values where the system undergoes bifurcations by solving the equation when $T = 0$. This leads to solving $3a^2 - 5ab - 125 = 0$. We use sympy by python to solve for this. Our solution looks like this: $(a, b) = (\frac{5b}{6} \pm \frac{5}{6}\sqrt{b^2 + 60}, b)$
By plugging in different values for b, you can find the a values. If you don't trust me, look at the plot below.

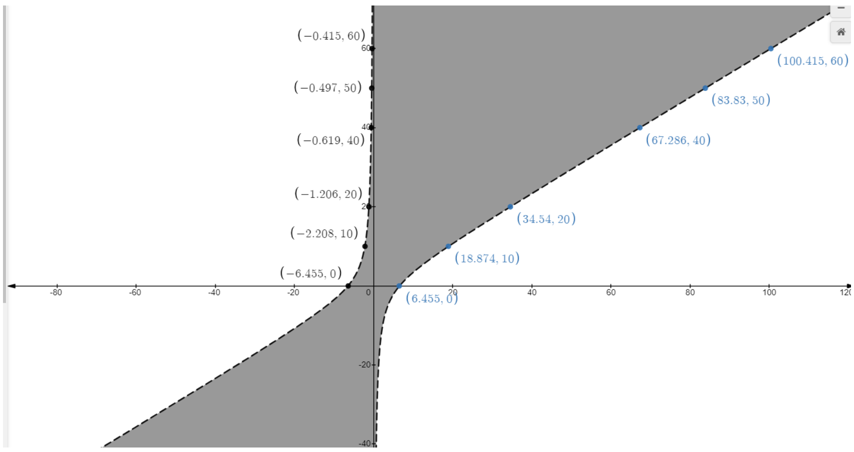

Figure 8: Finding Bifurcation points on ab-plane

6. Using the nullclines for the system together with the Poincare–Bendixson Theorem, find the ab-values for which a stable limit cycle exists. Why do these values correspond to oscillating chemical reactions?
We want to find an unstable equilibrium first around which we build an annulus region D and then we would use corollary 2 from chapter 10.6(See Appendix[2]) to claim that given the region which we will prove to be positively invariant doesn't have an equilibrium point, It must have a stable limit cycle.
We want to pick equilibriums where we can get spiral sources, these are unstable equilibriums that fit our purpose of finding a stable limit cycle. From our ab-plane analysis we can find the (a, b) values which correspond to spiral sources.

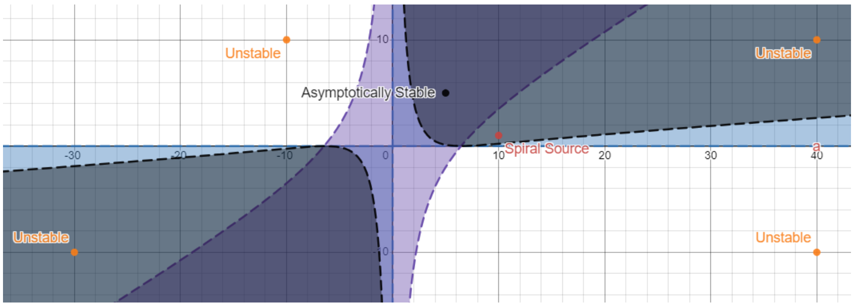

Figure 9: Spiral sources region is important

From this plane, we can tell (a,b)=(6.7,0.1) will correspond to spiral sources. Plugging in these parameters we can solve for our equilibrium points $(\frac{a}{5}, 1 + \frac{a^2}{25})$ to be (1.34,2.7956). We want to investigate the phase portrait corresponding to these values we have, first.To confirm via visuals we use Fieldplay's useful features. When you reset the particle reset probability to be really low, the existence of limit cycles become more apparent.

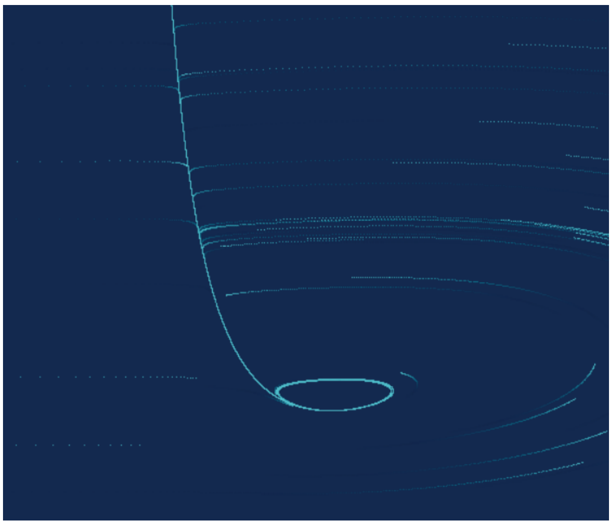

Figure 10: Limit Cycle Visualized for (a,b)=(6.7,0.1) in Fieldplay

So we find from our (a,b) plane that (6.7,0.1) corresponds to a spiral source. This corresponds to an unstable equilibrium at (x,y)=(1.34,2.7956). By the use of **linearization theorem** we know that there exists a neighborhood around (1.34,2.7956) where the vector field within that neighborhood points away from (1.34,2.7956) due to our system having eigenvalues with positive real parts, indicating that trajectories move away from the equilibrium.

Define γ to be an open neighborhood around (1.34,2.7956) such that within γ, the vector field is directed away from (1.34,2.7956). By construction, any trajectory that starts in D immediately moves outwards and cannot return to (1.34,2.7956).
What's next?: Now we want to build a closed rectangle ABCD that is positively invariant, as in any vector by the region gets absorbed by the ABCD region.
We propose the ABCD region as drawn below which is parametrized by:

$$ABCD := \begin{cases} x = 0 \\ y = 1 \\ y = 37.69 \\ x = 6.057 \end{cases}$$

We then draw vector field directions along the sides of ABCD by computing (x', y') in corresponding regions.

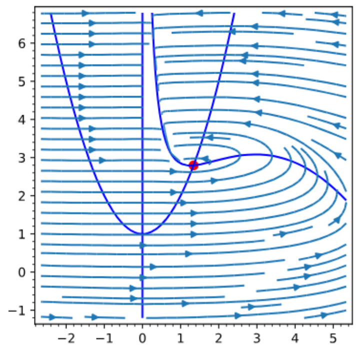

Figure 11: Streamlines along our nullclines and Unstable Equilibrium

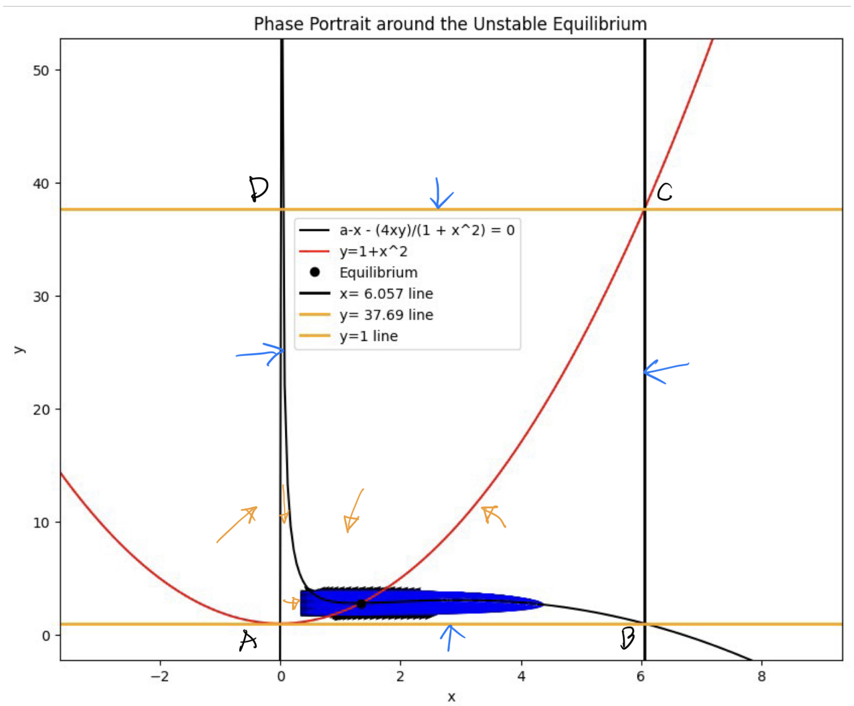

Figure 12: Vector field directions by nullclines and ABCD

From the vector field computation around region ABCD, it's obvious that vectors in our $x - y$ plane point inwards in the ABCD region. The way to check that is the vector field

arrows in resulting regions between the nullclines– you see that they gravitate towards our unstable equilibrium. Now, check the sides of ABCD- notice that the vector arrows gravitate inwards ABCD and not outwards of ABCD. We then have our closed positively invariant region ABCD because for each $(x, y) \in ABCD, \phi_t(x, y)$ is defined and contained in ABCD for $t > 0$ as guaranteed by the vector field in the ABCD region.
We can then define an annulus closed region $K = ABCD - \gamma$. This region now is closed and bounded and positively invariant by construction. Corollary 2 from chapter 10.6 (See Appendix[2]) reads that, "A closed and bounded set K that is positively or negatively invariant contains either a limit cycle or an equilibrium point." So we are guaranteed that K contains either a limit cycle or an equilibrium point. But we know K doesn't have an equilibrium point because it's disjoint from γ and our equilibrium point is in γ. Hence, we know that K must contain a limit cycle and not an equilibrium. So we are done.
Similarly it can be shown for other (a,b) values that correspond to spiral sources/ real sources, limit cycles can exist. To generalize our proof then we just need a more general parametrization of our positive invariant set.
For our general positive invariant set, notice that $x = 0$ and $y = 1$ will naturally be two sides because they have vector field arrows always pointing inwards, this can be checked by computing x', y' in these respective sides. So we have the left and bottom sides of our general invariant set ABCD for the sources of our dynamical system. This gives us bottom left corner A(0,1). Let's find the other 3 corners. For the bottom right corner B, we know that this will be the intersection of our nullcline $a - x - \frac{4xy}{1+x^2}$ and $y = 1$ line. Solving for its real root gives us: $x = k = \frac{1}{3}\,a + \frac{a^2-15}{3\left(a^3-9\,a+9\,\sqrt{\frac{1}{3}\,a^4-\frac{22}{3}\,a^2+\frac{125}{3}}\right)^{\frac{1}{3}}} + \frac{1}{3}\left(a^3-9\,a+9\,\sqrt{\frac{1}{3}\,a^4-\frac{22}{3}\,a^2+\frac{125}{3}}\right)^{\frac{1}{3}}$
So we have our bottom right corner $B(k, 1)$
For the top right corner C, we are looking for the intersection point of $x = k$ line and $y = 1 + x^2$ nullcline. So, C will be $(k, 1 + k^2)$.
For the top left corner D, we are looking for the intersection point of $x = 0$ line and $y = 1 + k^2$. So D will be $(0, 1 + k^2)$
So, our general positive invariant set $ABCD$ will be a rectangle bounded by these four points:

1. $A(0, 1)$
2. $B(k, 1)$ where $k = \frac{1}{3}\,a + \frac{a^2-15}{3\left(a^3-9\,a+9\,\sqrt{\frac{1}{3}\,a^4-\frac{22}{3}\,a^2+\frac{125}{3}}\right)^{\frac{1}{3}}} + \frac{1}{3}\left(a^3-9\,a+9\,\sqrt{\frac{1}{3}\,a^4-\frac{22}{3}\,a^2+\frac{125}{3}}\right)^{\frac{1}{3}}$
3. $C(k, 1 + k^2)$
4. $D(0, 1 + k^2)$

Now similarly as to our proof $(a, b) = (6.7, 0.1)$, you can show how stable limit cycle exists for the general case too.

Conclusion and Chemical Reaction Relevance

In conclusion, for the values $a = 6.7$ and $b = 0.1$, our dynamical system exhibits a stable limit cycle. This limit cycle represents sustained oscillations in the phase portrait, corresponding to periodic behavior in the chemical concentrations. In our context, this corresponds to iodine ion (I^-) and chlorine dioxide (ClO_2^-) concentrations reaching particular equilibriums after a period. This equilibrium is no longer steady, rather periodic. Such behavior is characteristic of certain oscillating chemical reactions, where the system does not settle into a steady state but rather continues to exhibit periodic fluctuations. These oscillations are a hallmark of non-equilibrium thermodynamics in chemical systems, exemplifying how dynamic interactions between reactants can lead to complex, self-sustaining patterns over time.

Appendix

1. For a more detailed discussion on the derivations of these differential equations, please see: "Experimental and Modeling Study of Oscillations in the Chlorine Dioxide-Iodine-Malonic Acid Reaction" by Lengyel et al., 1990.
2. Differential Equations, Dynamical Systems, and an Introduction to Chaos By Morris W. Hirsch, Stephen Smale, and Robert L. Devaney.