Chemical kinetics in well-mixed reactors*

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1 Material Balance for the well-mixed, batch reactor

The batch reactor is assumed to be well stirred, so there are no concentration gradients anywhere in the reactor volume. In this case it is natural to consider the entire reactor contents to be the reactor volume element as in Figure 1, and $V = V_R$.

The statement of conservation of moles for component j is

$$\frac{d\left(c_j V_R\right)}{dt} = R_j V_R \qquad (1)$$

Equation 1 applies whether the reactor volume is constant or changes during the course of the reaction. If the reactor volume is constant, which is sometimes a good approximation for liquid-phase reactions, V_R can be divided out of both sides of Equation 1 to give

$$\frac{dc_j}{dt} = R_j \qquad (2)$$

Be sure to use Equation 1 rather than Equation 2 if the reactor volume changes significantly during the course of the reaction.

Figure 1: Batch reactor volume element.

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*Parts of these notes are taken from Rawlings and Ekerdt (2012)

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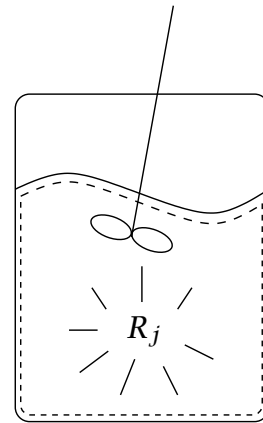
1.1 Analytical Solutions for Simple Rate Laws

In complex and realistic situations, the material balance for the batch reactor must be solved numerically. However, if the reactor is isothermal, and the rate laws are assumed to be quite simple, then analytical solutions of the material balance are possible. Analytical solutions are valuable for at least two reasons. First, due to the closed form of the solution, analytical solutions provide insight that is difficult to achieve with numerical solutions. The effect of parameter values on the solution is usually more transparent, and the careful study of analytical solutions can often provide insight that is hard to extract from numerical computations. Secondly, even if one must compute a numerical solution for a problem of interest, the solution procedure should be checked for errors by comparison to known solutions. Comparing a numerical solution procedure to an analytical solution for a simplified problem provides some assurance that the numerical procedure has been constructed correctly. Then the verified numerical procedure can be used with more assurance on the full problem for which no other solution is available.

The next several sections derive analytical solutions for some simple rate laws. Of course, the batch reactor is assumed to be operating at constant temperature in this discussion.

First-order, irreversible. Consider the first-order, irreversible reaction

$$A \xrightarrow{k} B \tag{3}$$

in which the reaction rate is given by $r = kc_A$. The units of the first-order rate constant are $(\text{time})^{-1}$. Application of the material balance for a constant-volume reactor gives the following differential equation

$$\frac{dc_A}{dt} = -kc_A \tag{4}$$

in which the negative sign arises because the production rate of A is $R_A = -r$ due to the stoichiometry of the reaction. Equation 4 requires an initial condition to have a unique solution. We denote the initial concentration of A in the reactor as c_{A0},

$$c_A(t) = c_{A0}, \qquad t = 0$$

The solution to the differential equation with this boundary condition is

$$c_A = c_{A0}e^{-kt} \tag{5}$$

which is plotted in Figure 2 for several values of the rate constant k. Because the reaction is irreversible, the A concentration decreases exponentially from its initial value to zero with increasing time. The rate constant determines the shape of this exponential decrease. Rearranging Equation 5 and taking logarithms gives
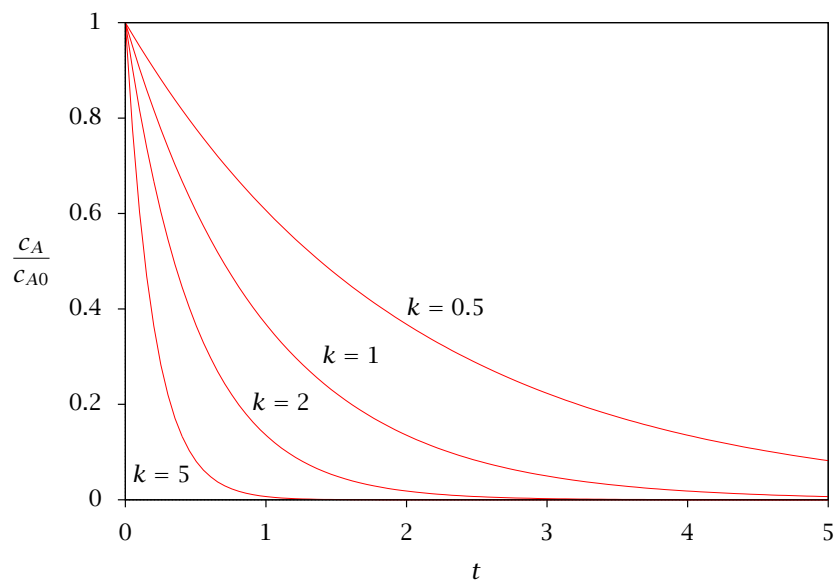
$$\ln(c_A/c_{A0}) = -kt$$

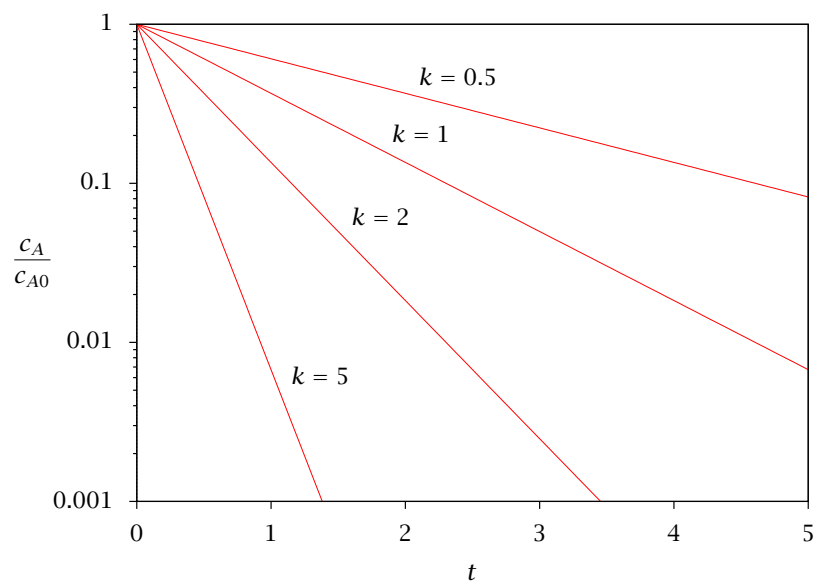Figure 2: First-order, irreversible kinetics in a batch reactor.

Figure 3: First-order, irreversible kinetics in a batch reactor, log scale.

3

which is plotted by using a log scale in Figure 3. Notice one can get an approximate value of the rate constant by calculating the slope of the straight line given by $\ln(c_A/c_{A0})$ versus t. This procedure is sometimes recommended as a way to determine rate constants for first-order reactions by plotting experimental concentration data and determining this slope. As will be discussed later this procedure is a poor way to determine a rate constant and should be viewed only as a rough approximation.

The B concentration is easily determined from the A concentration. One could write down the material balance for component B,

$$\frac{dc_B}{dt} = R_B = kc_A \tag{6}$$

and solve this differential equation with the initial condition for B, $c_B(0) = c_{B0}$, after substituting the known solution for $c_A(t)$. It is simpler to note, however, that the sum of concentrations A and B is a constant. Adding Equations 4 and 6 gives

$$\frac{d(c_A + c_B)}{dt} = R_A + R_B = 0$$

Therefore, $c_A + c_B$ is a constant and independent of time. The value of this constant is known at $t = 0$,

$$c_A + c_B = c_{A0} + c_{B0}$$

which can be rearranged for the B concentration,

$$c_B = c_{A0} + c_{B0} - c_A \tag{7}$$

First-order, reversible. Consider now the same first-order reaction, but assume it is reversible

$$A \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} B \tag{8}$$

and the reaction rate is $r = k_1 c_A - k_{-1} c_B$. The material balances for A and B are now

$$\frac{dc_A}{dt} = -r = -k_1 c_A + k_{-1} c_B$$
$$\frac{dc_B}{dt} = r \quad = k_1 c_A - k_{-1} c_B$$

with the same initial condition $c_A(0) = c_{A0}$, $c_B(0) = c_{B0}$. Notice that $c_A + c_B$ remains constant, so c_B can be computed from Equation 7. Substituting Equation 7 into the material balance for A gives

$$\frac{dc_A}{dt} = -k_1 c_A + k_{-1}(c_{A0} + c_{B0} - c_A)$$

which can be rearranged into

$$\frac{dc_A}{dt} + (k_1 + k_{-1})c_A = k_{-1}(c_{A0} + c_{B0}) \tag{9}$$

Equation 9 is a nonhomogeneous, linear differential equation. The solution can be written as the sum of what is called the particular solution and the solution to the homogeneous equation Boyce and DiPrima (1997). One particular solution to the equation is the constant solution

$$c_{Ap} = \frac{k_{-1}}{k_1 + k_{-1}}(c_{A0} + c_{B0})$$

You should substitute this back into Equation 9 to check that it is indeed a solution. The homogeneous equation refers to the differential equation with a zero forcing term on the right-hand side,

$$\frac{dc_{Ah}}{dt} + (k_1 + k_{-1})c_{Ah} = 0$$

The solution to this equation already has appeared in the previous section, $c_{Ah} = a \exp(-(k_1+k_{-1})t)$, in which a is an arbitrary constant to be determined from the initial condition. The full solution to Equation 9 is then $c_A = c_{Ah} + c_{Ap}$,

$$c_A = ae^{-(k_1+k_{-1})t} + \frac{k_{-1}}{k_1 + k_{-1}}(c_{A0} + c_{B0}) \tag{10}$$

The constant a is now determined from the initial condition. Writing Equation 10 for $t = 0$ gives

$$c_{A0} = a + \frac{k_{-1}}{k_1 + k_{-1}}(c_{A0} + c_{B0})$$

Solving this equation for a yields

$$a = c_{A0} - \frac{k_{-1}}{k_1 + k_{-1}}(c_{A0} + c_{B0})$$

Substituting in this value of a into Equation 10 and rearranging terms gives the final solution

$$c_A = c_{A0}e^{-(k_1+k_{-1})t} + \frac{k_{-1}}{k_1 + k_{-1}}(c_{A0} + c_{B0})\left[1 - e^{-(k_1+k_{-1})t}\right] \tag{11}$$

The B concentration can be determined by substituting Equation 7 into 11 and rearranging, or more simply, by switching the roles of A and B and k_1 and k_{-1} in Reaction 8, yielding

$$c_B = c_{B0}e^{-(k_1+k_{-1})t} + \frac{k_1}{k_1 + k_{-1}}(c_{A0} + c_{B0})\left[1 - e^{-(k_1+k_{-1})t}\right] \tag{12}$$

Equations 11 and 12 are plotted in Figure 4. Notice that with the reversible reaction, the concentration of A does not go to zero as in the irreversible case, but goes to a nonzero steady-state value. We next calculate the values of the steady-state concentrations. Taking the limit $t \longrightarrow \infty$ in Equation 11 gives

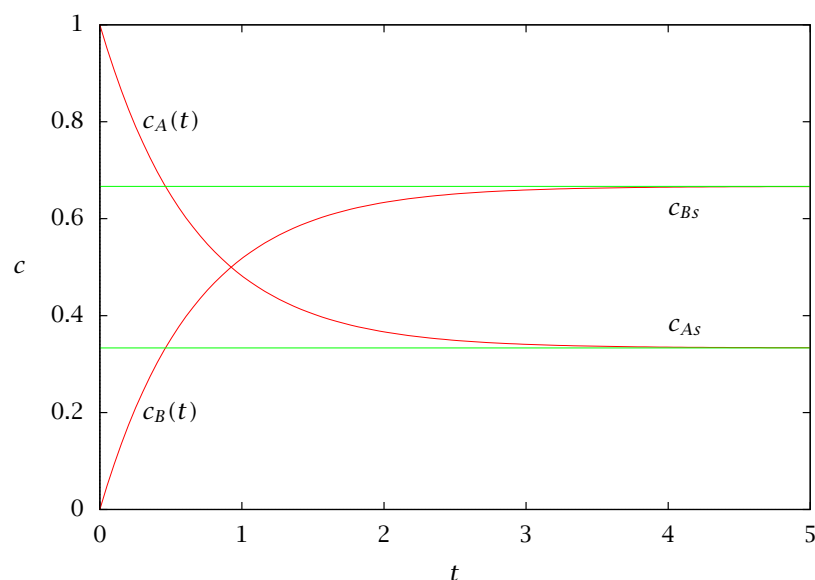$$c_{As} = \frac{k_{-1}}{k_1 + k_{-1}}(c_{A0} + c_{B0})$$

Figure 4: First-order, reversible kinetics in a batch reactor, $k_1 = 1$, $k_{-1} = 0.5$, $c_{A0} = 1$, $c_{B0} = 0$.

in which c_{As} is the steady-state concentration of A. Defining $K_1 = k_1/k_{-1}$ allows us to rewrite this as

$$c_{As} = \frac{1}{1 + K_1}(c_{A0} + c_{B0})$$

Performing the same calculation for c_B gives

$$c_{Bs} = \frac{K_1}{1 + K_1}(c_{A0} + c_{B0})$$

These results are shown in Figure 4 for $K_1 = 1/0.5 = 2$ and $c_{A0} = 1$, $c_{B0} = 0$. Notice that because K_1 is larger than 1, the forward reaction is favored and the steady state favors the product B, $c_{Bs} = 2/3$, $c_{As} = 1/3$. For small K_1 values, the steady state would favor the reactant A.

Example 1: Radioactive Decay[1]

Radium was used in the formation of phosphorescent watch faces. The radium decays according to the scheme (half lives are shown):

$$_{88}\text{Ra}^{226}(1620\text{years}) \longrightarrow {}_{86}\text{Rn}^{222}(3.83\text{days}) + {}_{2}\text{He}^{4} \tag{13}$$
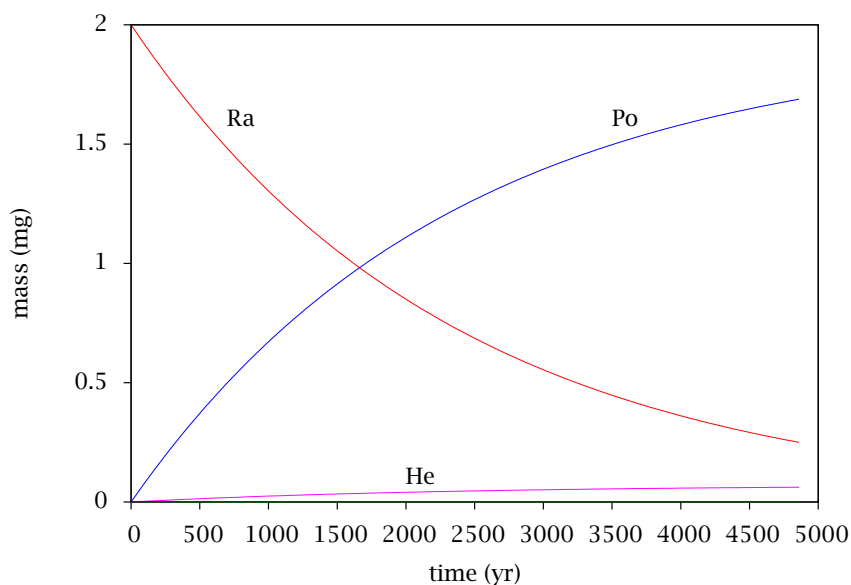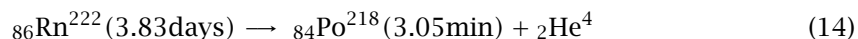
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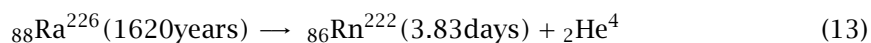
[1]Example suggested by T.F. Kuech

Figure 5: Concentrations of species in Reactions 13–14 versus time.

The alpha particle, $_2$He^4, which is a doubly ionized He atom, hits a phosphor which then emits light. The radon, $_{86}$Rn^{222}, has a half life of only 3.83 days. It will also decay through the reaction:

$$_{86}\text{Rn}^{222}(3.83\text{days}) \longrightarrow \; _{84}\text{Po}^{218}(3.05\text{min}) + \, _2\text{He}^4 \tag{14}$$

Note that Po^{218} further decays to radioactive isotopes of Pb, Bi and other isotopes of Po before finally decaying to stable Pb. We will ignore these further steps in this example.

Assuming no Po and Rn were present in the initial 2 milligram sample of Ra, what is the mass of $_{84}$Po^{218} and $_{86}$Rn^{222} present as a function of time? Plot the mass of $_{84}$Po^{218} and $_{86}$Rn^{222} as a function of time.

Solution

First we convert the 1/2 lives of the two reactants to first-order rate constants with consistent time units using the formula $k = \ln 2 / t_{1/2}$, which gives

$$
\begin{aligned}
k_1 &= \frac{\ln 2}{1620 \text{ yr}} & &= 4.28 \times 10^{-4} \text{ yr}^{-1} \\
k_2 &= \frac{\ln 2}{3.83 \text{ day}} \, \frac{365 \text{ day}}{1 \text{ yr}} & &= 66.1 \text{ yr}^{-1}
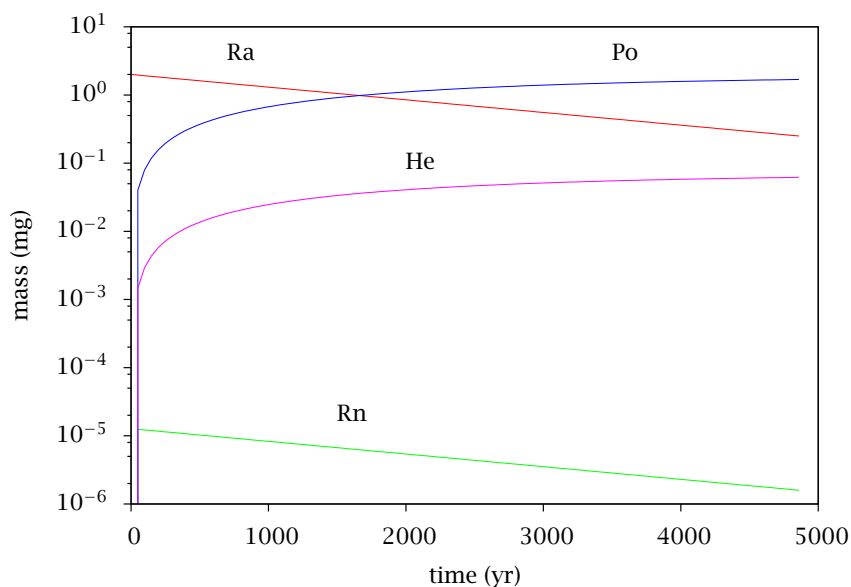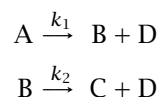\end{aligned}
$$

Figure 6: Concentrations (log scale) versus time

We can summarize the two reactions as

$$A \xrightarrow{k_1} B + D$$
$$B \xrightarrow{k_2} C + D$$

Notice the two rate constants have quite different magnitudes. If we assume the reactions take place in a well-mixed environment and neglect transport of the species away from the sources, the mass balances for all species are

$$\frac{dc_A}{dt} = -r_1 \qquad = -k_1 c_A$$
$$\frac{dc_B}{dt} = r_1 - r_2 \quad = k_1 c_A - k_2 c_B$$
$$\frac{dc_C}{dt} = r_2 \qquad = k_2 c_B$$
$$\frac{dc_D}{dt} = r_1 + r_2 \quad = k_1 c_A + k_2 c_B$$

Since the problem asks for the *mass* of each component in the sample, we multiply the solution in molar concentration by the molecular weights of each species.
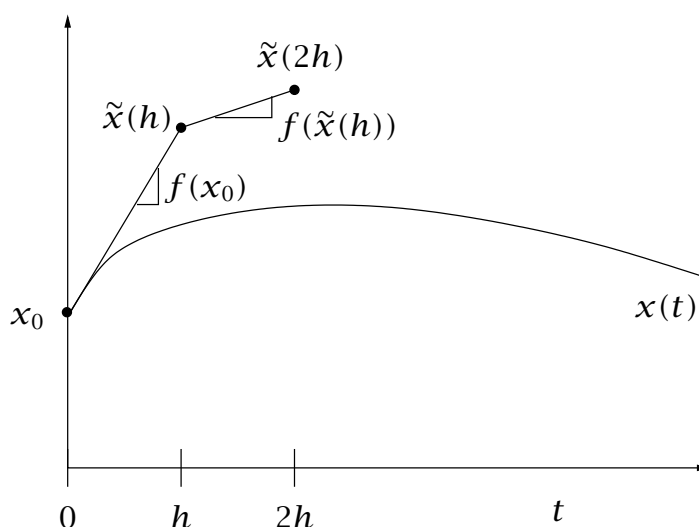
Figure 7: Depiction of the explicit Euler method for solving ordinary differential equation $dx/dt = f(x)$ with initial condition $x(0) = x_0$.

You can solve this problem analytically because the differential equations are *linear*. But we compute a numerical solution so the solution method still applies when we change the reactions to something besides linear, first-order reactions.

The results are shown in Figures 5–6. Notice Figure 6 uses a log-scale on the y-axis to show the low mass concentration of Rn. Exercise 5 asks you to think about why the Rn concentration is so low in this set of two reactions.

<div align="right">□</div>

2   Numerical Solution for Complex Rate Laws

2.1   Explicit Euler Method

We first construct our own simple ODE solver so that you have a basic understanding of what modern numerical ODE solvers are doing. Say we wish to solve the following differential equation numerically.

$$\frac{dx}{dt} = f(x)$$
$$x(0) = x_0$$

The simplest scheme for solving this equation is the Euler method. In the Euler method we partition the time axis into small increments of size h, known as the stepsize. We

then make a very simple approximation. We assume that over a small enough stepsize, the function $f(x)$ does not change significantly. We approximate it with the value at the beginning of the time interval. Then we project across the time interval using the constant slope approximation for dx/dt. This idea is illustrated in Figure 7. To start the procedure, we know the value of x at time $t = 0$, $x(0) = x_0$. So our approximate solution $\tilde{x}$ at time $t = h$ is given by

$$\tilde{x}(h) = x_0 + hf(x_0)$$

Now we have the approximate solution at time $t = h$, and we repeat the procedure to obtain

$$\tilde{x}(2h) = \tilde{x}(h) + hf(\tilde{x}(h))$$

We continue in this fashion until we have marched the solution across the entire time interval of interest. We summarize the procedure as follows

$$
\begin{aligned}
\tilde{x}(0) &= x_0 \\
\tilde{x}(h) &= x_0 &&+ hf(x_0) \\
\tilde{x}(2h) &= \tilde{x}(h) &&+ hf(\tilde{x}(h)) \\
\tilde{x}(3h) &= \tilde{x}(2h) &&+ hf(\tilde{x}(2h)) \\
&\cdots \quad \cdots &&\cdots \\
\tilde{x}((n+1)h) &= \tilde{x}(nh) &&+ hf(\tilde{x}(nh))
\end{aligned}
\tag{15}
$$

Notice that this approximate numerical solution is *recursive* in that each $\tilde{x}((n+1)h)$ depends only on $\tilde{x}(nh)$. That means we can write an efficient loop for implementing this scheme. The following code performs this loop for `nsteps`.

```
tout = (0:nsteps)'*h;
x = zeros(nsteps+1, numel(x0));
%force x0 to be a row vector
x(1,:) = x0(:)';
for i = 1: nsteps
  t = i*h;
  fval = f(t, x(i,:));
%force evaluated function to be a row vector
  frow = fval(:)';
  x(i+1,:) = x(i,:) + frow*h;
end
```

The command `plot(tout, x)` should give a plot of the resulting approximate numerical solution using Euler's method.

2.2 MATLAB's ODE Solvers

Although useful for illustration, the Euler method is unable to cope with many of the issues that arise in solving complex, large-dimensional ODEs. Languages such as MATLAB and

Octave have much better built-in ODE solvers available. We recommend `ode15s` as a general purpose ODE solver. Try `help ode15s` for more information about MATLAB's ODE solvers.

Exercise 2 provides an introduction into using `ode15s` for solving ODEs. If you click on the figure caption of Figure 5, your browser should open a window with the code that produced this figure. This code and Exercise 2 should lead you through how to use `ode15s` to solve a set of nonlinear differential equations.

Solving ODEs remains an active research area in scientific computing although the current methods are highly developed. The interested reader may wish to consult Brenan, Campbell, and Petzold (1989) for more information on these methods.

Notation

A	heat transfer area
c_j	concentration of species j
c_{jf}	feed concentration of species j
c_{js}	steady-state concentration of species j
c_{j0}	initial concentration of species j
$\hat{C}_P$	constant-pressure heat capacity per mass
E	activation energy (divided by the gas constant)
k_i	reaction rate constant for reaction i
k_m	reaction rate constant evaluated at mean temperature T_m
K_i	equilibrium constant for reaction i
M_j	molecular weight of species j
n	reaction order
n_j	moles of species j, $V_R c_j$
n_r	number of reactions in the reaction network
n_s	number of species in the reaction network
P	pressure
Q	volumetric flowrate
Q_f	feed volumetric flowrate
Q	volumetric flowrate
Q_f	feed volumetric flowrate
$\dot{Q}$	heat transfer rate to reactor, usually modeled as $\dot{Q} = U^o A(T_a - T)$
r_i	reaction rate for ith reaction
r_{tot}	total reaction rate, $\sum_i r_i$
R	gas constant
R_j	production rate for jth species
t	time
T	temperature
T_a	temperature of heat transfer medium
T_m	mean temperature at which k is evaluated

U^o overall heat transfer coefficient
V reactor volume variable
V_R reactor volume
x_j molar conversion of species j
ε_i extent of reaction i
ν_{ij} stoichiometric coefficient for species j in reaction i
ρ mass density
τ reactor residence time, V_R/Q_f

3   Exercises

Exercise 1: Passing arguments to a function with the `global` statement

Often we use functions with input arguments, but we require other parameters to evaluate the function. These parameters do not appear in the input argument list. For example in solving ODEs

$$\frac{dx}{dt} = f(x)$$

If we call the right-hand side function f, the call to the ODE solver looks like

```
[tout, x] = ode15s (@f, time, x0)
```

Now the function f has been assumed to have input arguments corresponding to x and t, so f's first line will look like

```
function dcadt = f(t, x)
```

But assume this problem is a first-order irreversible reaction so $x = c_A$ and the differential equation of interest is

$$\frac{dc_A}{dt} = -kc_A$$

Obviously the right-hand side function requires c_A, which is passed in as the variable x, but it also requires the rate constant k, which is not passed to the function. In this case we use a global statement. In the script that calls the ODE solver, we declare k to be global and assign it a value. Then in the function f, we also declare k to be global. Then we have access to it inside the function. The first two lines of the function then look like

```
function dcadt = f(t, x)
global k
```

To make sure you understand the idea, write a function `firstorder` that takes the concentration c_A and time t as the two arguments and returns dc_A/dt for the first-order irreversible reaction. Call this function from a script called `call_firstorder.m` for the

following values of c_A and k

$$c_A = 1 \quad k = 1$$
$$c_A = 0 \quad k = 1$$
$$c_A = 1 \quad k = 0$$
$$c_A = 2 \quad k = 3$$

Check that the function `firstorder` returns the correct values for dc_A/dt.

Exercise 2: Solving ordinary differential equations (ODEs) in MATLAB

Look at the code for Figure 5 as a guide to solving differential equations with MATLAB. The call to the ODE solver `ode15s` is the following line:

       `[tout, x] = ode15s (@rates, time, x0);`

in which `ode15s` is the name of the ODE solver, `rates` is the name of a user-supplied function, `time` is the vector of times at which output is requested and `x0` is the vector of initial conditions. The @ prepended to the function name `rates` in the call to `ode15s` signifies that `rates` is a user-supplied function. The return arguments are `tout`, the vector of times at which the solution was computed[2], and `x`, the vector of states at the times `tout`. The output is arranged conveniently for plotting the states versus time by the command

       `plot(tout, x)`

(a) Write an external function defining the right-hand side of the ODEs for the first-order irreversible reaction and plot the numerical solution determined by `ode15s`. Use parameter values

$$k = 1 \text{ s}^{-1} \quad c_{A0} = 1 \text{ mol/L}$$

(b) Also plot the analytical solution given in Equation 5. How well do the numerical and analytical solutions compare?

Exercise 3: Second-order, irreversible reaction

Consider the irreversible reaction

$$A \xrightarrow{k} B$$
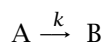
in which the rate expression is second order, $r = kc_A^2$. The units of the second-order rate constant are $(vol/mol)(time)^{-1}$. The material balance and initial condition are

$$\frac{dc_A}{dt} = -kc_A^2, \qquad c_A(0) = c_{A0}$$

---

[2]Often the output times in `tout` are the same as the requested times in `time`, but these may not be the same if the ODE solver experiences numerical difficulties solving the ODEs.

Find the analytical solution to this differential equation. Plot this solution and the first-order solution for $c_{A0} = 1$ mol/L and $k = 1$ min^{-1} for the first-order reaction and $k = 1$ L/(mol min) for the second-order rate constant.

Exercise 4: More ODE solving in MATLAB

Consider again the second-order, irreversible reaction taking place in a well-stirred batch reactor

$$\text{A} \xrightarrow{k} \text{B} \qquad r = kc_A^2$$

Compute the solution numerically using MATLAB's ode15s program for the parameter values given in Exercise 3. Compare the numerical and analytical solutions. Plot the relative error in the two solutions versus time. Relative error is defined as

$$e(t) = \frac{x(t) - \tilde{x}(t)}{x(t)}$$

in which $x(t)$ is the true solution and $\tilde{x}(t)$ is the approximate numerical solution.

Exercise 5: Radioactive decay with fast intermediate species

Consider again the radioactive decay reactions in Example 1. Examine the species concentrations depicted Figures 5–6, and the magnitudes of the rate constants and provide responses to the following questions and statements.

(a) What single reaction do you suppose can accurately represent the complete model with two reactions? (hint: think about the quasi-steady-state assumption)

(b) Solve the mass balances for this single reaction and plot the concentrations of radium, radon, polonium and alpha particles versus time. Compare your solution for this single reaction model to the results for the two-reaction case displayed Figures 5–6. Comment on any differences between the two solutions.

Exercise 6: Writing your own simple ODE solver: Euler's method

In this exercise, you are asked to write your your own ODE solver using the Euler method. Let's provide your ODE solver by defining the following function

```
function [tout, x] = euler (@oderhs, nsteps, h, x0)
```

in which oderhs is the name of the function that defines the right-hand side, nsteps is the number of time steps, h is the step size in the Euler method, and x0 is the initial condition. The function returns tout, the vector of times at which the solution was computed and x, a matrix in which the ith row is the solution vector x at the ith time in vector tout. We solve the ODEs by calling euler, much like we called the MATLAB solver ode15s.

Use the same form for the user-provided right-hand side function `oderhs` as used by `ode15s`; that is assume the ODE is of the form

$$\frac{dx}{dt} = f(t, x) \qquad \texttt{function\quad retval = oderhs(t, x)}$$

(a) Write function `euler` to implement Equations 15 defining the explicit Euler method.

(b) Test your ODE solver by calling it for a first-order, irreversible reaction with rate constant and initial condition parameters given in Exercise 2. Use the following step sizes
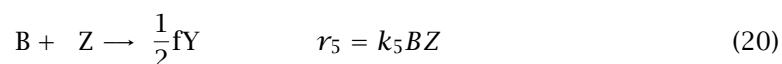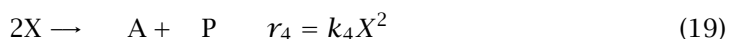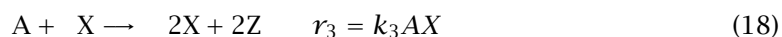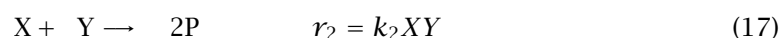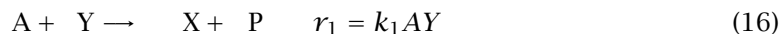
$$h = 0.5 \qquad h = 0.1 \qquad h = 0.01 \qquad h = 0.001$$

You can reuse the `firstorder` function that you wrote in Exercise 1 for evaluating the right-hand side of the ODE.

(c) Plot all four $c_A(t)$ numerical solutions on the same graph and label the four curves. Replot the four solutions using a log scale on the y-axis. Which step size do you recommend for solving this problem?

Exercise 7: Complex dynamic behavior with nonlinear ODEs. Belousov-Zhabotinsky reaction.

Belousov and Zhabotinsky discovered chemical reactions that can remain far from equilibrium for long periods of time. The following mechanism due to Field and Noyes (1974) while working at the University of Oregon, known as the Oregonator, is the simplest model that explains some of the observed behavior

$$
\begin{align}
A + Y &\longrightarrow \quad X + \quad P & r_1 &= k_1 AY & (16)\\
X + Y &\longrightarrow \quad 2P & r_2 &= k_2 XY & (17)\\
A + X &\longrightarrow \quad 2X + 2Z & r_3 &= k_3 AX & (18)\\
2X &\longrightarrow \quad A + \quad P & r_4 &= k_4 X^2 & (19)\\
B + Z &\longrightarrow \quad \tfrac{1}{2}fY & r_5 &= k_5 BZ & (20)
\end{align}
$$

in which A=$HBrO_3^-$, B is the sum of all oxidizable organic species, P=HOBr, X=$HBRO_2$, Y=Br, and Z=metal oxides. We may assume the A and B concentrations are much higher than the intermediates X, Y, and Z and can be assumed constant at A=0.06M and B=0.02M.

We wish to solve this model for the intermediates using the following values of rate constants and initial conditions

$$
\begin{align*}
\frac{dX}{dt} &= \alpha(Y - XY + X - \beta X^2)\\
\frac{dY}{dt} &= (Z - XY - Y)/\alpha\\
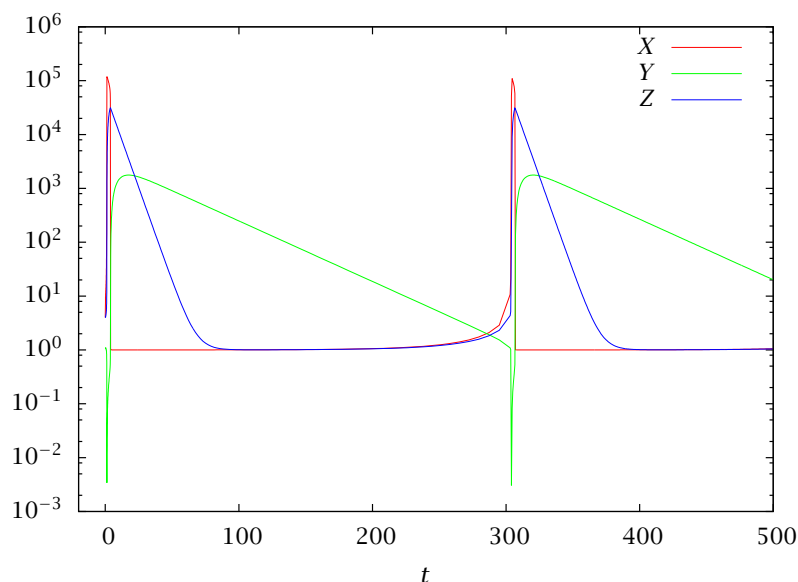\frac{dZ}{dt} &= \gamma(X - Z)
\end{align*}
$$

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Figure 8: Complex dynamic behavior of the Oregonator model of the Belousov-Zhabotinsky reaction.

in which

$$\alpha = 77.27 \qquad \beta = 8.375 \times 10^{-6} \qquad \gamma = 0.161$$
$$X_0 = 4 \qquad Y_0 = 1.1 \qquad Z_0 = 4$$

Be prepared, your solution is going to look something like Figure 8. In order to capture the sudden transient occurring at about $t = 303$, try using the following times for reporting the ODE solution in your call to `ode15s`

```
time = [0, ...
     (logspace (-1, log10 (303), 300)), ...
     (logspace (log10 (303.01), log10 (500), 300))]';
```

echo `time` back to the command line so you can see where these time points are placed. The command `logspace` is handy for dividing an interval evenly on a log scale. Contrast its behavior to the command `linspace`.

Exercise 8: More oscillations. Coupled mass and energy balance in a continuous well-stirred reactor. Default error tolerances in MATLAB's `ode15s` unreliable

Consider again the irreversible reaction

$$A \xrightarrow{k} B \qquad r = kc_A$$

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The mass and energy balances for a continuous-stirred-tank reactor (CSTR) are given by (Rawlings and Ekerdt, 2012, p. 298)

$$\frac{dc_A}{dt} = \frac{c_{Af} - c_A}{\tau} - kc_A \tag{21}$$

$$\frac{dT}{dt} = \frac{U^o A}{V_R \rho \hat{C}_P}(T_a - T) + \frac{T_f - T}{\tau} - \frac{\Delta H_R}{\rho \hat{C}_P}kc_A \tag{22}$$

$$k(T) = k_m e^{-E(1/T - 1/T_m)} \tag{23}$$

in which c_A is the reactor A concentration and T is the reactor temperature. Notice the rate constant k also depends on the reactor temperature. Including the energy balance to describe the reactor temperature allows the reactor to exhibit complex behavior. We wish to solve the model for the following parameter values

Param.	Value	Units
T_f	298	K
T_a	298	K
T_m	298	K
$\hat{C}_P$	4.0	kJ/(kg K)
c_{Af}	2.0	kmol/m^3
$k_m(T_m)$	0.004	min^{-1}
E	1.5×10^4	K
ρ	10^3	kg/m^3
ΔH_R	-2.2×10^5	kJ/kmol
$U^o A/V_R$	340	kJ/(m^3 min K)
τ	73.1	min

(a) Solve the two differential equations describing the reactor from the following initial condition using MATLAB's default parameters

$$c_{A0} = 0.36 \text{ mol/L} \qquad T_0 = 315 \text{ K}$$

Plot c_A, T versus t for this solution out to $t = 20\tau$.

Next plot c_A versus T for this solution. This type of plot is called a phase plot or phase portrait. Notice it gives you a clear indication when a system is approaching a persistent oscillation known as a limit cycle.

(b) Next we tighten the absolute and relative error tolerance for ode15s using the odeset function. Learn more about this function by typing at the command line

```
help odeset
```

The machine precision is stored in the variable eps. Try setting both the absolute and relative error tolerances to the square root of the machine precision. The odeset command is

```
opts = odeset ('AbsTol', sqrt (eps), 'RelTol', sqrt (eps));
```

After setting `opts`, you pass this extra argument to the ODE solver to use the tighter tolerances with

```
[tout, x] = ode15s (@oderhs, tout, x0, opts);
```

Resolve the ODEs with the same initial conditions and the tighter tolerances. Plot the solution with both loose and tight tolerances on the same graph. What do you conclude about MATLAB's default error tolerances?

(c) Try your function `euler` on this problem. Can you obtain an accurate solution? If so, what step size h do you recommend? Note: I have not tried this part myself so I am not sure what happens here.

(d) Resolve the Oregonator with tighter tolerances and compare to your solution in Exercise 7. Do you notice a difference in the two solutions?

Exercise 9: Estimating rate constant and activation energy from rate constant measurements at different temperatures

Assume a reaction rate has been measured at several different temperatures in the range $300\,\text{K} \le T \le 500\,\text{K}$. Model the rate (rate constant) as

$$k = k_0 \exp(-E/T) \tag{24}$$

in which k_0 (min^{-1}) is the pre-exponential factor and E (K) is the activation energy scaled by the gas constant. To make the estimation problem linear, transform the data by taking the logarithm of Equation 24

$$\ln k = \ln k_0 - E/T$$

(a) Estimate the parameters $\ln k_0$ and E using least squares given the following single experiment consisting of nine rate constant measurements at the following temperatures

T	k
300	0.01658
325	0.06151
350	0.09822
375	0.2751
400	0.9982

```
425     2.113
450     4.401
475     4.505
500     13.42
```

What are the least squares estimates of $\ln k_0$ and E for this experiment?

(b) Plot the data and least squares fit on two plots: one plot of k versus T and a separate plot of $\ln k$ versus $1/T$. How well does Equation 24 represent these data?

(c) Next we wish to analyze the following 50 replicate experiments in which each experiment consists of nine measurements of k at different T. The first four of these experiments are shown here

T1	k1	T2	k2	T3	k3	T4	k4
303	0.01145	302	0.0175	302	0.01208	301	0.00955
323	0.0483	321	0.04742	326	0.06483	329	0.05799
351	0.167	345	0.1456	354	0.2289	354	0.1729
376	0.3197	379	0.5643	375	0.436	376	0.2612
402	1.221	396	0.9718	401	0.877	404	0.8787
429	1.278	425	2.166	427	2.152	422	1.052
453	3.844	447	2.853	452	2.354	448	3.882
479	4.519	476	5.098	477	4.685	475	5.931
501	13.8	504	12.05	496	8.29	496	6.235

Download these data from the file

<div align="center">kt_lotsmeas.dat</div>

Calculate a least squares estimates for each experiment. Plot the 50 estimates using the estimate of $\ln k_0$ as the abscissa and the estimate of E as the ordinate.

(d) Next combine all 50 experiments into one dataset of k, T values and estimate $\ln k_0$ and E using all 450 measurements. What are the values of the estimates?

(e) Plot all 450 measurement and the least squares fit on two plots: one plot of k versus T and a separate plot of $\ln k$ versus $1/T$. How well does Equation 24 represent all of the measurements.

Exercise 10: Multiple steady states. Coupled mass and energy balance in a continuous well-stirred reactor

Consider again the irreversible reaction

$$A \xrightarrow{k} B \qquad r = kc_A$$

The mass and energy balances for an *adiabatic* (no heat transfer to the surroundings), continuous-stirred-tank reactor (CSTR) are given by (Rawlings and Ekerdt, 2012, p. 298)

$$\frac{dc_A}{dt} = \frac{c_{Af} - c_A}{\tau} - kc_A$$
$$\frac{dT}{dt} = \frac{T_f - T}{\tau} - \frac{\Delta H_R}{\rho \hat{C}_P} kc_A$$
$$k(T) = k_m e^{-E(1/T - 1/T_m)}$$

in which c_A is the reactor A concentration and T is the reactor temperature. Notice the rate constant k also depends on the reactor temperature. Including the energy balance to describe the reactor temperature allows the reactor to exhibit complex behavior. We wish to solve the model for the following parameter values

Parameters	Values
τ	10 min
c_{Af}	2 kmol/m^3
T_f	298 K
k_m	0.001 min^{-1}
E	8000 K
T_m	298 K
$\Delta H_R/(\rho \hat{C}_P)$	-75 m^{3}K/kmol

(a) Solve the reactor differential equation model for the following 11 initial conditions:

$$c_A(0) = c_{Af}$$
$$T(0) = \begin{bmatrix} 300 & 310 & 320 & 330 & 340 & 350 & 360 & 370 & 380 & 390 & 400 \end{bmatrix}$$

Plot all eleven solutions $c_A(t)$ versus t on one graph and all eleven solutions $T(t)$ versus t on a second graph.

Some of these initial conditions should lead to an extinguished steady state (low conversion, low temperature), and some of the initial conditions should lead to an ignited steady state (high conversion, high temperature).
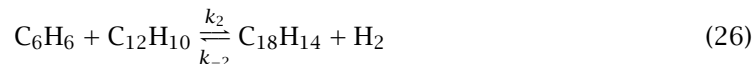
(b) If you wanted to start the rector full of feed, what is the smallest temperature at which you could start the reactor and still achieve the ignited steady state?

Exercise 11: Benzene pyrolysis and stopping time

Hougen and Watson (1947) analyzed the rate data for the pyrolysis of benzene by the following two reactions. Diphenyl is produced by the dehydrogenation of benzene,

$$2C_6H_6 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} C_{12}H_{10} + H_2 \tag{25}$$

Triphenyl is formed by the secondary reaction,

$$C_6H_6 + C_{12}H_{10} \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} C_{18}H_{14} + H_2 \tag{26}$$

The reactions are assumed to be elementary so that the rate expressions are

$$r_1 = k_1 \left(c_B^2 - \frac{c_D c_H}{K_1} \right) \qquad r_2 = k_2 \left(c_B c_D - \frac{c_T c_H}{K_2} \right) \tag{27}$$

in which the subscripts, B, D, T and H represent benzene, diphenyl, triphenyl and hydrogen, respectively. The reactor operates at 1033 K and 1.0 atm. The rate and equilibrium constants at $T = 1033$ K and $P = 1.0$ atm are given in Hougen and Watson,

$$k_1 = 7 \times 10^5 \text{ L/mol} \cdot \text{hr} \qquad K_1 = 0.31$$
$$k_2 = 4 \times 10^5 \text{ L/mol} \cdot \text{hr} \qquad K_2 = 0.48$$

The reactor is initially full of benzene. The gas constant is $R = 0.08205$ lit atm/mol K.

(a) Plot the mole fractions of the four components versus time.

(b) Use the ODE solver to calculate precisely the time required to reach 50% total conversion of the benzene.

Exercise 12: Chemical reaction in a batch reactor — limiting reagant

The reaction of interest is the dehalogenation of a dihalogenated starting material to form the divinyl product, which is used in photographic film production (Rawlings and Ekerdt, 2012). It is assumed that the halide groups (X) are removed from the starting material in two consecutive reactions:

$$A + B \overset{k_1}{\longrightarrow} C + B \cdot HX$$
$$C + B \overset{k_2}{\longrightarrow} D + B \cdot HX$$
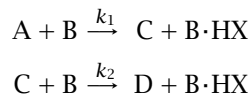
A	$XH_2CCH_2RCH_2CH_2X$
B	Organic base
C	$H_2C{=}CHRCH_2CH_2X$
D	$H_2C{=}CHRCH{=}CH_2$

The dihalogenated starting material (A) loses HX to the base (B) to form the mono-halogenated intermediate (C), which subsequently loses HX to the base to produce the desired final product (D).

(a) Write down the differential equations describing the concentrations of A, B, C, and D for this reaction in a well-stirred batch reactor of constant volume.

(b) Solve the differential equations numerically for the following values of initial concentrations and rate constants

$$c_{A0} = 2.35 \, \text{mol/L} \qquad c_{B0} = 3.5 \, \text{mol/L} \qquad c_{C0} = 0 \qquad c_{D0} = 0$$
$$k_1 = 25.0 \, \text{L/mol} \cdot \text{hr} \qquad k_2 = 12.5 \, \text{L/mol} \cdot \text{hr}$$

Plot the concentrations of all species versus time with (i) standard axes and (ii) with a logarithmic scale on the y-axis (semilog plot). Label A, B, C and D curves on the plot. Choose an appropriate time interval for the solution of the differential equations to display the final steady state of the system.

(c) What species are present at long times? To increase the production of final product D, what initial reactant concentration must be increased? Why?

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O. A. Hougen and K. M. Watson. *Chemical Process Principles. Part Three: Kinetics and Catalysis.* John Wiley & Sons, Inc., New York, 1947.

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