Lesson 15: Oregonator, Chemical Reactions and ode15s

15.1 Applied Problem.

The chemical reaction with bromous acid, bromide ion and cerium ion exhibits a remarkable chemical attributes, which oscillate with changes in color and structure. The rate of changes of the concentrations are very large and have spikes similar to those in the Van der Pol equation solution. Such systems are called **stiff** and require special numerical methods. The Matlab command odedemo illustrates this (see chm9ode) and other stiff differential equations and two stiff solvers called ode23s and ode15s.

15.2 Differential Equation Model.

The chemical reaction can be described in five stages with known reaction rates. Upon suitable time and concentration scaling this is modeled by three coupled differential equations. Let $s = 77.27$, $w = .161$, $q = 8.375\times10^{-6}$, $y_1(0) = 4$, $y_2(0) = 1.1$ and $y_3(0) = 4$.

\[
y_1' = s(y_2 - y_1 y_2 + y_1 - q y_1^2) \]
\[
y_2' = (-y_2 - y_1 y_2 + y_3)/s \quad \text{and} \]
\[
y_3' = w(y_1 - y_3). \]

Matlab's ode23s and ode15s can be used to solve such systems.

As a first step in the study of this system, we consider the steady state solutions, which are defined by all three derivatives being set equal to zero so that

\[
0 = s(y_2 - y_1 y_2 + y_1 - q y_1^2) = f_1(y_1, y_2, y_3),
\]
\[
0 = (-y_2 - y_1 y_2 + y_3)/s = f_2(y_1, y_2, y_3) \quad \text{and}
\]
\[
0 = w(y_1 - y_3) = f_3(y_1, y_2, y_3).
\]

The three positive steady state solutions are
These may be found by using the symbolic Matlab command solve as follows

\begin{verbatim}
EDU» [y1,y2]=solve('y2 -y1*y2+y1 - q*y1*y1=0','-y2-y1*y2+y1=0')
y1 =
[ 0]
[ 1/2/q*(-q+(q^2+8*q)^(1/2))]
[ 1/2/q*(-q-(q^2+8*q)^(1/2))]
y2 =
[ 0]
[ 1+1/4*q-1/4*(q^2+8*q)^(1/2)]
[ 1+1/4*q+1/4*(q^2+8*q)^(1/2)]
\end{verbatim}

The Jacobian of \([f_1 \ f_2 \ f_3]'\) is

\[
J = \begin{bmatrix}
  f_{y_1} & f_{y_2} & f_{y_3} \\
  f_{2y_1} & f_{2y_2} & f_{2y_3} \\
  f_{3y_1} & f_{3y_2} & f_{3y_3}
\end{bmatrix}
= \begin{bmatrix}
  s(-y_2 +1-q2y_1) & s(1-y_1) & 0 \\
  - y_2 / s & (-1- y_1)/ s & 1 / s \\
  w & 0 & -w
\end{bmatrix}.
\]

The eigenvalues of \(J\), evaluated at the steady state solutions, are easily found by using the Matlab command eig. The following code is in the Matlab m-file called \texttt{oregjac.m}.

\begin{verbatim}
y1 = 488.18;
y2 = .99796;
y3 = y1;
s = 77.27;
w = .161;
q = 8.375*10^-6;
J = [s*(-y2+1-q*2*y1) s*(1-y1) 0,
    -y2/s (-1-y1)/s 1/s,
    w 0 -w];
eig(J)
\end{verbatim}
The output from the execution of this file shows some large positive and negative eigenvalues so that the steady state solutions are unstable and the system is stiff near the steady state solutions.

```matlab
EDU» oregjac

ans =

-25.7146
18.7473
0.0013
```

### 15.3 Method of Solution.

We will use Matlab's stiff solver called `ode15s`. This is much more sophisticated than the simple Euler-trapezoid method that was used a previous lesson. However, its formulation is somewhat similar to the implicit nature of each time step in the Euler-trapezoid method. Further details about this method are described in the Matlab's helpdesk (also see the link to the ODE suite on the homepage for Math 302).

### 15.4 Matlab Implementation.

The m-files for this system are called `yporeg.m` and `oreg.m`. In the first calculation we used the final time $tf = 300$, and the second calculation used $tf = 1000$ so as to show the oscillations over three periods. The graph is for the scaled concentrations versus time. The `oreg.m` file uses semilogy graphing, and so it reveals very significant spikes in the solutions.
function yporeg=yporeg(t,y)
    yporeg(1) = 77.27*(y(2) - y(1)*y(2) + y(1) - (8.375*10^-6)*y(1)*y(1));
    yporeg(2) = (-y(2) - y(1)*y(2) + y(3))/77.27;
    yporeg(3) = .161*(y(1) - y(3));
    yporeg=[yporeg(1) yporeg(2) yporeg(3)]';

% your name , your student number, lesson number
clear;

   tf = 1000;
   yo = [4 1.1 4];
   [t y] = ode15s('yporeg',[0 tf],yo);
   semilogy(t,y(:,1),t,y(:,2),t,y(:,3));
   title('your name, your student number, lesson number')
   xlabel('time')
   ylabel('solutions one, two and three')
15.5 Numerical Experiments.

In the calculation below we decreased $w$ from .161 to .04. Notice the period increased and the steepness of the spikes decreased.
Next the initial conditions will be chosen closer to the steady state solution so that $y_1(0) = 480$, $y_2(0) = 1.1$ and $y_3(0) = 480$. The first calculation reveals the same oscillating pattern is established. The second calculation is for a much smaller time interval where $t_f$ has been decreased from $t_f = 1000$ to 10.
15.6 Additional Calculations.

Consider the above oregonator chemical reaction with variable

\[ w = \frac{S}{10}, \quad S \text{ and } 2S. \]

(a). State the new system of differential equations.

(b). Modify the yporeg.m file.

(c). Insert your name and student number into the oreg.m file.

Execute the oreg.m file for the three choices of w.

(d). Print the yporeg.m and oreg.m files and the graphs.