Computational Study of Chemical Kinetics (GIDES) Using VenSim PLE
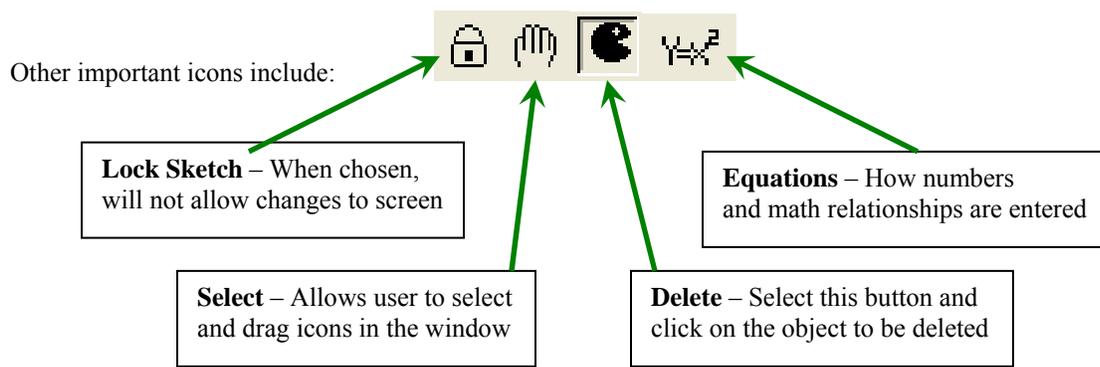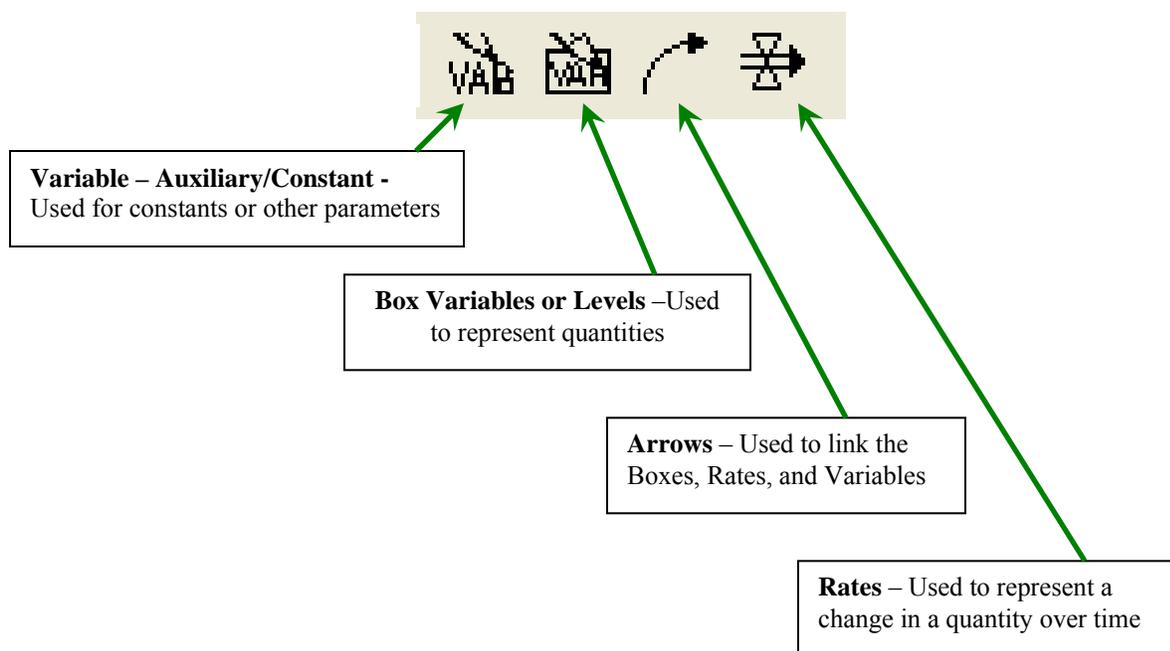
Software Introduction

VenSim Personal Learning Edition (PLE) software is an icon-based systems dynamics modeling package that is available for free (http://www.vensim.com/venple.html). The construction of models in VenSim PLE is similar to that of programs such as STELLA and Berkeley-Madonna. The great advantage of VenSim PLE is the free version available for educational and personal (non-commercial) use.

If you open VenSim PLE you will either see a blank screen or the program will open the last model that was used. From the "File" pull down menu at the top of the page, select "New Model". A "Model Settings" window will open. For now we will accept the default values by clicking "OK".

At the top of the page you will see two horizontal toolbars. The uppermost toolbar contains some familiar icons for opening a new model page, opening an existing model file, saving, printing, etc., and also contains icons used to run a model. The second toolbar contains the icons used to construct a model. The main ones we will be using include:

Variable – Auxiliary/Constant - Used for constants or other parameters

Box Variables or Levels –Used to represent quantities

Arrows – Used to link the Boxes, Rates, and Variables

Rates – Used to represent a change in a quantity over time

Other important icons include:

Lock Sketch – When chosen, will not allow changes to screen

Select – Allows user to select and drag icons in the window

Delete – Select this button and click on the object to be deleted

Equations – How numbers and math relationships are entered

Listed below are some general directions on using the icons described on the previous page:

1) Drawing a "Box Variable"
  a) Click the icon on the toolbar
  b) Click in the work area in the desired location. A text box appears.
  c) Type in the name of the quantity (e.g. "Reactant A"). Hit Enter.
  d) Resize the box by clicking and dragging the circle in the lower right corner.
  e) Right clicking allows font, color, name position, and box type changes.
  f) Clicking elsewhere in the workspace will add more box variables.

2) Drawing a "Rate" between two Boxes
  a) Click the icon on the toolbar.
  b) Click and release inside of the first Box, then click and release inside the second box.
  c) At this point a text box opens. Type in the name of the Rate, hit Enter.
  d) The rate icon can be "bent" between two Boxes by clicking on the triangular portion and
      dragging to the appropriate location.
  d) Right clicking on the icon allows font color and name position changes.

3) Drawing a "Variable"
  a) Click the icon on the toolbar.
  b) Click in the work area in the desired location. A text box appears.
  c) Type in the name of the variable (e.g. Rate constant) and hit Enter.
  d) Right clicking on the small circle allows changes in icon shape, font type and color, and
      name position.

4) Drawing an "Arrow"
  a) Click the icon on the toolbar.
  b) Click and release inside the "box" or variable" icon where the arrow will originate.
  c) Click again on the "rate" or "variable" icon where the arrow will end.
  d) The small blue circle at the arrow midpoint can be used to "curve" the arrow.
  e) Right clicking in the small blue circle allows changes to arrow thickness, etc.

During the execution of a completed model, any difference equations (generated by connecting icons in the workspace) describing the time dependence of the quantity y are solved using one of two numerical methods based on a Taylor series.

$$y(t_m + \Delta t) = y_m + \frac{\Delta t}{1!}\left(\frac{dy}{dt}\right)_{t=t_m} + \frac{\Delta t^2}{2!}\left(\frac{d^2 y}{dt^2}\right)_{t=t_m} + \frac{\Delta t^3}{3!}\left(\frac{d^3 y}{dt^3}\right)_{t=t_m} + \frac{\Delta t^4}{4!}\left(\frac{d^4 y}{dt^4}\right)_{t=t_m} + \ldots$$

$$= y_m + F(t_m, y_m) + \frac{\Delta t^2}{2} F'(t_m, y_m) + \frac{\Delta t^3}{6} F''(t_m, y_m) + \frac{\Delta t^4}{24} F'''(t_m, y_m) + \ldots$$

Where y_m represents the value of the "Box Variable" at time $t = t_m$ and $y(t_m + \Delta t)$ represents the value of the "Box Variable" at time $t_m + \Delta t$. Unless changed, Euler's method is the default method used by VenSim PLE:

$$y(t_m + \Delta t) = y_m + \Delta t \, F(t_m, y_m)$$

which is based on the first two terms of the above series. VenSim PLE also offers the Runge-Kutta 4 method which is based on the first five terms of the series:

$$y(t_m + \Delta t) = y_m + \frac{\Delta t}{6}(\alpha_1 + 2\alpha_2 + 2\alpha_3 + \alpha_4) \qquad \alpha_1 = F(t_m, y_m)$$

$$\alpha_2 = F\left(t_m + \frac{\Delta t}{2}, y_m + \frac{\alpha_1 \Delta t}{2}\right) \qquad \alpha_3 = F\left(t_m + \frac{\Delta t}{2}, y_m + \frac{\alpha_2 \Delta t}{2}\right)$$

$$\alpha_4 = F(t_m + \Delta t, y_m + \alpha_3 \Delta t)$$

For chemical kinetics we will normally use the "RK4" method because it produces the most accurate results for these types of calculations. Note that VenSim PLE cannot solve "stiff" systems that other programs such as Berkeley-Madonna can handle.

Chemical Kinetics Studies

Simple First Order Reaction

Consider the reaction:
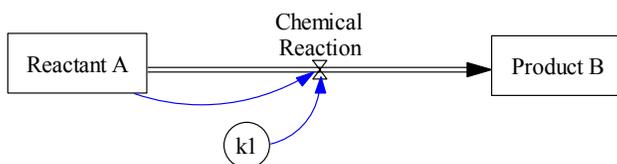
$$A \xrightarrow{k_1} B$$
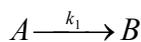
which is first order in A. The differential rate equations are:

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

The integral rate equations are:

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

The model is shown below, along with the steps used to create it.

1) Create and name the two reservoirs "Reactant A" and "Product B" in the work area. Right clicking on the icon will let you choose where the name will appear, font size, etc.

2) Choose the "Rate" icon, click and release inside the "A" reservoir, then click inside "B". Type in the name "Chemical Reaction" for the rate and hit Enter.

3) Choose the "Variable" icon and click in the workspace. Type in the name "k1", hit Enter. You can right click on the small blue circle and choose the shape of this icon and where the label appears, as shown above.

4) Choose the "Arrow", click inside the "Reactant A" box, then click on the "Chemical Reaction" icon. Repeat this process to draw an arrow between the "k1" and the "Chemical Reaction" icons.

5) You are now ready to enter the appropriate numbers into the model so it will run. To do this, click on the "Equations" icon ![icon]. The icons highlighted in black indicate that no numerical values or formulas have been added to the model.
        a) Click on "Reactant A", and type in "1000" for the initial value. Click "OK".
        b) Click on 'Reactant B", and type in "0" for the initial value. Click "OK".
        c) Click on "k1", and type in "1" in the "=" box. Click "OK".
        d) Click on "Chemical Reaction", and then click on "k1" in the lower box so that it moves into the upper box. Use the calculator pad to put in "*" (multiplication), then click on "Reactant A" in the lower box so that it moves to the upper box. See the next page:
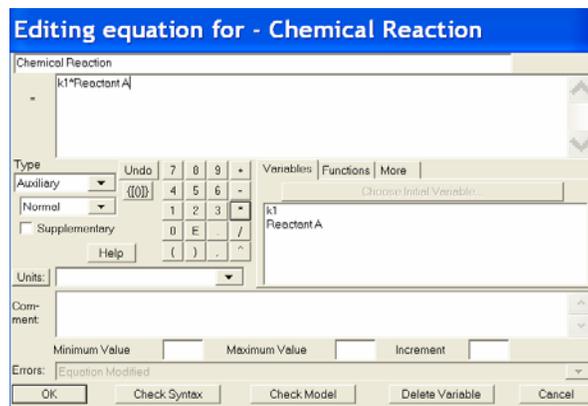
Note in the model above that the "Chemical Reaction" arrow coming out of Reactant A will cause the amount to decrease, while the same arrow entering Product B causes it to increase. This takes care of the signs for the differential equations on the previous page.

Before running the model, we have a few things left to specify. We need to change the time limits, the time step (dt), and the integration method used in the model. Follow these steps to change the model settings:

1) Click on "Model" and "Settings".

2) Change the "FINAL TIME" to 10. Change "Units of Time" to seconds. Change "TIME STEP" to 0.0625

3) To change the integration method, click on the "Set" button. Just to the left you can click on "Eule" to toggle between the Euler method and the Runge-Kutta 4 method. Select "RK4".

Now we should be ready to run the model. This is easily done by clicking on the picture of the running figure on the top tool bar. The model <u>did</u> run, but we have not told the program how we want to view the results! Follow the steps below to set up a graph of the model output:

1) Click on the "Control Panel" icon on the top toolbar.

2) Click on the "Graphs" tab. Click the "New" button.

3) Give the graph a name (e.g. "First Order A to B") near the top of the dialog box.

4) Click on "Sel" next to "X-Axis", and choose "time". Click "OK". Type in "Time" for "X Label".

5) The lower left side is where you select what variables to plot.
        a) Next to the first "Variable" box, click "Sel", then click on "Reactant A". Click "OK".
        b) In the second box below "Variable", click "Sel" and choose "Product B". Click "OK".
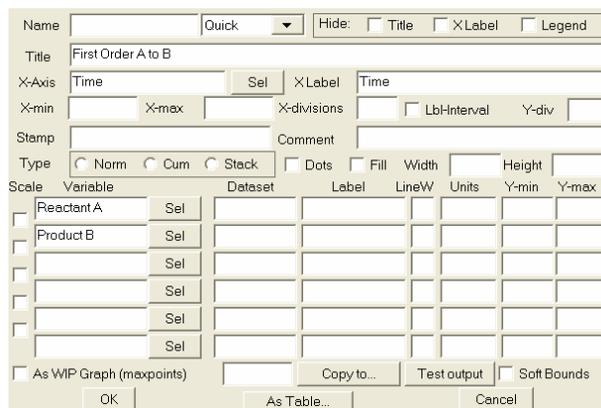
6) Click "OK" on the dialog box to close it.

7) Click Display in the "Control Panel" window and close the "Control Panel" to see the graph.

First Order A to B

Reactant A : Current
Product B : Current
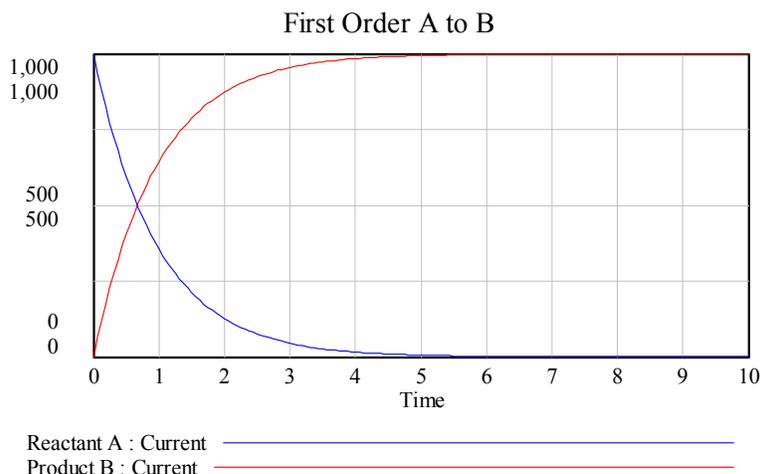
Answer the following questions:

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 clicking on the "Set" button ![SET]. This highlights the k_1 icon. Clicking on the k_1 icon will allow you to change the value to 2. Run the model again and display the graph.

Adding Interactivity

On the top toolbar next to the standard "Run" button ![run] is the *SyntheSim* button ![synthesim]. The *SyntheSim* utility will make a model interactive by changing all constant-valued auxiliary variables into slider bars. In addition, small graphs will appear inside the box variables and rates. Any changes made to the slider bar values will instantly appear as changes in these small graphs.

Click on the *SyntheSim* button. A sliderbar appears below the k1 icon for the rate constant, and you will see small graphs appear in the A, Chemical Reaction, and B areas of the model.
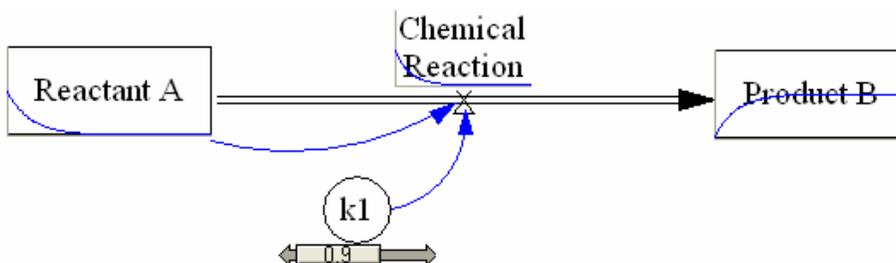
You can move the slider bar and observe what happens to the small graphs. You can also set slider bar limits and increments by clicking one of the arrows at either end of the bar. Clicking on the "Stop" button ![stop] will exit the *SyntheSim* mode and return the model to the original state.

Parallel First Order Reactions Involving the Same Reactant

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

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

Some examples of this reaction type include radioactive decay where the parent nucleus can undergo different decay processes and also during some organic reactions where byproducts are formed. The differential rate equations are:

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

The integrated rate equations are:

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

The model is shown below. Set $k_1 = k_2 = 1$ with initial values of $A = 1000$ and $B = C = 0$. Be sure that the formulas you enter correspond to the differential rate equations. Run the model and set up an appropriate graph to see how A, B, and C change with time. Note that if A and B are plotted on the same scale, they will be superimposed.
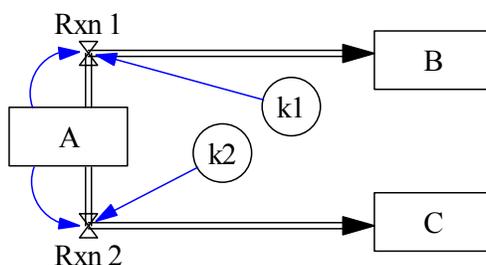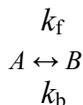

Answer the following questions:

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

2) How will the graph change if $k_1 = 2$. Change the model and see.

3) After reaction completion (steady state), is the ration of C/B the same as k_2/k_1?

*Reversible First Order Reactions*

Consider the reversible system:

$$\begin{array}{c} k_{\mathrm{f}} \\ A \leftrightarrow B \\ k_{\mathrm{b}} \end{array}$$

The differential rate equations are:

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

The integrated rate equations are:

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

Build the model as shown below. Set $k_1 = k_2 = 1$ and the initial values of $A = 1000$ and $B = 0$. Be sure that the formulas you enter correspond to the differential rate equations. Run the model and set up an appropriate graph to see how A, B, and C change with time.
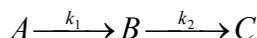
Forward Rxn

Reverse Rxn
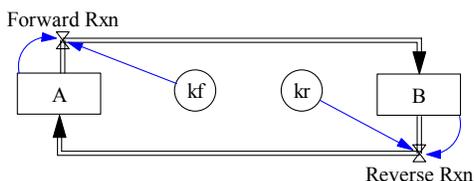
Run the model and answer the following questions:

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

      2) How will the graph change if $k_1 = 2$ and $k_2 = 1$? Change the model and see.

      3) Once equilibrium is established, is the ratio 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:

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

The integrated rate equations are:

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

Construct the model as shown below. Set $k_1 = k_2 = 1$ and the initial values of $A = 1000$ and $B = C = 0$. Be sure that the formulas you enter correspond to the differential rate equations. Run the model and set up an appropriate graph to see how A, B, and C change with time.
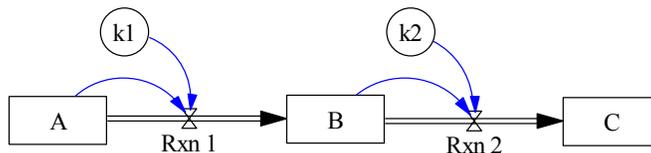

Run the model and answer the following questions:

      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 $k_2 = 1$? Change the model and see. 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 $k_2 = 5$? Change the model and see. 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 $k_2 = 10$? Change the model and see. Under these conditions, the series of reactions are known to be in "secular equilibrium".

Reversible Consecutive First-Order Reactions

Consider the reversible reaction system:

$$\begin{array}{ccc} k_1 & & k_3 \\ A \leftrightarrow B & \leftrightarrow & C \\ k_2 & & k_4 \end{array}$$
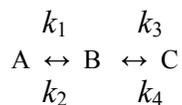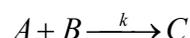
Write the differential equations for dA/dt, dB/dt, and dC/dt. Construct the model for this system of reactions. Set the initial value of $A = 1000$ and $B = C = 0$ and use $k_1 = k_2 = k_3 = k_4 = 1$. Be sure that the formulas you enter correspond to the differential rate equations. Run the model and set up an appropriate graph to see how A, B, and C change with time.

This model can be used to illustrate the "steady state" and "equilibrium" approximations often used in stepwise (complex) mechanisms by setting $k4 = 0$. 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, $(k_2 + k_3) \gg k_1$. 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, $(k_2 + k_3) \gg k_1$ and $k_2 \gg k_3$. 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:

$$A + B \xrightarrow{\ k\ } C$$

Write the differential equations for dA/dt, dB/dt, and dC/dt. Construct the model for this reaction system, as shown below. Note that the "Variable" icon must be used for A and B and the entries are A_o-C and B_o – C, respectively.
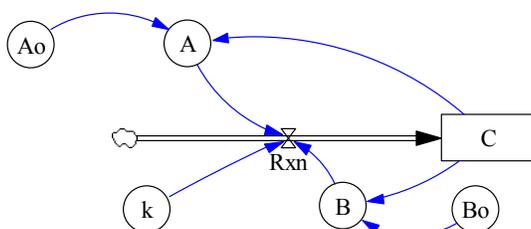
Set the values $A_o = B_o = 1000$ and $C = 0$ and use $k = 0.001$. Be sure that the formulas you enter correspond to the differential rate equations. Run the model and set up an appropriate graph to see how A, B, and C change with time.