Chemistry 4010 Fall 2019
Test 2 Solutions

1. In panel (A), we appear to have a limit cycle. This limit cycle undergoes a period doubling going from panel (A) to panel (B). Panel (B) thus shows a period-doubled limit cycle. Going from panel (B) to panel (C), the attractor has gone through at least one more period doubling. We still have a limit cycle in panel (C), although a more complex one, with at least four distinct loops. Panel (D) appears to show a chaotic time series. An infinite number of period doublings would have occured between panels (C) and (D).

2. (a) If $a = 0$, the equations to solve to find the equilibrium point are

$$y + z = 0$$
$$x = 0$$
$$b + xz - cz = 0$$

   Substituting $x = 0$ into the last equation, we get $z = b/c$. The first of the equilibrium conditions then gives $y = -z = -b/c$. The equilibrium point for $a = 0$ is therefore $(0, -b/c, b/c)$.

   (b) For $a = 0$, $b = 0.2$ and $c = 5.7$, the equilibrium point is roughly $(0, -0.0351, 0.0351)$. I used a very simple XPPAUT input file for to carry out the bifurcation analysis:

```
dx/dt=-(y+z)
dy/dt=x+a*y
dz/dt=b+x*z-c*z

x(0)=0
y(0)=-0.0351
z(0)=0.0351

param a=0, b=0.2, c=5.7

done
```

   Even starting close to the equilibrium point as I did, I had to run `Xppaut` for a long time to get to equilibrium. I therefore set `Total`

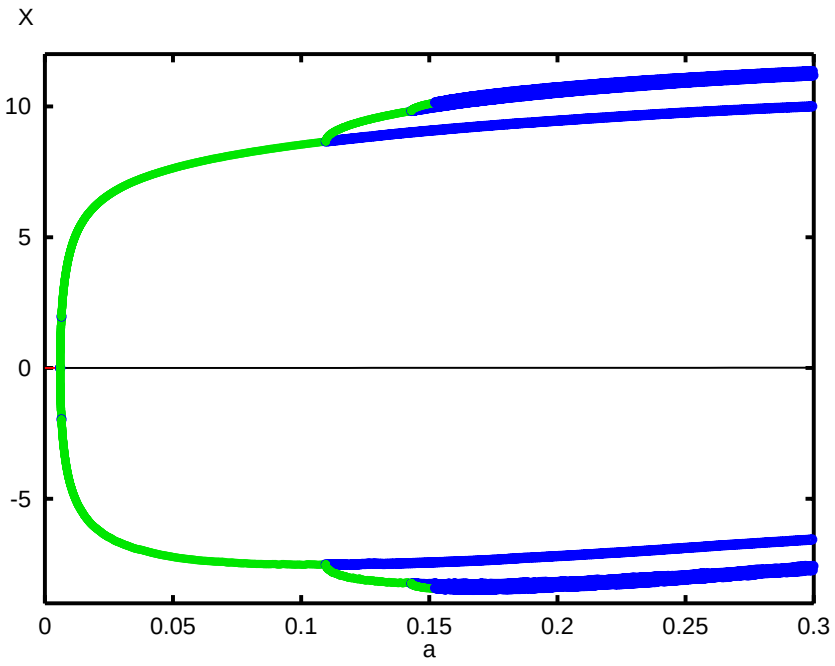

Figure 1: Bifurcation diagram for the Rössler model

to 2000 in the `Numerics` menu. This got me to equilibrium after clicking on `Initialconds`→`Last` just a couple of times.

After starting AUTO, I set `Par Max` to 0.3. Following the hints in the question, I reduced `Ds`, `Dsmin` and `Dsmax` to 0.001, 0.0001 and 0.01 respectively. After I started computing the branch of limit cycles, I found that I didn't get very far with the default 200 points, so I increased `Nmax` to 2000 before continuing. My bifurcation diagram is shown in figure 1. I found the following bifurcation points:

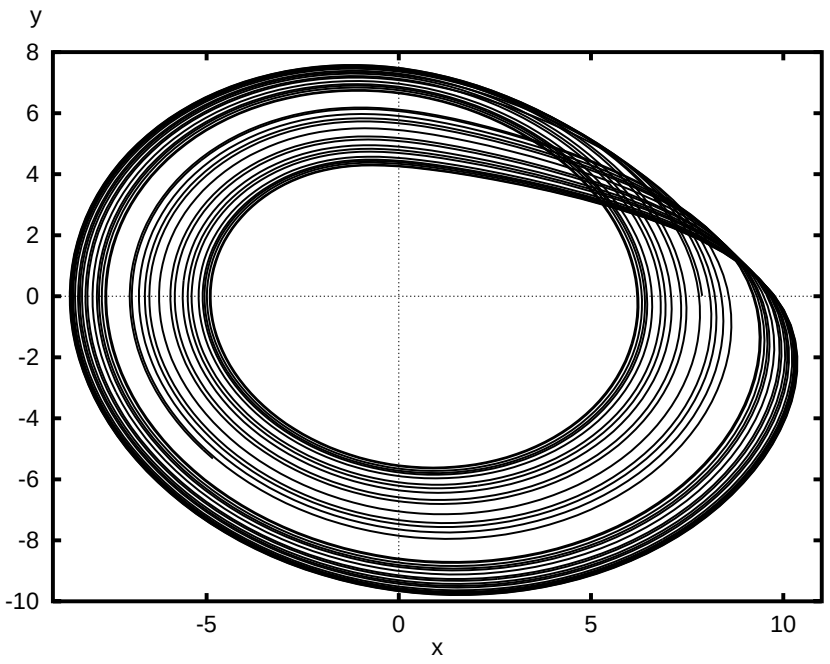

Figure 2: Chaotic attractor found at at $a = 0.16$, $b = 0.2$ and $c = 5.7$.

Type	$\boldsymbol{a}$
Andronov-Hopf	0.0060
Period-doubling	0.1096
Period-doubling	0.1430
Period-doubling	0.1520

(c) Figure 2 shows the attractor found at $a = 0.16$, $b = 0.2$ and $c = 5.7$. (It was not necessary to show the attractor in your response.) I guessed a good value of a based on the values at the period-doubling points I had observed. Many other values of a would have done just as nicely.

3. (a)

$$\frac{d[\mathrm{I}_2]}{dt} = -k_1[\mathrm{I}_2] + k_{-1}[\mathrm{I}]^2$$
$$\frac{d[\mathrm{I}]}{dt} = 2k_1[\mathrm{I}_2] - 2k_{-1}[\mathrm{I}]^2 - 2k_2[\mathrm{H}_2][\mathrm{I}]^2$$

Note: We could also write down an equation for [HI], but since it only appears as a product, it is not needed to study this model.

(b)
- The transformation to dimensionless equations is optional here, but let's suppose we decided to go ahead with it. The following are possible dimensions of the various quantities appearing in the equations:

$[\mathrm{I}_2]$:	bar	k_1: s^{-1}
$[\mathrm{I}]$:	bar	k_{-1}: $\mathrm{bar}^{-1}\mathrm{s}^{-1}$
$[\mathrm{H}_2]$:	bar	k_2: $\mathrm{bar}^{-2}\mathrm{s}^{-1}$
t:	s	

Define the dimensionless variables

$$x = k_{-1}[\mathrm{I}_2]/k_1,$$
$$y = k_{-1}[\mathrm{I}]/k_1,$$
$$\tau = k_1 t.$$

Inserting these quantities into the differential equations, we get

$$\frac{dx}{d\tau} = -x + y^2,$$
$$\frac{dy}{d\tau} = 2x - 2y^2 - 2\frac{k_2[\mathrm{H}_2]}{k_{-1}}y^2.$$

Define the dimensionless parameter

$$\alpha = \frac{k_2[\mathrm{H}_2]}{k_{-1}}.$$

Then

$$\frac{dx}{d\tau} = -x + y^2,$$
$$\frac{dy}{d\tau} = 2x - 2y^2(1+\alpha).$$

The rest of the solutions will be based on these dimensionless equations, although you could have chosen to work with the original differential equations.

- To find the equilibrium points, solve the equations

$$-x + y^2 = 0,$$
$$2x - 2y^2 - 2\alpha y^2 = 0.$$

The first of these equations gives $x = y^2$. Substituted into the second equation, we find that $y = 0$, so $x = 0$. The equilibrium point is therefore $(x^*, y^*) = (0, 0)$.

- The Jacobian is

$$J = \begin{bmatrix} -1 & 2y \\ 2 & -4(1+\alpha)y \end{bmatrix}.$$

At the equilibrium point, we have

$$J^* = \begin{bmatrix} -1 & 0 \\ 2 & 0 \end{bmatrix}.$$

The eigenvalues of the Jacobian are therefore -1 and 0. The stability of the equilibrium point is undecidable by linear stability analysis because of the zero eigenvalue. The negative eigenvalue means that the centre-manifold theorem will apply, i.e. that the initial relaxation will bring the composition to the centre manifold, and that subsequent motion on this manifold will determine the stability.

- If linear stability analysis doesn't resolve the stability issue, phase-plane analysis might. I usually start by determining the nullclines. The x nullcline is

$$y_{\mathcal{X}} = \sqrt{x}.$$

The y nullcline is

$$y_{\mathcal{Y}} = \sqrt{\frac{x}{1+\alpha}}.$$

Note that, since $\alpha > 0$, $y_{\mathcal{Y}} < y_{\mathcal{X}}$ at any given value of x. Figure 3 shows a sketch of the vector field. The y nullcline is

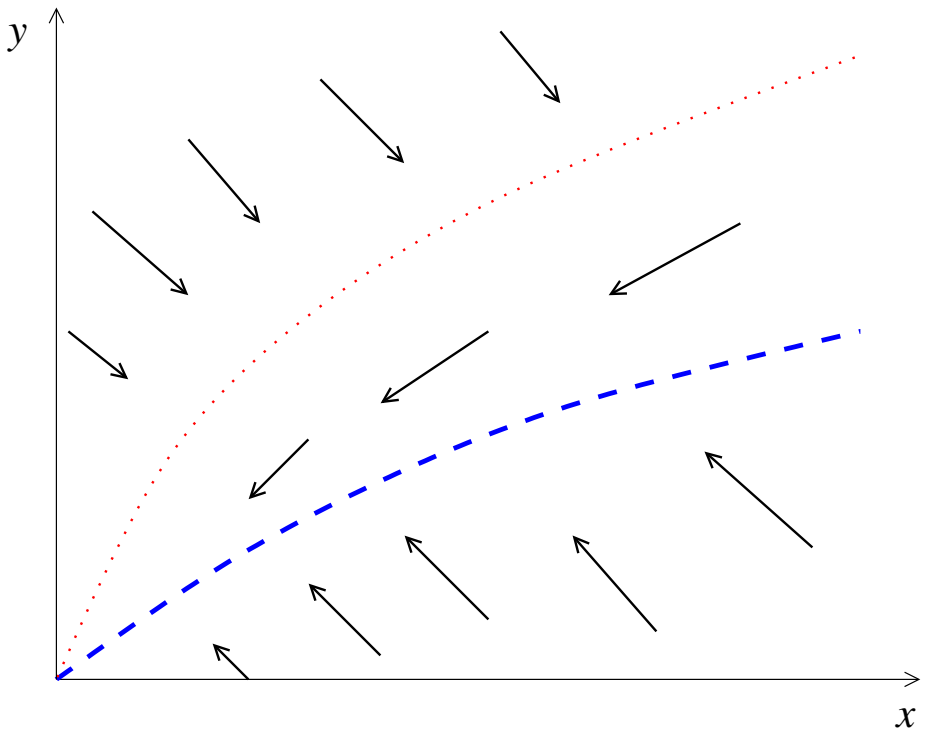

Figure 3: Velocity field for the reaction of H_2 with I_2 at fixed $[H_2]$. The dashed blue curve is the y nullcline. The dotted red curve is the x nullcline.

represented by the blue dashed curve, and the x nullcline is the red dotted curve. Along the x axis, $\mathbf{v} = (-x, 2x)$. The same qualitative sign pattern is found everywhere below the y nullcline. The sign of $dy/d\tau$ changes as the composition crosses this nullcline. Similarly, on the y axis, $\mathbf{v} = (y^2, -2y^2(1+\alpha))$. Again, this overall orientation of the velocity vector is maintained until the composition crosses the x nullcline.
Once we have the velocity field, we can trace out trajectories, as shown in figure 4. It becomes clear from the sketch of the trajectories that all trajectories started from the physically realizable quadrant must reach the equilibrium point, i.e. the equilibrium point is a global (within the positive quadrant) attractor.

- To carry out the centre-manifold analysis, we need the eigen-

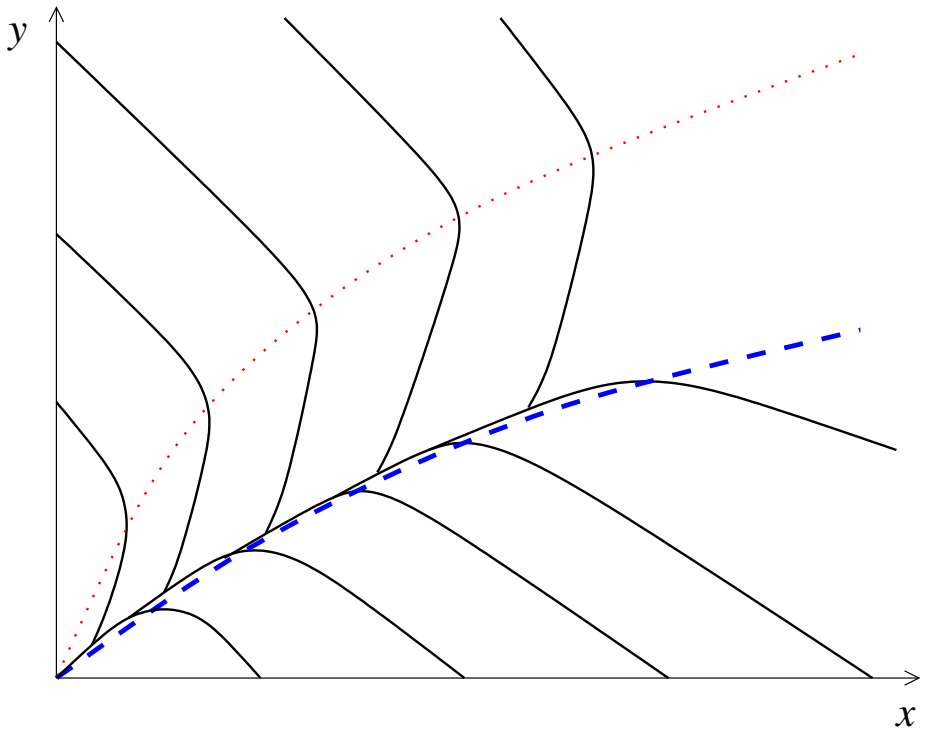

Figure 4: Sketch of the trajectories for the reaction of H_2 with I_2

vector of the Jacobian belonging to the zero eigenvalue. An eigenvector satisfies $\mathbf{J}^*\mathbf{u} = \lambda\mathbf{u}$. For $\lambda = 0$, this becomes $\mathbf{J}^*\mathbf{u} = \mathbf{0}$:

$$\begin{bmatrix} -1 & 0 \\ 2 & 0 \end{bmatrix} \begin{bmatrix} u_x^{(0)} \\ u_y^{(0)} \end{bmatrix} = \begin{bmatrix} -u_x^{(0)} \\ 2u_x^{(0)} \end{bmatrix} = \begin{bmatrix} 0 \\ 0 \end{bmatrix}.$$

Thus, $(0, 1)$ is an eigenvector. This leads to a slight complication, namely that the centre manifold enters the equilibrium point vertically. A simple way to address this problem is to write the centre manifold in the form $x = x_{\mathrm{CM}}(y)$, which will have a proper Taylor expansion. Written in this form, x_{CM} has the representation

$$x_{\mathrm{CM}}(y) = a_2 y^2 + a_3 y^3 + O(y^4).$$

(a_0 is zero because the equilibrium point is $(0, 0)$, and a_1 is zero because the centre manifold enters the equilibrium point vertically.) The invariance equation in this case is

$$\left.\frac{dx}{d\tau}\right|_{\mathrm{CM}} = \frac{dx_{\mathrm{CM}}}{dy} \left.\frac{dy}{d\tau}\right|_{\mathrm{CM}}.$$

Using the rate equations and the Taylor series representation of the centre manifold, we get

$$\begin{aligned} &- \left[a_2 y^2 + a_3 y^3 + O(y^4)\right] + y^2 \\ &\quad = \left[2a_2 y + 3a_3 y^2 + O(y^3)\right] \\ &\qquad\qquad \times \left\{2\left[a_2 y^2 + a_3 y^3 + O(y^4)\right] - 2y^2(1+\alpha)\right\}. \end{aligned}$$

If we now collect terms in y^2 on both sides of this equation, we get

$$-a_2 + 1 = 0$$

which of course implies that $a_2 = 1$. Accordingly, on the centre manifold

$$\left.\frac{dy}{d\tau}\right|_{\mathrm{CM}} = 2\left[y^2 + O(y^3)\right] - 2y^2(1+\alpha) = -2\alpha y^2 + O(y^3).$$

For any positive value of y, $dy/d\tau < 0$, so y decreases toward the equilibrium point. It follows that the equilibrium point is semi-stable.

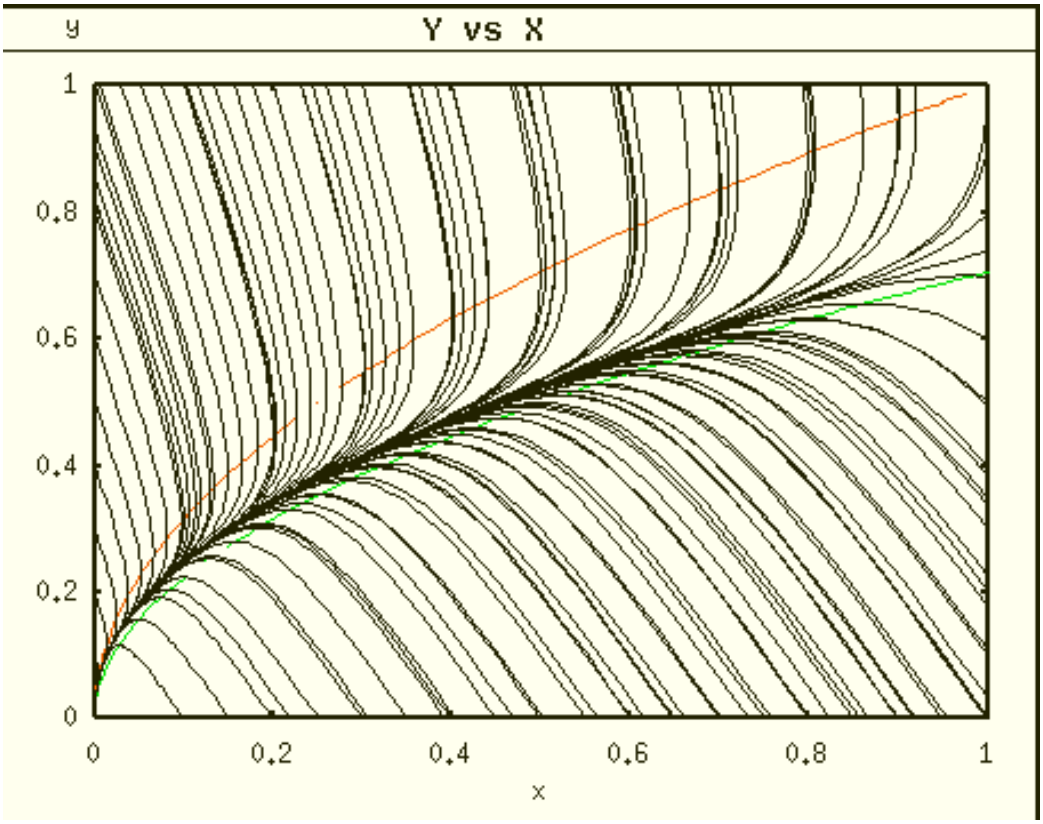

Figure 5: Phase-plane flow computed by `Xppaut` for the H_2/I_2 model with $\alpha = 1$.

- We could have done something like a phase-plane analysis using XPPAUT using the `Nullcline` function along with the `Dir.field/flow`→`Flow` function. My XPPAUT input file is the following:

```
dx/dt=-x+y^2
dy/dt=2*x-2*y^2*(1+alpha)

param alpha=1

done
```

  My computation of the flow is shown in figure 5. (We could also have plotted the vector field.) The resulting figure is,

in essence, a graphical proof of stability of the equilibrium point. The only catch is that we can't be sure from this result alone that the qualitative behavior is independent of α. We still need to look at the equations to convince ourselves that nothing changes qualitatively when α changes.