Exploring Exotic Kinetics: An Introduction to the Use of Numerical Methods in Chemical Kinetics

Michelle M. Francl
Bryn Mawr College
101 N. Merion Ave
Bryn Mawr, PA 19010 USA
mfrancl@brynmawr.edu

Copyright M.M. Francl, 2004. You are welcome to use this in your classroom. The author appreciates suggestions for improvement. Commercial use or sale requires permission of the author.

The use of numerical methods to solve systems of partial differential equations for chemical kinetics is introduced using a Mathematica notebook. The principles of numerical integration are briefly presented. The Runge-Kutta algorithm is used to explore two simple mechanisms as well as an autocatalyzed system (Lotka-Volterra) which exhibits exotic kinetic behaviors. The exercise can be used in the introductory physical chemistry course as a capstone exercise for chemical kinetics, or in the lecture to introduce numerical methods and/or exotic kinetic behaviors such as oscillatory reactions and chaotic behavior. An exercise for mastery based on the Gray-Scott mechanism for glycolysis is included.

Keywords: chemical kinetics, numerical integration, oscillating reactions, chaotic reactions, Lotka-Volterra reaction, computer-based learning, symbolic mathematics, upper division undergraduates, physical chemistry
Introduction

Background

When I was a graduate student TA for a physical chemistry course, the instructor gave a final exam problem that consisted of a dozen graphs with instructions to label the axes, briefly describe what the graph represented and comment on why this particular graph was important in the course. A similar exercise from a recent final I gave showed the graph in Figure 1, and of course, you immediately associate it with chemical kinetics, can identify it as illustrating first order kinetics (in this case a first order equilibrium $A \rightleftharpoons B$), would label the abscissa with units of time and the ordinate with concentration units and note that the blue line was the product and the orange, the reactant. What about the graph in Figure 2? This is not so immediately recognizable. However, just as in Figure 1, the graph shows the time dependence of the concentrations of two species, but where their behavior can no longer be characterized in the classical fashion as "first order" or "second order". How do such exotic behaviors arise? Are they rarities, of interest only to the specialist, or commonplace? How can we predict the concentration as a function of time when we cannot use the simple relationships we are accustomed to writing?

![Figure 1](image-url)

Michelle M. Francl  
Created: April 2000  
Modified: June 2004
The second question is easily answered by taking your own pulse. Many biological processes are clearly oscillatory, and at the most fundamental level are run by chemical reactions that therefore must oscillate as well. Larger reaction systems, such as the atmosphere, can also exhibit complex behavior, for example, the seasonal development of a "hole" in the tropospheric ozone layer over the poles. A half-century ago, researchers were not convinced that chemical reactions could exhibit oscillatory or other complex behaviors. The assumption was that the concentrations of species either decayed or increased monotonically, except for intermediates, which reached a maximum sometime during the reaction, then decayed to zero. In the 1950s, while searching for a model for the Krebs cycle, a Russian chemist, Belousov, discovered a reaction which clearly cycled from reactant to products multiple times before ultimately reaching equilibrium. The Belousov-Zhabotinsky reaction is spectacular to watch [see the Further Reading section for a link to a movie], flashing various colors, and has a complex autocatalytic mechanism, a model for which was first developed by Noyes' group at the University of Oregon. These reactions, while fascinating in and of themselves, opened the door to the exploration of "exotic kinetics", reactions that exhibit oscillatory patterns, or even chaotic kinetics. Alan Turing, a computer scientist, proposed that such reactions could be used to produce regular patterns, such as those seen in nature, and suggested that these sorts of reactions could give rise to biomorphogenesis. More systems probably exhibit these complex behaviors than do not, so to label them "exotic" might be a bit of a stretch, but as they do fall outside the bounds of what is studied in most introductory physical chemistry courses, I'll continue to use the term.

The chemical kinetics of complex reactions such as these can be difficult to model mathematically. Once a reaction mechanism reaches more than a few steps, it becomes difficult or impossible to integrate the differential rate equations analytically. Many studies of complex mechanisms rely either on simplifying the reaction mechanism by identifying rate determining steps or by applying steady state approximation to one or more intermediates. These approaches are important, but can fail when no one step dominates the reaction, or when the conditions for using the steady state approximation are not met. When the equations cannot be simplified and solved analytically, it is necessary to turn to numerical techniques to solve the rate equations. Numerical integration of the differential rate expressions can also produce more accurate models, even for situations where the steady state approximation can be used or where there is a clear rate determining step.

The drawback to using numerical integration is that for any system of equations of significant size or complexity it requires a computer. Even for small systems and short time scales, it is tedious to do by hand. Since my days as a student, where an 80Mb hard drive was the size of a washing machine, computers have gotten smaller and faster so for systems which have only a few steps, you can do this on a laptop at Starbucks. Larger systems obviously can require a bigger computer, some of the world's fastest supercomputers (see http://www.top500.org/ for the current list of the top 500 fastest machines) are used to tackle such problems as modeling the reactions in the troposphere. Recent advances in computer science are even making it possible to model larger systems by temporarily creating a supercomputer - then I could do the whole thing at Starbucks by inviting the 10 other people who are here with me right now to link up their laptops (see http://www.flashmobcomputing.org/).

There are many ways to integrate a set of coupled differential equations, ranging from the very simple to the more complex. You don't actually need to know much about how numerical integration works to be able to use it to solve differential rate equations. This notebook uses two methods for numerical integration, one where it is easy to see how numerical integration works, and another (a Runge-Kutta method) which is more sophisticated and in many situations works better. I've included a section about numerical integration if you want to learn the basics (or if your instructor wants you to).
In this notebook, we will see how numerical techniques can complement and extend our ability to predict the concentration of species during a reactions and use numerical techniques to try to understand how exotic kinetics might develop, and how complex a reaction mechanism is required before we can see these behaviors.

**Goals**

When you finish this exercise, you will be able to explain how numerical integration schemes can be used to calculate the concentrations of species in a reaction as a function of time and be able to numerically integrate the rate equations for simple mechanisms to obtain concentration versus time graphs for various species in a reaction. You will have seen examples of exotic kinetic behavior and be able to describe some conditions when exotic behaviors might be manifested.

**Objectives**

After completing this workbook you will be able to:

- explain how numerical integration can be used to find the concentration of species in a reaction, given the mechanism, rate constants and concentrations of species.
- explain how simple numerical integration schemes work.
- write a Mathematica notebook to do a simple integration.
- explain the concept of time step and how it affects the results of a numerical integration.
- use the Runge-Kutta method to find concentration as a function of time for a multi-step mechanism.
- explain the limitations of the customary approximations such as the steady state approximation.
- explain the concept of induction period (rise time).
- describe some exotic kinetic behaviors, such as sustained oscillation and chaos, and the conditions under which they might arise

**Test yourself**

When you have completed the exercise, you can test your mastery of the material by doing the two "test yourself" exercises provided under "Reprise and Revise"

**Going further**

Interested in more information? Check out the additional reading under "Reprise and Revise"
Getting Started

■ Note to the student

Questions and exercises are highlighted in grey boxes, you will get more from the exercise if you tackle these questions than if you just hit "enter" and look at the graphs. If the question asks to explain or describe something, and you are working in pairs, discuss the question with your partner, then each write in your notebook what you agree on. Can't agree? Write down the points you can't settle and go back to your text or course notes to try to sort it out. I have also included questions which ask you to sketch a graph in your notes, and you may wonder why not just print out the graph, or look at it on the screen. Mathematica does such a nice job of plotting. As you probably know, there are many ways to learn. Some people are auditory learners, others visual, and still others are kinetic learners. Most of us use several such approaches as we master new skills and concepts. Discussing and writing the answers to questions engages the auditory process, sketching the graphs involves both visual and kinetic approaches. Some of my students print out the raw notebook and write their answers on this, others do it on separate sheet of paper and staple the notebook onto it, your instructor may have a preference, but whatever you do - write and write by hand! You are more likely to master and retain the concepts presented here.

If you are a Mathematica novice, don't panic. Even after using it for almost 15 years, I still feel like I've hardly scratched the surface of what is possible and am always discovering new and useful tidbits. If you work in pairs, switch off each section who controls the keyboard -- lest one of you become more expert than the other. Finally, if you are a novice, remember that Mathematica (like all computer languages) is picky -- for example it thinks that A[t] means find the value of the function A at the point t, if you type A(t) instead, it will not understand you. If you get the dreaded "beep", have a friend check your input (it's hard to see your own errors). The Mathematica tidbits below introduce various commands that I found useful to solve the problems set out in this notebook. My students report that having examples to study and modify is the best way to learn more about Mathematica. Finally, the help menu can be a big help - many examples are given that you can edit for your own use.

At the end of this notebook, I've included two problems you can use to test your mastery of the material and a section called "The Culture of Chemistry." There is more to physical chemistry and the people who do it than you can find in your physical chemistry book. See if you can find the physical chemistry in CSI or ER, or read a novel or short story that features physical chemistry! If you want to see more "Culture of Chemistry" vignettes, check out (www.brynmawr.edu/Acads/-Chem/mfrancl/PChemResources/).

■ Warming-up

What you might want to read before you start

The specific references given below will provide appropriate background, but you can also read the chapters on chemical kinetics in any junior level physical chemistry text.

McQuarrie and Simon (1997): Ch. 28, sections 1, 3-5; Ch. 29, sections 1, 4.

Atkins and dePaula (2002): Ch. 25, sections 6-7; Ch. 26, sections 7-10.
What you should refresh before you start

It would be useful to refresh the following concepts: elementary steps and mechanisms; steady state; the distinction between integrated rate expressions and differential rate laws; how to integrate a simple differential rate expression to find the integrated rate expression; the effect of a catalyst on reaction rate; what is the difference between catalysis and autocatalysis; what constitutes a recursive relationship; how to determine the frequency of oscillation from a graph of a periodic function.

Mathematica tidbits

*Mathematica* is a sophisticated system for symbolic mathematics. Some commands that could be useful in solving the problems embedded in this exercise are given below. These tidbits may not represent the most elegant methodology, or even the most direct, and are almost certainly not the only way to use *Mathematica* to solve the problem. Remember, too, that your head contains an extraordinarily sophisticated computing resource as well, don't forget to engage it when the situation warrants. Sometimes it is easier to solve a simple piece of algebra, than to ask *Mathematica* to do it for you!

Comments have been placed directly in the *Mathematica* code in places where I thought they might be helpful in figuring out why I approached something in a particular way, they are formatted as

(* THIS IS  A COMMENT *)

Useful packages

The two packages invoked here allow you to add legends to plots and to make multiple plots of data lists. See the Mathematica help browser for more information about options to use with these commands. The key here is that you need to load the packages before you use any of the commands in them. If you try the command first, then load the package, *Mathematica* gets somewhat confused. I've set these as initialization cells (under the Cell/Cell Properties menu) to guarantee this.

```
In[57]:= << Graphics`Legend`
    << Graphics`MultipleListPlot`
```

Turning off spelling errors

Often I don't want to see this error, particularly when reminding me that when I say "sec" (and mean seconds) I really don't mean "secant" or "Sec"....

```
In[59]:= Off[General::spell1]
     Off[General::spell]
```

Assigning values to variables

Want R to always be 8.314? (The ; keeps *Mathematica* from echoing the value. You can take it out and it will do the same thing.)

```
In[61]:= R = 8.314;
```

Need to check the value of variable, just type it's name

```
In[62]:= R
Out[62]= 8.314
```

Change your mind? Clear the variable out and reset it.

```
In[63]:= Clear[R]
      R = 8.314 / 4.184
Out[64]= 1.98709
```

Just need the value of A to be specified in this one place? use /.
In[65]:= A + 18 /. A -> 4
Out[65]= 22

You can even use the /.substitution syntax with Plot and other more complex commands

In[66]:= Plot[Cos[A x] /. A -> 4, {x, -Pi, Pi}]

Out[66]= - Graphics -

You can specify multiple variables using the substitution syntax.

In[67]:= A + B /. {A -> 4, B -> 3}
Out[67]= 7

Defining and using functions

Note the := format and use of the underscore only on the left hand side.

Standard functions are capitalized (Sin, Cos, etc.)

Log[x] is natural log
Log[10,x] is log base 10

In[68]:= B[t_] := (k1 / (k2 - k1)) (Exp[-k1 t] - Exp[-k2 t]) A

In[69]:= Psi[x_, n_] := (2 / a) ^ 1 / 2 Sin[(n Pi x) / a]

To evaluate a function at a particular value, type the value(s) in the brackets

In[70]:= Sin[Pi]
Out[70]= 0

In[71]:= Exp[-Infinity]
Out[71]= 0

In[72]:= Sqrt[2]
Out[72]= \sqrt{2}
\[ \text{In[73]}=\Psi[a/2,1] \]
\[ \text{Out[73]}=\frac{1}{a} \]

To see the definition of a function (either a \textit{Mathematica} built-in or one you have defined)

\[ \text{In[74]}=?\text{Exp} \]
\text{Exp[z]} \text{ is the exponential function. More...} \]
\[ \text{In[75]}=?\Psi \]
\text{Global`\Psi} \]
\[ \Psi(x_,n_):=\frac{1}{2}(\frac{2}{a})^n\sin[\frac{n\pi x}{a}] \]

Labeling graphs

Physical chemistry instructors frequently have a bee in their bonnets about labeling graphs! \textit{Mathematica} makes it easy to do that, and it's good to get into the habit of doing so, even when you are making graphs purely for your own pleasure. You can label both the abscissa and the ordinate.

\[ \text{In[88]}=\text{Plot}[x^2,\{x,-4,4\},\text{AxesLabel}\rightarrow\{"x","y"\}] \]

\[ \text{Out[88]}=\text{Graphics} \]

You can also label the overall plot
Multiple graphs on the same plot

How to plot multiple graphs on the same plot when you have their analytical form

Notice that it is hard to tell which curve is which? Use colors to distinguish the three. Hue[0] is red, Hue[.3] is green and Hue[.6] is blue (think ROYGBIV as you vary the value input to Hue from 0 to 1).

Michelle M. Francl
Created: April 2000
Modified: June 2004
\textbf{In[91]}: \begin{verbatim}
Plot[{x, \frac{1}{x}, x^2}, \{x, -4, 4\}, PlotStyle -> \{(Hue[0]), (Hue[.3]), (Hue[.6])\}]
\end{verbatim}

\textbf{Out[91]}: - Graphics -

Still confused? Add a legend.

\textbf{In[92]}: \begin{verbatim}
Plot[{x, \frac{1}{x}, x^2}, \{x, -4, 4\}, PlotStyle -> \{(Hue[0]), (Hue[.3]), (Hue[.6])\},
PlotLegend \rightarrow \{"x", \frac{1}{x}, \text{x}^2\}, LegendPosition \rightarrow \{1.1, -0.4\}]
\end{verbatim}

\textbf{Out[92]}: - Graphics -

Printer doesn’t do color? You’re color blind (my sons are so I’m sensitive to this!)? Use dashes and solid lines.
To try: Plot \( \sin(x) \), \( x^2 \) and \( x^4 \) on the same graph from \(-\pi\) to \(\pi\).

**How to plot multiple sets of points on the same plot**

Have data from an experiment or from a numerical integration you need to plot as points? Need to plot several such data points on a single graph? The command of choice is `MultipleListPlot`

I'll generate a set of \((x,y)\) data to use.

\[
\begin{align*}
\text{In[94]=} & \quad \text{Data1 = Table}\{\{x, \sin(x)\}, \{x, 0, 4 \pi, \pi/8\}\}; \\
\text{Data2 = Table}\{\{x, \sin(0.5x) + \sin(0.45x)\}, \{x, 0, 4 \pi, \pi/8\}\};
\end{align*}
\]

This plots just the points, using different symbols for each set. I used the legend command as in the previous section.

\[
\begin{align*}
\text{In[95]=} & \quad \text{MultipleListPlot[Data1, Data2, PlotLegend \rightarrow \{"set \#1", "set \#2"\}]}
\end{align*}
\]
In[97]:= MultipleListPlot[Data1, Data2, 
   PlotLegend -> {"set #1", "set #2"}, PlotJoined -> True]

Out[97]= - Graphics -

Color is also an option

In[98]:= MultipleListPlot[Data1, Data2, 
   SymbolStyle -> {Hue[.1], Hue[.6]}, PlotLegend -> {"set #1", "set #2"}]

Out[98]= - Graphics -

How to combine multiple types of graphs on the same plot (points and analytical functions, for example)

Want to compare an analytical function and a set of data points? Show can help.

Again, I'll generate some point data to use

In[99]:= Data1 = Table[{x, Sin[x] + (Random[] - 0.5) / 4}, {x, 0, 4 Pi, Pi / 16}];

I use names for each plot to make them easier to refer to. I've turned off the display of the two plots when they are created, and turn it back on when I want to show them both together by changing the value of DisplayFunction
In[100]:= Plot1 = ListPlot[Data1, DisplayFunction -> Identity]
Plot2 = Plot[Sin[x], {x, 0, 4 Pi}, DisplayFunction -> Identity]
Show[Plot1, Plot2, DisplayFunction -> $DisplayFunction]

Out[100]= - Graphics -
Out[101]= - Graphics -

The Do command, repeating a calculation

Sometimes it's useful to be able to repeat a series of calculations, while varying the values of a parameter, for example, or when computing a recursive function. To see how Do works, try the following example, which just writes "Done" 10 times.

In[103]:= Do[Print["Done"], {10}]
          
          Done
          Done
          Done
          Done
          Done
          Done
          Done
          Done
          Done
          Done

To see how this works in a more complex example, let's try to construct the Fibonacci sequence. Each value in the Fibonacci sequence is the sum of the two preceding terms. In this example I've used "first" and "second" to indicate the values of the two numbers. Note that I have to do a switch at each step. If you have a hard time seeing how the switch works, make a table of the values of first, second and new at each step. I can't see the intermediate results unless I use the Print command.
In[104]:= first = 1;
second = 1;
Do[{new = first + second, first = second, second = new, Print[new]}, {10}]

2
3
5
8
13
21
34
55
89
144

This is great, but what if I want to use the list somewhere else? I need to create a place to store it. Let's say I want the first 100 values. I make a list of all zeros (FibList), then fill it up using my Do. Now instead of first and second I use the actual locations in the list. The [[ ]] notation is how you tell Mathematica where items are located in a list. Note that I start with the 3rd item (I already have the first two), and that I can skip the swap, since I have the previous values permanently stored in FibList and the print, since again, I've got it all in the list.

In[107]:= NumberWant = 100;
FibList = Table[0, {NumberWant}];
FibList[[1]] = 1;
FibList[[2]] = 1;
Do[FibList[[i]] = FibList[[i-1]] + FibList[[i-2]], {i, 3, NumberWant}]

To see the whole thing

In[112]:= FibList

Out[112]= {1, 1, 2, 3, 5, 8, 13, 21, 34, 55, 89, 144, 233, 377, 610, 987, 1597, 2584, 4181, 6765, 10946, 17711, 28657, 46368, 75025, 121393, 196418, 317811, 514229, 832040, 1346269, 2178309, 3524578, 5702887, 9227465, 14930352, 24157817, 39088169, 63225986, 102334155, 165560141, 267914296, 433494437, 701408733, 1134903170, 1836311903, 2971215073, 4807526976, 7778742049, 12586269025, 20365011074, 32951280099, 53316291173, 86267571272, 139583682445, 225851433717, 365435296162, 591286729879, 956722026041, 1548008755920, 2504730781961, 4052739537881, 6557470319842, 1061020957723, 17167680177565, 27777890035288, 44945570212853, 72723460248141, 11766903046994, 190392490709135, 308061521170129, 498454011879264, 80651553304393, 1304969544928657, 2111485077978050, 3416454622906707, 5527939700884757, 8944394323791464, 14472334024676221, 23416728348467685, 3789062373143906, 61305790721611591, 99194853094755497, 160550643816367088, 259695496911122585, 420196140727489673, 679891637638612258, 1100087778366101931, 1779979416004714189, 2880067194370816120, 4660046610375530309, 7540113804743646429, 12200160415121876738, 19740274219868223167, 31940434634990099905, 51680708854858323072, 83621143489848422977, 13530185234470646049, 218922995834555169026, 354224848179261915075}
To see the 89th

```
In[113]:= FibList[[89]]
Out[113]= 1779979416004714189
```

**Warm up problems**

The following problems give you a chance to ramp-up for the longer, more complex exercises that follow.

**WU-1** Given the mechanism below, write down the differential rate law for \( \text{CH}_4 \), \( \text{H} \) and \( \text{CH}_3 \).

\[
\text{CH}_4 \rightleftharpoons \text{CH}_3 + \text{H} \\
\text{H} + \text{CH}_4 \rightleftharpoons \text{CH}_3 + \text{H}_2 \\
2\text{CH}_3 \rightleftharpoons \text{C}_2 \text{H}_6
\]

**WU-2** For the mechanism given in **WU-1**, find expressions for [H] and [CH₃] assuming that the steady state approximation can be applied to both species.

**WU-3** Given the differential rate law \( \frac{d[\text{SO}_2 \text{Cl}_2]}{dt} = k_1 [\text{SO}_2 \text{Cl}_2] \) for the reaction \( \text{SO}_2 \text{Cl}_2 \rightarrow \text{SO}_2 + \text{Cl}_2 \) where \( k_1 = 2.20 \times 10^{-5} \text{ sec}^{-1} \) at 593K. Graph the percentage of \( \text{SO}_2 \text{Cl}_2 \) that has decomposed as a function of time.

**WU-4** The number of leaves on the ground \( l \) at time \( t \) depends on the number of leaves that have already fallen. The dependence is captured in the recursive relationship \( l_{i+1} = l_i + \sqrt{l_i^2 + 1} \). Assuming there are no leaves on the ground initially, how many leaves will there be after 10 steps? If you start with 5 leaves, how many leaves after 10 steps?

**WU-5** What is the frequency of oscillation of the wave in the figure below?

![Wave Figure](image.png)
Before you begin

Say "yes" when asked if you want to initialize!

1. Sequential reactions:
Comparing the exact analytical solution for a two step mechanism with solutions from two different numerical integration schemes
How to numerically integrate

Consider the following two step mechanism:

\[ A \rightarrow B \]
\[ B \rightarrow C \]

We can easily write down the differential rate expressions for each species in that appears in the mechanism:

\[ \frac{d[A]}{dt} = -k_1 [A] \]
\[ \frac{d[B]}{dt} = k_1 [A] - k_2 [B] \]
\[ \frac{d[C]}{dt} = k_2 [B] \]

We are now in a position to solve this system of partial differential equations to find how the concentration of A, B and C varies with time.
A. The analytical solution

Analytical expressions for \([A], [B]\) and \([C]\) as a function of time can be found that simultaneously satisfy all these differential equations. This set of differential equations can be solved exactly. The approach is covered in many physical chemistry books (see for example Atkins and de Paula, 7th edition, pp 883-884). The precise form of the solution depends on the boundary conditions specified and the values of the rate constants for the elementary steps. The boundary conditions for a chemical kinetics problem are generally set by specifying the initial concentrations of the various species. The analytical solutions given here (and in most introductory physical chemistry texts) for this mechanism are derived given that the initial concentration of \(A\) is \(A_o\) and that the initial concentrations of \(B\) and \(C\) are zero.

\[
A(t) = A_o e^{-k_1 t}
\]

\[
B(t) = \frac{k_1}{k_2 - k_1} (e^{-k_1 t} - e^{-k_2 t}) A_o
\]

\[
C(t) = A_o - B(t) - A(t)
\]

1. Given that \(A_o = 3.6\) M, and that \(k_1 = 1.2/\text{sec}\) and \(k_2 = 1.5/\text{sec}\) plot (on the same graph) the concentrations of \(A\), \(B\) and \(C\) as a function of time for 10 seconds. It will be convenient if you give the plot a name so that you can easily compare it to the graphs of the numerical solutions you will make shortly. Sketch the graph in your notebook, label each of the curves.

   [Hint: It is probably useful to plot this using different colors or types of lines and to have a legend, check the "Mathematica tidbits" section under "What you should know before you start" to see examples.]

B. A very simple numerical integrator

A simple straightforward algorithm for numerical integration can be constructed by assuming that if you consider a very small interval on the concentration versus time graph, the curve will appear linear.

1. Using the values we established in problem 1-1 for \(A_o\), \(k_1\) and \(k_2\), plot the \([A]\) as a function of time from \(t=1.8\) sec to \(t=2.0\) sec. Does the graph appear linear? What happens if you take a larger interval, say \(t=1.0\) to \(t=2.0\)? Does the graph still appear linear?

Now suppose I did not know the formula for \([A]\), but did have an expression for the slope \(\frac{d[A]}{dt} = -k_1 [A]\). I also know the initial value of the concentration. If I take a very short time step, the curve looks like a straight line and I can just use the slope of that line (given me by my rate expression) to find the next point. Let's take a time step of 0.2 seconds (we saw in question 1-2 that the graph appeared linear over a 0.2 second interval, so that seems a reasonable place to start).

\(A_o = 3.6\) M

The slope of the line at this point is

\[
\text{slope} = -k_1 [A] = -1.2/\text{sec} (3.6\text{ M}) = -4.32\text{ M/sec}
\]

so if I wanted to find \([A]\) 0.2 seconds later I could use as an estimate

\[A(0.2\text{ sec}) = A_o \text{ M} + \text{slope} \times \Delta t\]

\[
\ln[114]:= 3.6 \text{ M} + (-4.32 \text{ M/sec} \times 0.2 \text{ sec})
\]

\[\text{Out[114]} = 2.736 \text{ M}\]

1-3 How does this value compare with the analytical solution for the \([A]\) for \(t=0.2\) seconds?
\[ \text{In[115]} = A[0.2] \]
\[ \text{Out[115]} = 2.83186 \]

1-4 Use a shorter time step, say 0.02 seconds. Compute an estimate of the \([A]\) at this time, and compare it with the analytical value for the same time. Is this an improvement? Why do you think shortening the time step helps? Using this time step, how many calculations would you have to do to compute the concentration versus time curve for 10 seconds?

1-5 Using the estimate you calculated in 1-4 for the \([A]\) at 0.02 seconds, compute the next point on the curve (\([A]\) at 0.04 seconds. Remember that you need to recalculate the slope at the new point! How does it compare to the analytical value? Write the general recursion relationship for the \(i^{th}\) point along the curve. Using this recursion relationship plot your estimated graph for \([A]\) for a period of 10 seconds. Compare it to the analytical graph. Are you convinced you can use this very simple method to solve the differential equation for \([A]\)?

Hints: Use the Do function to generate a list of the points for 10 seconds. The Show command can put both graphs onto a single plot for comparison, the DisplayIdentity setting is used to suppress the plotting of the preliminary graphs on the screen (you really only want to see the combination). See the Mathematica tidbits heading in the Introduction for more information.
In[116]:= timestep = 0.05; TotalTime = 10;
(* create an empty matrix to hold the results as {t, [A]} points *)
Num = Table[{t, 0}, {t, 0, TotalTime, timestep}];
(* initialize the first point in the list with the initial concentration of A *)
Num[[1, 2]] = Ao;
Do[Num[[i, 2]] = Num[[i - 1, 2]] + timestep (-k1 Num[[i - 1, 2]]),
   {i, 2, Length[Num]}]
(* Use the DisplayFunction \[\rightarrow\] Identity to turn off the plots if you only want to see the final comparison *)
(* In order to see the points from the numerical solution on top of the analytical line, I've only plotted every 10th point that was computed in the numerical solution, that's what the Part[Num,Range....] bit does, to make it take fewer points, change 10 to a smaller number *)
NumPlot = ListPlot[Part[Num, Range[1, Length[Num], 10]],
   DisplayFunction \[\rightarrow\] Identity];
AnalPlot = Plot[A[t], {t, 0, 10}, DisplayFunction \[\rightarrow\] Identity];
(* Use the DisplayFunction \[\rightarrow\] $DisplayFunction to turn back on the display of plots *)
Show[NumPlot, AnalPlot, PlotRange \[\rightarrow\] {0, Ao},
   AxesLabel \[\rightarrow\] {"time", "concentration"}, DisplayFunction \[\rightarrow\] $DisplayFunction]

Out[122]= -Graphics-

1-6 What happens if you use a larger time step? Try using Δt=0.2 sec. To see more points plotted, change the value "10" in Part[Num,Range[1,Length[Num],10] to 2. Try various values for Δt, both larger and smaller than those already suggested. What can you conclude about the relationship between the accuracy of your results and the size of the time step? Is there any disadvantage to using a very small time step? How might you tell in a system where you didn't know the answer (the usual situation) what a suitable time step might be?
C. A more sophisticated numerical integrator: Runge-Kutta

In section B you discovered that you had to use a small time step (and lots of steps) because you needed the graph to be well approximated by a line over the periods of the time step. If you used a method that assumed the graph was curved, you might be able to use larger time steps, and thus have to compute fewer steps. Many more sophisticated methods use this approach, or a variant of it. One algorithm in wide-spread use is Runge-Kutta. There is no real advantage to using this method for the mechanism we are looking at here, but since this method is in such wide-spread use it is worthwhile knowing a little bit about it. See "Further Reading" for additional information on this method. This is the method used to look at the more complex chemical kinetics in the next section.

I’ve installed a function in the notebook to do the actual Runge-Kutta solution for you (if you’d like to look at it, it’s under the heading “Runge-Kutta package”). The command has the format \texttt{RK}\{expression for dA/dt, expression for dB/dt, expression for dC/dt...\},{a,b,c},{Ao,Bo,Co},{total,incr}\}

\{a,b,c\} are a set of variables that are used internally by the program, you need one for each species you have a rate expression for. (The \texttt{Block} command lets you use a,b and c “locally”, in other words, the values they are set to while the \texttt{RK} package runs do not spill over into the rest of the \texttt{Mathematica} notebook.)

\{Ao, Bo, Co\} are the initial values of [A], [B] and [C]

\texttt{TotalTime} is the total time to run the reaction

\texttt{Dt} is the timestep

\texttt{data} ends up being a list of the concentrations at each point in time, so the first point is data \{3.6, 0, 0\}, the initial concentrations of A, B and C

I take apart the data array to make it easier to plot in the same format as the analytical forms.

The example shown below is for the two step mechanism for which we considered the analytical solution in section 1A.

\[ A \rightarrow B \]
\[ B \rightarrow C \]

where the differential rate expressions are

\[ \frac{d[A]}{dt} = -k_1 [A] \]
\[ \frac{d[B]}{dt} = k_1 [A] - k_2 [B] \]
\[ \frac{d[C]}{dt} = k_2 [B] \]

1-7 Using the values we established in problem 1-1 for \( A_0, k_1 \) and \( k_2 \), use the Runge-Kutta method to integrate [A], [B] and [C] as a function of time for a total of 10 seconds. Choose a time step of 0.5 seconds. How accurate is RK at this time step compared to the simple integrator developed in section 1B? What do you think the advantage of using RK is?
\[\text{In[123]}=\]
\[
(* \text{here is the data} *)
\]
\[
\text{TotalTime} = 10 ;
\]
\[
\Delta t = 0.5 ;
\]
\[
A_0 = 3.6 ; B_0 = 0 ; C_0 = 0 ;
\]
\[
k_1 = 1.2 ;
\]
\[
k_2 = 1.5 ;
\]
\[
(* \text{do the RK integration} *)
\]
\[
data = \text{Block}\{\{a, b, c\},
\quad \text{RK}\{-k_1 a, k_1 a - k_2 b, k_2 b\},
\quad \{a, b, c\}, \{A_0, B_0, C_0\}, \{\text{TotalTime}, \Delta t\}\};
\]
\[
time = \text{Table}[i, \{i, 0, \text{TotalTime,} \Delta t\}] ;
\]
\[
(* \text{Plot the data} *)
\]
\[
\text{holding} = \text{Transpose[data] ;}
\]
\[
\text{holding}[[1]] ;
\]
\[
\text{Adata} = \text{Transpose}\{\{\text{time, holding[[1]]}\}\};
\]
\[
\text{Bdata} = \text{Transpose}\{\{\text{time, holding[[2]]}\}\};
\]
\[
\text{Cdata} = \text{Transpose}\{\{\text{time, holding[[3]]}\}\};
\]
\[
\text{SeqRxnRKSoln} = \text{MultipleListPlot}\{\text{Adata, Bdata, Cdata,}
\quad \text{SymbolStyle} \to \{\text{Hue}[0.1], \text{Hue}[0.6], \text{Hue}[0.9]\},
\quad \text{DisplayFunction} \to \text{Identity}\}
\]
\[
\text{SeqRxnAnalSoln} = \text{Plot}\{\{A[t], B[t], Cee[t]\}, \{t, 0, 10\},
\quad \text{PlotRange} \to \{0, 4\},
\quad \text{DisplayFunction} \to \text{Identity}\}
\]
\[
\text{Show}[\text{SeqRxnRKSoln, SeqRxnAnalSoln, AxesLabel} \to \{"time", "concentration"\},
\quad \text{DisplayFunction} \to \$\text{DisplayFunction}]
\]
\[
\text{Out[138]}= \quad \text{Graphics} -
\]
\[
\text{Plot::plnr} :
\quad B[t] \text{ is not a machine-size real number at } t = 4.1666666666666667 \times 10^{-7}. \text{ More…}
\]
\[
\text{Plot::plnr} :
\quad B[t] \text{ is not a machine-size real number at } t = 0.40566991572915795. \text{ More…}
\]
\[
\text{Plot::plnr} :
\quad B[t] \text{ is not a machine-size real number at } t = 0.8480879985937368. \text{ More…}
\]
\[
\text{General::stop} : \text{Further output of}
\quad \text{Plot::plnr will be suppressed during this calculation. More…}
\]
\[
\text{Out[139]}= \quad \text{Graphics} -
\]
\[
\text{out[140]}= \quad \text{Graphics} -
\]

Michelle M. Francl
Created: April 2000
Modified: June 2004
2. Some more complex reaction mechanisms: What happens when you can't derive an exact analytical solution? Exotic kinetics and autocatalysis

Now consider a more complex reaction, an 'equilibrium' followed by a single step. The rate equations for this mechanism cannot be solved analytically by direct integration as we did above, though we can make some approximations that make it easier to find an approximate analytical solution in this way. (See Further Reading under Revise and Refine if you are interested in how you might come up with an exact solution for this problem.) Applying a numerical approach, we can both get an accurate solution and gauge the quality of the approximate analytical solution. We are confident based on the work we did in sections 1B and 1C that the numerical solutions are as accurate as analytical ones -- as long as we have made the proper choice of a time step. This shows the power of the numerical approach: we can get accurate solutions to problems that cannot be solved in the way usually taught in physical chemistry. We can also develop a sense for how accurate the traditional approximations really are.

Here is a simple mechanism where the first step is an equilibrium between A and B:

\[
A \overset{k_f}{\rightarrow} B \\
B \overset{k_r}{\rightarrow} A \\
B \overset{k_3}{\rightarrow} Pr
\]

2-1 Write down the differential rate expressions for each of the three species.

■ A. Approximate analytical solution

Let's begin by assuming that we can apply the steady state approximation to the intermediate species B. This situation will arise when the forward reaction is rapid compared to the reverse reaction and to the step that forms product, i.e. when \( k_f \gg k_r, k_3 \).

2-2 Using the steady state approximation for the [B] in the mechanism given above, find an expression for [B] in terms of the 3 rate constants and [A].

2-3 Substitute the expression you derived for [B] in 2-2 into the differential rate equation for [A] you wrote down in 2-1. Derive an integrated rate expression for [A]. Substitute your expression for [A] as a function of time into what you derived for [B] in 2-2 to yield an expression for the [B] in terms of the three rate constants, the initial concentration of A and time. Finally, make use of the mass balance conditions (i.e. that \( [A]_o = [A] + [B] + [Pr] \)) to find an expression for the concentration of product as a function of time.

2-4 Using your results from 2-3, plot the concentrations of A, B and C as a function of time for 10 seconds. Use the conditions \( A_o = 3.7 \text{ M}; k_f = 120/\text{sec}; k_r = 500/\text{sec}; k_3 = 0.8/\text{sec} \). Sketch the result in your notebook. Is it apparent from this plot that the steady state approximation is appropriate? Explain.
B. Numerical solution

Following the procedures laid out in section 1C, we will use the Runge-Kutta method to compute accurate concentrations of A, B and C for the mechanism given in section 2A.

2-5 Using the Runge-Kutta method, and the following conditions, plot the concentrations of A, B and C for 10 seconds. \( A_o = 3.7 \text{ M}; \ B_o = C_o = 0 \text{ M}; \ k_f = 120/\text{sec}; \ k_r = 500/\text{sec}; \ k_3 = 0.8/\text{sec}. \) You might need to adjust the time step to get good results! Sketch the result in your notebook. Does it differ qualitatively from the plot in section 2-A? Based on this graph, do you still think the steady state approximation is a good one for this set of conditions?

2-6 What happens when the conditions are not such that a steady state of B is established. Using the Runge-Kutta method, and the following conditions, plot the concentrations of A, B and C for 20 seconds. \( A_o = 3.7 \text{ M}; \ B_o = C_o = 0 \text{ M}; \ k_f = 0.5/\text{sec}; \ k_r = 20.4/\text{sec}; \ k_3 = 0458/\text{sec}. \) Sketch the graph. What do you notice?

2-7 Compare the results for the [B] from 2-6 with those for the approximate analytical solution for the same conditions. Sketch the two in your notebook. How do the two compare? Is the approximation better earlier in the reaction or toward the end? What phenomenon does the approximate solution miss?

C. Oscillating Reactions: The Lotka-Volterra mechanism

So far the reactions we have considered have had "normal" kinetics. That is, the concentration of reactants falls off monotonically, while that of the product grows. Intermediate concentrations rise during an induction period, then also fall off smoothly as the reaction progresses. The Lotka-Volterra mechanism describes an autocatalytic reaction. Autocatalysis can result in exotic kinetic behaviors. This system illustrates the principles of these types of mechanisms well, though there are no known chemical examples of this particular mechanism. These differential equations are often used by biologists to describe predator prey relationships (on the large scale, such as mice and snakes, and on the smaller scale, such as hosts and parasites). Typical reaction conditions are such that \( [A] \) is constant. B is typically removed from the system, but since the differential rates don't depend on [B], this is immaterial to our solutions. For more information on related reactions see the references given in Reprise and Revise.

The proposed mechanism is:

\[
\begin{align*}
A + X & \xrightarrow{k_1} 2X \\
X + Y & \xrightarrow{k_2} 2Y \\
Y & \xrightarrow{k_3} B
\end{align*}
\]

If we want to understand how the concentrations of X and Y vary with time, we must use numerical techniques. We could apply the steady state approximation to X and Y, but all that would show is that X and Y are constant, which is definitely not the most interesting behavior exhibited by this reaction!

Modeling oscillatory reactions can help us untangle reactions ranging from those that control our heartbeat, to those that produce the stripes on a tiger.

2-8 Write down the differential rate expressions for X and Y.
2-9 Using the Runge-Kutta methods, integrate the Lotka-Volterra rate equations for X and Y for the following conditions: \( A_o = 3.0 \, \text{M} \), \( X_o = 0.8 \, \text{M} \), \( Y_o = 2.0 \, \text{M} \), \( k_1 = 1.0/\text{M-sec} \), \( k_2 = 1.5/\text{M-sec} \) and \( k_3 = 1.2/\text{sec} \). I’d suggest a time step of 0.01 seconds and a total reaction time of 5.0 seconds. Sketch the graph in your notebook. What conditions do these rate constants and initial concentrations lead to?

2-10 Vary the initial concentrations of X and Y very slightly and again use the Runge-Kutta method to integrate the Lotka-Volterra rate equations for X and Y. The conditions are: \( A_o = 3.0 \, \text{M} \), \( X_o = 0.9 \, \text{M} \), \( Y_o = 2.1 \, \text{M} \), \( k_1 = 1.0/\text{M-sec} \), \( k_2 = 1.5/\text{M-sec} \) and \( k_3 = 1.2/\text{sec} \). I’d suggest a time step of 0.01 seconds and a total reaction time of 20 seconds. Sketch the graph in your notebook. How has the behavior changed? Given the small changes in the concentrations, did you expect this?

2-11 You can increase the oscillatory behavior by changing the conditions. Try these values: \( A_o = 3.0 \, \text{M} \), \( X_o = 0.85 \, \text{M} \), \( Y_o = 3.2 \, \text{M} \), \( k_1 = 1.0/\text{M-sec} \), \( k_2 = 1.5/\text{M-sec} \) and \( k_3 = 1.2/\text{sec} \) or others of your own choosing.

2-12 Using the graph above, estimate the frequency with which the concentrations of X and Y change. Are they roughly the same? Why do you think this should be? It might help to think about what happens to predator populations when their prey starts to vanish as a result of an increase in the predator population.
Reprise and Revise

■ References and Further Reading

Physical Chemistry Background:


Atmospheric Chemistry:

Barbara J. Finlayson-Pitts and James N. Pitts, *Chemistry of the Upper and Lower Atmosphere*, Academic Press, 2000. A very detailed look at the chemistry of the atmosphere and the experimental methods used to study it. The introduction and sections on policy are very accessible to the beginning physical chemistry student, if you find the rest intriguing, contact UCIrvine for information about going to grad school there!

Mathematics/Mathematica:


MathBasics.nb, an introduction to Mathematica for my physical chemistry course. Available at www.brynmawr.edu/-Acads/Chem/mfranc1/PChemResources/

Exotic Kinetics:


A good film of a demonstration is at Oxford's site: http://www.chem.ox.ac.uk/vrchemistry/FilmStudio/oscillating/ -HTML/page03.htm

■ Test Yourself for Mastery

TY-1 The Belousov-Zhabotinsky reaction has an extremely complicated mechanism, even the simplified versions such as the Oregonator have many steps, so perhaps it isn't surprising that the kinetics can be so richly varied. Similarly,
oscillatory kinetics have been observed in biological systems, which are also very complex. Are complex mechanisms a necessary condition for complex kinetic behavior?

The two step autocatalytic mechanism given below was explored mathematically by Gray and Scott in the mid 1980s [see P.Gray and S.K. Scott, J.Phys.Chem. 1985, 89,22-32], and was based on a simple model for glycolysis (which had been observed to be oscillatory in the 1950s). The system is set up to be an open system (consider a cell, which is getting a continuous infusion of glucose), so the differential rate expressions need to include a term for the intake of both the substrate A and the catalyst B.

Gray-Scott mechanism:

\[ A + 2B \xrightarrow{k_1} 3B \]
\[ B \xrightarrow{k_2} C \]

(a) Write down the differential rate expressions for the [A] and [B] given Gray-Scott mechanism assuming a closed system, that is assume that no A or B is being added to the system as the reaction progresses. (Despite how I've stated it, this is easy. The assumption of a closed system is the one you usually make in chemical kinetics, it's just generally unstated!)

(b) The differential rate expressions for the open system are

\[ \frac{d[A]}{dt} = -k_1[A][B]^2 + k_f([A]_o - [A]) \]
\[ \frac{d[B]}{dt} = k_1[A][B]^2 - k_2[B] + k_f([B]_o - [B]) \]

Compare these to what you found in (a) to find the terms describing the flow. Are both A and B assumed to be flowing in at the same rate? What are the units on \( k_f \) ?

(c) Numerically integrate the differential equations given in (b) for the three sets of conditions given below and plot the [A] and [B] as a function of time. Sketch each of the graphs. What do you notice? In their article, Gray and Scott wrote that "it does not need a complicated pattern of auxiliary reactions to generate very exotic behavior indeed, despite much folklore to the contrary." Do you agree with them?

(i) \( A_o = 1; B_o = 0.075 \); \( C_o = 0 \); \( k_1 = 1 \); \( k_2 = 0.05 \); \( k_f = 1/5 \); total time 100 units
(ii) \( A_o = 1; B_o = 0.075 \); \( C_o = 0 \); \( k_1 = 1 \); \( k_2 = 0.05 \); \( k_f = 1/40 \); total time 500 units
(iii) \( A_o = 1; B_o = 0.075 \); \( C_o = 0 \); \( k_1 = 1 \); \( k_2 = 0.05 \); \( k_f = 1/60 \); total time 500 units

(d) Can you find other conditions that lead to further "exotic behavior", such as kinetics that oscillate for longer periods of time? Can you find conditions where the [A] and [B] behave chaotically? Try to think about the competing processes and see if you can make educated guesses about the behaviors. Consider reading the paper by Gray and Scott. It is at a level a physical chemistry student could read, though it will take time and it would be helpful to have this notebook so you can work along with the authors.

TY-2 What are the advantages of using numerical integration? When might you choose to look at a reaction using numerical techniques? What are the potential challenges?
Culture of Chemistry

■ It's all spheres in motion: Chlorine Atoms and Baseballs

F. Sherwood Rowland playing for University of Chicago, used with permission.

F. Sherwood Rowland won the Nobel prize in Chemistry in 1995 for his work on chlorofluorocarbons and ozone in the upper atmosphere. Prof. Rowland got his Ph.D. at the University of Chicago in 1952 working under Willard Libby (who also won the Nobel prize, in 1960 for C-14 dating). While at Chicago Rowland evinced a clear interest in many areas of kinetics, both inside and outside the lab. He played basketball and baseball for the University of Chicago's team and spent two summers with a semi-pro baseball team in Canada. When I was a graduate student in the 1980s, Rowland played with our intramural softball team, his speed around the bases might not have equaled his performance playing semi-pro ball, but he hit the ball so far, it never mattered! He was also the author of the exam referred to in the introduction to this workbook.

For more information on Rowland's work see:

http://magazine.uchicago.edu/9708/9708FeatRowland.html

The Inner Workings

Runge-Kutta package

Copyright Notice

Copyright 1989 by Roman Maeder.

Adapted from Roman E. Maeder: Programming in Mathematica, Addison-Wesley, 1989.

Permission is hereby granted to make copies of this file for any purpose other than direct profit, or as part of a commercial product, provided this copyright notice is left intact. Sale, other than for the cost of media, is prohibited.

Permission is hereby granted to reproduce part or all of this file provided that the source is acknowledged.

Implementation

In[141]= BeginPackage["RMPackages`RK`"]

Out[141]= RMPackages`RK`

In[142]= RK::usage = "RK[{e1,e2,..}, {y1,y2,..}, {a1,a2,..}, {t1, dt}] numerically integrates the ei as functions of the yi with initial values ai.

The integration proceeds in steps of dt from 0 to t1.
RungeKutta[{e1,e2,..}, {y1,y2,..}, {a1,a2,..}, {t, t0, t1, dt}] integrates
a time-dependent system from t0 to t1."

Out[142]= RK::shdw : Symbol RK appears in multiple contexts {RMPackages`RK`, Global`}; definitions in context RMPackages`RK` may shadow or be shadowed by other definitions. More...

In[143]= Begin["`Private`"]

Out[143]= RMPackages`RK`Private`
\textbf{In[144]} := \texttt{RKStep[f_, y_, y0_, dt_]} :=
\begin{verbatim}
    Block[{k1, k2, k3, k4},
        k1 = dt \texttt{N[f /. Thread[y \rightarrow y0]]};
        k2 = dt \texttt{N[f /. Thread[y \rightarrow y0 + k1/2]]};
        k3 = dt \texttt{N[f /. Thread[y \rightarrow y0 + k2/2]]};
        k4 = dt \texttt{N[f /. Thread[y \rightarrow y0 + k3]]};
        y0 + (k1 + 2 k2 + 2 k3 + k4)/6
    ]
\end{verbatim}
\textbf{In[145]} := \texttt{RK[f_List, y_List, y0_List, \{t1_, dt\}]} :=
\begin{verbatim}
    \texttt{NestList[RKStep[f, y, #, \texttt{N}\texttt{[dt]}]&, \texttt{N}\texttt{[y0]}, \texttt{Round}\texttt{[N[t1/dt]]}]} /;
    \texttt{Length[f] == Length[y] == Length[y0]}
\end{verbatim}
\textbf{In[146]} := \texttt{RK[f_List, y_List, y0_List, \{t_, t0_, t1_, dt\}]} :=
\begin{verbatim}
    \texttt{Block[\{res\},
        res = RK[Append[f, 1], Append[y, t], Append[y0, t0], \{t1 - t0, dt\}]
    ];
    \texttt{Drop[\#, -1] \& /\@ res}
    ] /; \texttt{Length[f] == Length[y] == Length[y0]}
\end{verbatim}
\textbf{In[147]} := \texttt{End[]}
\texttt{Out[147] := \texttt{RMPackages`RK`Private`}}
\textbf{In[148]} := \texttt{Protect[RK]}
\texttt{Out[148] := \{RK\}}
\textbf{In[149]} := \texttt{EndPackage[]}
Notes to the instructor

Using these materials

I've attempted to set the material in this exercise in a broad chemical context in three ways: through two mastery exercises that are linked to actual problems, with a "Culture of Chemistry" piece on F. Sherwood Rowland, and by an introduction that keys students to the applications of the techniques presented. There is some evidence to show that context-rich curricula, which embed new material in a wide context and/or which provide students multiple entry points into a subject, result in increased student interest as well as improved performance. In this vein, I have included some references to the primary literature for interested students to pursue, suggested links to other courses students might be enrolled in, provided a "culture of chemistry" section, and created a problem which draws on the primary literature. I have been surveying my students in the past few years about these strategies. Students report that they enjoy the "Culture of Chemistry" pieces, and say that reading them often gets them more interested, not only in the general subject area, but in solving the problems! Students also note that the engagement with the primary literature is a motivating factor, to see that physical chemistry is not just something to be survived, but is part of a broader scaffold that impinges on many areas of chemistry and science. I am currently working on an NSF funded project to develop context-rich auxiliary materials for physical chemistry and to assess their impact on student interest and performance. More information on this project can be found at http://www.brynmawr.edu/Acads/Chem/NSFpchem/. A description of a literature exercise linked to this Mathematica notebook can be found at http://www.brynmawr.edu/Acads/Chem/NSFpchem/exotic.html; the exercise itself (as PDF) is at http://www.brynmawr.edu/Acads/Chem/NSFpchem/DraftModules.html.

I've used the notebook as the basis for a lecture, then had students follow-up by completing the exercises embedded in the notebook. I've also used the notebook in lieu of lecture, and followed-up with a brief discussion that hit the points I most wanted them to retain (see Objectives). I always have students hand write the answers to the questions in their class notebooks, and sketch the graphs they get. Engaging their kinetic sense by sketching the graphs seems particularly helpful, and students who do this rather than just look at the graphs on the screen appear to have better retention of the information. To help overcome the resistance of the "I don't have graph paper" or "I'm not a very good artist", I provide a PDF of graph paper on the course web site (see http://www.mathematicahelpcentral.com/graph_paper.htm for a nice assortment) and point out that while art is not my forte either, I do draw things on the board and they do understand what I'm saying, the point being to learn to communicate effectively in this way! Students have done the BZ reaction in class as a demonstration, they have also taken the demo on the road to their differential equations course, which was studying numerical solutions. If you do the demonstration in class, consider making a video of it and sharing it with your colleagues in general chemistry or mathematics.

The notebook as it appears here is what I would use with my students as an in class exercise, in lieu of lecture. Most of the Mathematica commands are not included (to reduce the opportunity for inducing the "hit enter" trance). I have included the codes for the numerical integration schemes where they first occur. I expect and encourage students to use the cut, paste and edit technique to complete the notebook. I generally follow up by posting a completed notebook for them to review. I either produce a set of notes entitled "important things to know from..." or spend 10 minutes in lecture getting them to give me the highlights of what they've done (easy in the classroom I teach in where I can pull up any screen on the main projector) to help them return to the forest from the trees. You might want to include more of the skeleton for them to use, or less, as the skill level of your class indicates.

I have a solution for the "mastery exercises" if you want them! Just send me an e-mail.

If you are pressed for time (aren't we all?), you could skip the section on how numerical integrators work, as well as the one on Lotka-Volterra kinetics and still give students a viable introduction to the use of numerical integration methods in chemical kinetics. The "test for mastery" problem assumes only knowledge from those sections (1A and C; 2A and B).

As always, I would appreciate comments, corrections, clarifications, which can be sent to nfrancl@brynmawr.edu.
Software information

This notebook was created using Mathematica v. 5.0.0.0 on a Macintosh running Mac OS 10.3.