Computational Study of Chemical Kinetics (GIDES)

Software Introduction

Berkeley Madonna (http://www.berkeleymadonna.com) is a dynamic modeling program in which relational diagrams are created using a graphical interface to which numerical values and mathematical functions may be assigned. A free evaluation version of the software (excluding the "Save" capability) is available for downloading.

The user interface of Madonna has modeling and equation windows–either can be used to directly solve the problem of interest. The equation window is updated by the construction in the model window. There is also a chemical reaction module useful for chemical kinetics.

Madonna offers both graphical and data input and automatically opens a graph/table window upon execution which can be easily toggled back and forth. There is a "Slider" input data option.

The execution in Madonna is very fast. Madonna offers Euler, RK2, RK4, auto-stepsize, and Rosenbrock (for stiff systems); provides a curve fit routine; and handles arrays.

Madonna comes with several "How do I" files and examples of its features using systems of interest to chemists.

When Madonna is opened, a partially filled "Equations" window appears. The construction of a model is done in a "Flowchart" window. Click the File / New Flowchart to open a blank flowchart window. A toolbar of 11 icons will appear across the top of this window. The ones that we will use primarily include:

The "Select" tool is the general purpose editing tool used for selecting, moving, opening, and editing various objects in the work area.
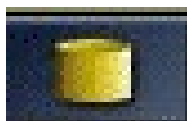

The "Reservoir" represents a value undergoing a change. For chemical kinetics, we will use a reservoir to represent the number of molecules of reactant or product present during a chemical reaction at a given time. Normally, we will set the initial number of reactant molecules at 1000 and the initial number of product molecules at 0.

A "Formula" contains constants and transformation equations. We will use "Formulas" to enter values of the rate constants for the chemical reactions being studied. Normally, we set the values of the rate constants in the range of 0 to 100.

An "Arc" links the various Reservoirs, Formulas, etc. within the model.
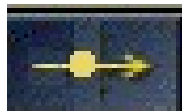
A "Flow" represents a change with respect to time of a Reservoir. During the process a Reservoir attached at the left decreases as time passes and one at the right increases. For our study of chemical kinetics, a Reservoir at the left represents a chemical reactant, a Reservoir at the right represents a chemical product, and the Flow represents the chemical reaction arrow.

Listed below are some simple directions on using the Graphical Interface icons described above:

   1) Drawing a "Reservoir".
            A) Click the Reservoir icon.
            B) Click in the work area at the desired location. A "R#" Reservoir appears.
            C) The Reservoir can be named by typing the name if the Reservoir is reddish.
            D) Double clicking or right clicking the Reservoir opens the dialog box for data
                entry.
            E) Clicking the Reservoir icon with the Control Key depressed will allow more
                than one Reservoir to be entered in the workspace.

   2) Drawing a "Flow" between two Reservoirs.
            A) Click the "Flow" icon.
            B) Move the cursor to the center of the outflow Reservoir.
            C) Click and drag to center of the inflow Reservoir.
            D) Release. A "J#" Flow appears.
            E) The Flow can be named by typing if the Flow is reddish.
   F) Double clicking or right clicking the Flow opens the dialog box for data entry.

   3) Drawing a "Formula".
            A) Click the "Formula" icon.
            B) Click in the work area at the desired location. A "F#" Formula appears.
            C) The Formula can be named by typing if the Formula is reddish.
            D) Double clicking or right clicking the Converter opens the dialog box for data
                entry.

   4) Drawing an "Arc".
            A) Click the "Arc" icon.
            B) Place the cursor inside the "from" object.
            C) Click and drag to the "target" object until the "target" is highlighted.
            D) Release.
            E) The locations of attachments can be adjusted, if desired.

Chemical Kinetics Studies

Simple First Order Reaction

Consider the reaction

$$A \xrightarrow{k_1} B$$
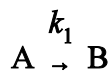
which is first order in A. The differential rate equations are
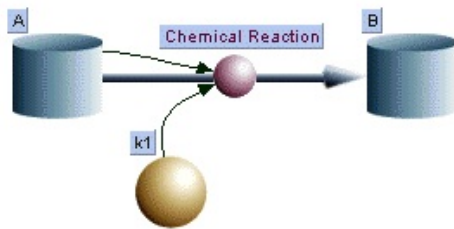
$$\frac{dA}{dt} = -k_1 A$$

$$\frac{dB}{dt} = k_1 A$$

and the integrated rate equations are

$$A = A_o e^{-k_1 t}$$

$$B = A_o (1 - e^{-k_1 t})$$

The model is created using the following steps:

1) Create and name Reservoir A in the work area.
      A) Double click the Reservoir and enter "1000 " for "Init A=".
      B) Click "OK".

2) Create and name Reservoir B in the work area. Enter "0" for "Init B=".

3) Draw the Flow connecting A to B and name it "Chemical Reaction". Do not worry about the question mark that appears on the Reservoir symbol–it will be eliminated later. The label can be moved by clicking and dragging to center it above the symbol.

4) Place a Formula in the work area.
      A) Name it "k1".
      B) Double click the Formula and enter "1" for "k1 = ".
      C) Click "OK".

5) Connect Reservoir A to the Flow using an Arc.

6) Connect Formula k1 to the Flow using an Arc.

7) Enter the kinetics of the reaction.
   A) Double click the "Flow".
   B) Double click on the k1 entry in the "Required Inputs" area.
   C) Type "*" or click on the "*" on the screen keypad for multiplication.
   D) Double click the "A" entry.
   E) The "Chemical_Reaction =" entry should read "k1*A".
   F) Click "OK".

8) Click Model / Equations. The differential equations that will be solved appear in the window as well as the initial amounts of A and B and the value of the rate constant.

9) Click the "Run" button in the equation window and the graph/table output is shown.
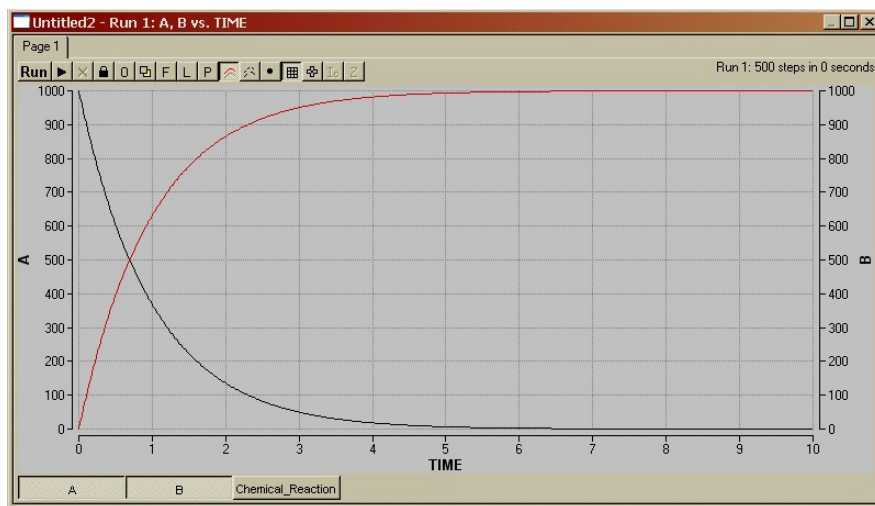
Answer the following questions:

1) What is the sum of A and B at any given time?

2) At what approximate time does $A = B$ (50 % completion)?

3) How would the graph change if $k_1 = 2$? You can check your answer by double clicking the k1 Formula, entering the value of "2", and rerunning the model.

The same kinetics may be studied without the use of the graphical interface.
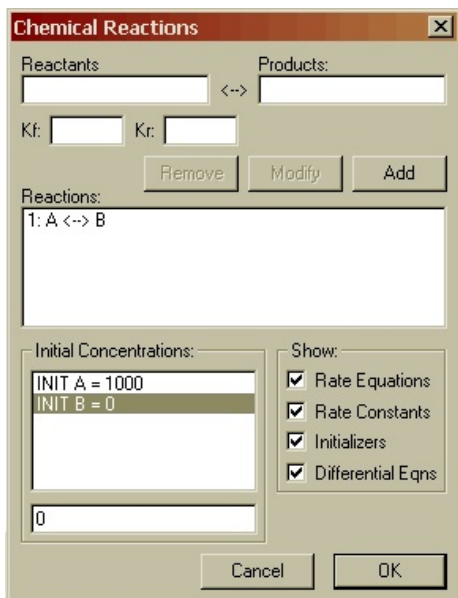
1) Click Model / Modules / Chemical Reactions.

2) Enter "A" in the Reactants area, "B" in the Products area, "1" in the Kf: area, and "0" in the Kr area.

3) Click "Add" and the equation appears in the Reaction: area.

4) Double click the "Init A=0" entry in the Initial Concentrations: area and enter "1000" in the bottom entry area. Click anywhere in the Initial Concentrations: area.

5) Click "OK" and the Equation window will open displaying the differential equations.

6) Click "Run" and the graph/table output is shown.

Parallel First Order Reactions Involving the Same Reactant

Consider the reactions in which A reacts to form two different products

$$A \xrightarrow{k_1} B$$

$$A \xrightarrow{k_2} C$$
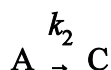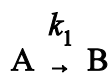
Such reactions are common in radioactive decay series when a parent can undergo decay by two different processes and during organic synthesis to give by-products. The differential rate equations are

$$\frac{dA}{dt} = -k_1 A - k_2 A = -(k_1 + k_2)A$$

$$\frac{dB}{dt} = k_1 A$$

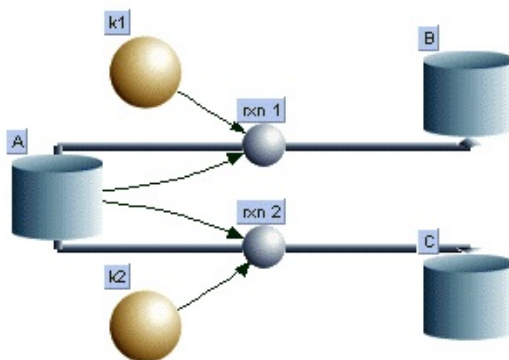$$\frac{dC}{dt} = k_2 A$$

and the integrated rate equations are

$$A = A_o e^{-(k_1+k_2)t}$$

$$B = A_o \frac{k_1}{k_1 + k_2}\left(1 - e^{-(k_1+k_2)t}\right)$$

$$C = A_o \frac{k_2}{k_1 + k_2}\left(1 - e^{-(k_1+k_2)t}\right)$$

$$\frac{C}{B} = \frac{k_2}{k_1}$$

Construct the model as shown. Set $k_1 = k_2 = 1$ and the initial values of $A = 1000$ and $B = C = 0$. Check the entries in the Equation window to assure that they agree with the differential rate equations. Run the model. The graph output may be modified by double clicking the left axis and responding to the pop-up window items. Note that if B and C are plotted on the same scale, they will be superimposed.
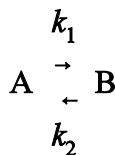

Answer the following questions:

    1) What is the sum of A, B, and C at any given time?

    2) How will the graph change if $k_1 = 2$? You can check this answer.

    3) After reaction completion (at long time), is the ratio of C/B the same as k_2/k_1?

(You might like to try the Chemical Reactions Module.)

Reversible First Order Reactions

Consider the reversible reaction system

$$A \underset{k_2}{\overset{k_1}{\rightleftharpoons}} B$$

The differential rate equations are

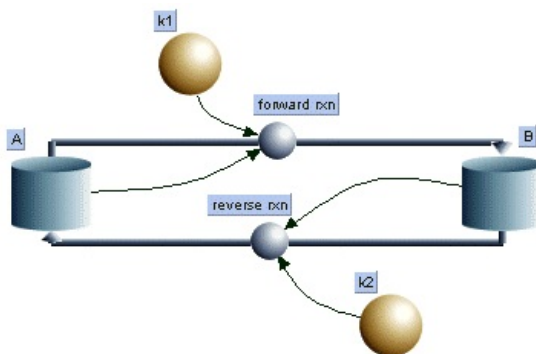$$\frac{dA}{dt} = -k_1A + k_2B$$

$$\frac{dB}{dt} = k_1A - k_2B$$

and the integrated rate equations are

$$A = A_o \frac{1}{k_1 + k_2}\left(k_2 + k_1 e^{-(k_1+k_2)t}\right)$$

$$B = A_o \frac{k_1}{k_1 + k_2}\left(1 - e^{-(k_1+k_2)t}\right)$$

$$\frac{B}{A} = \frac{k_1}{k_2} \quad \text{at equilibrium}$$

Construct the model as shown. Set $k_1 = k_2 = 1$ and the initial values of $A = 1000$ and $B = 0$. Check the entries in the Equation window to assure that they agree with the differential rate equations.
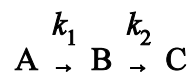

Run the model and answer the following questions:

1) What is the sum of A and B at any given time?

2) How will the graph change if $k_1 = 2$ and $k_2 = 1$? You can check this answer.

3) Once equilibrium is reached, is the ratio of B/A the same as k_1/k_2?

Consecutive First Order Reactions

Consider the series of two first-order reactions

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

The differential rate equations are

$$\frac{dA}{dt} = -k_1 A$$

$$\frac{dB}{dt} = k_1 A - k_2 B$$

$$\frac{dC}{dt} = k_2 B$$

and the integrated rate equations are

$$A = A_o \, e^{-k_1 t}$$

$$B = A_o \frac{k_1}{k_2 - k_1} \left(e^{-k_1 t} - e^{-k_2 t} \right)$$

$$C = A_o \left(1 - \frac{k_2}{k_2 - k_1} e^{-k_1 t} + \frac{k_1}{k_2 - k_1} e^{-k_2 t} \right)$$

Construct the model as shown. Set $k_1 = k_2 = 1$ and the initial values of $A = 1000$ and $B = C = 0$. Check the entries in the Equation window to assure that they agree with the differential rate equations.
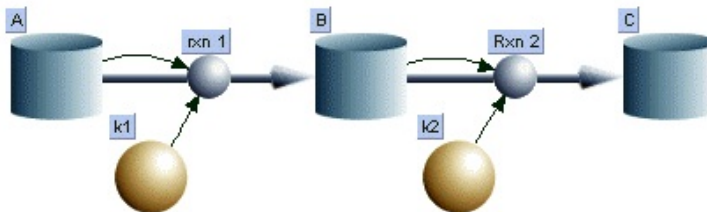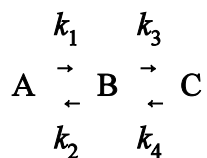

Run the model and answer the following questions:

1) What is the sum of A, B, and C at any given time?

2) How will the graph change if $k_1 > k_2$ such as $k_1 = 5$ and $k_2 = 1$? You can check this answer. Under these conditions, the series of reactions are known to be in "disequilibrium".

3) How will the graph change if $k_1 < k_2$ such as $k_1 = 1$ and $k_2 = 5$? You can check this answer. Under these conditions, the series of reactions are known to be in "transient equilibrium".

4) How will the graph change if $k_1 \ll k_2$ such as $k_1 = 0.5$ and $k_2 = 10$? You can check this answer. Under these conditions, the series of reactions are known to be in "secular equilibrium".

Reversible Consecutive First-Order Reactions

Consider the reversible reaction system

$$A \; \underset{k_2}{\overset{k_1}{\underset{\leftarrow}{\rightarrow}}} \; B \; \underset{k_4}{\overset{k_3}{\underset{\leftarrow}{\rightarrow}}} \; C$$

Write the differential rate equations for dA/dt, dB/dt, and dC/dt. Construct the model for this system of reactions. Set the initial value of $A = 1000$ and $B = C = 0$ and use $k_1 = k_2 = k_3 = k_4 = 1$. Check the entries in the Equation window to assure that they agree with the differential rate equations. Run the program.

This model can be used to illustrate the "steady state" and "equilibrium" approximations often used in stepwise (complex) mechanisms by setting $k_4 = 0$. The steady state approximation assumes that the intermediate B is very reactive so that at any given time B is very small and $dB/dt = 0$. Under these conditions $(k_2 + k_3) >> k_1$. Run the model with $k_2 = k_3 = 10$ and $k_1 = 0.1$ to observe the results for the steady state approximation. The equilibrium approximation assumes that B/A is constant. Under these conditions $(k_2 + k_3) >> k_1$ and $k_2 >> k_3$. Run the model with $k_2 = 10$, $k_3 = 1$, and $k_1 = 0.5$ to observe the results for the equilibrium approximation. Record your observations for each set of conditions.

Second Order Reactions

Consider the system
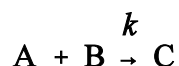
$$A + B \overset{k}{\rightarrow} C$$

Write the differential rate equations for dA/dt, dB/dt, and dC/dt. Construct the model for this system of reactions. Note that Formulas must be used for A and B and the entries are A_o-C and B_o-C, respectively.
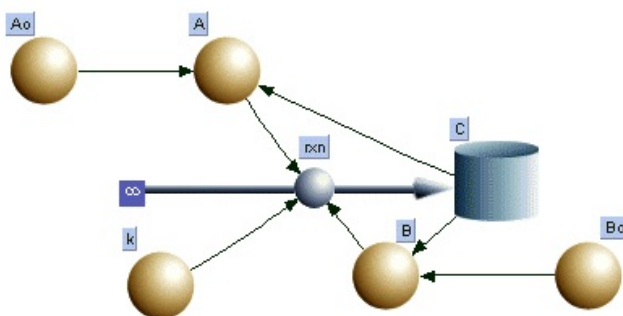
Set the initial value of $A = B = 1000$ and $C = 0$ and use $k = 0.001$. Check the entries in the Equation window to assure that they agree with the differential rate equations. Run the program.