First Order Rate Laws and Stella

The MacIntosh program Stella is useful for building models in a wide variety of areas, including population dynamics, chemistry, administrative science, biology, economics, and psychology. We will use Stella to build a model of a first-order reaction with stoichiometry:

$$A \rightarrow B$$

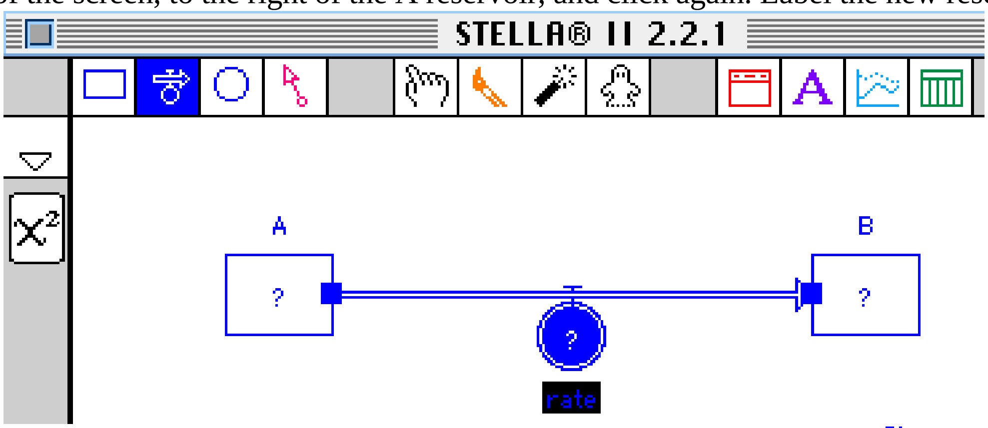
We will use a first-order rate constant k_1=0.3 sec^{-1} and an initial concentration of A of 1.0 M. In Stella, the concentration of A will be represented as a reservoir that empties through a pipe (the chemical reaction) to fill the B reservoir. A valve in the pipe controls the flow of reactants to products and will represent the rate law:

$$-\frac{d[A]}{dt} = k_1[A] .$$

Flow has the units of stuff per unit time as does a reaction rate, so flow and reaction rate are analogous.

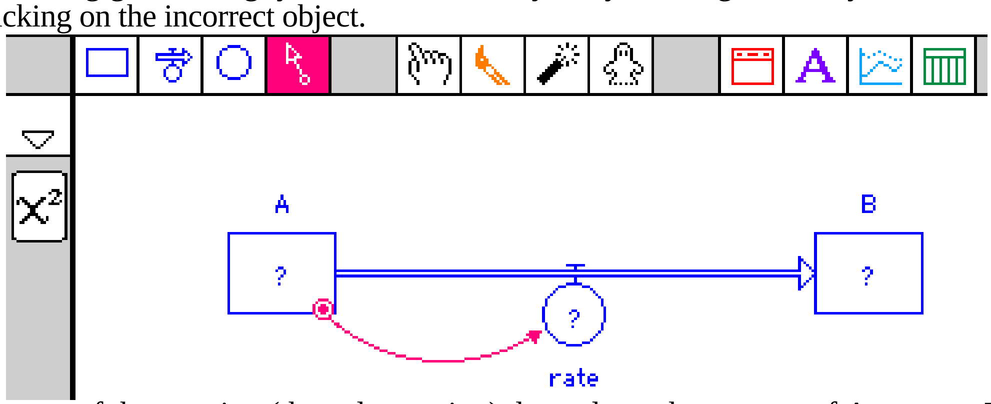
To build your model, do the following steps. Double click on the Stella II icon.

(1) The reservoir icon, a rectangle, is the first icon on the top of the of the screen. Click the mouse on the reservoir icon, then position the cursor on the screen and click again. Type in the name of the reservoir: call it "A". Click the mouse on the reservoir icon again, position the cursor in the center of the screen, to the right of the A reservoir, and click again. Label the new reservoir "B".



(2) Set up the pipe between the two reservoirs by clicking on the pipe icon, ,and then dragging the cursor from the middle of the A reservoir to the side of the B reservoir. Type in the label for the valve: "rate". The main window should now appear as shown above.

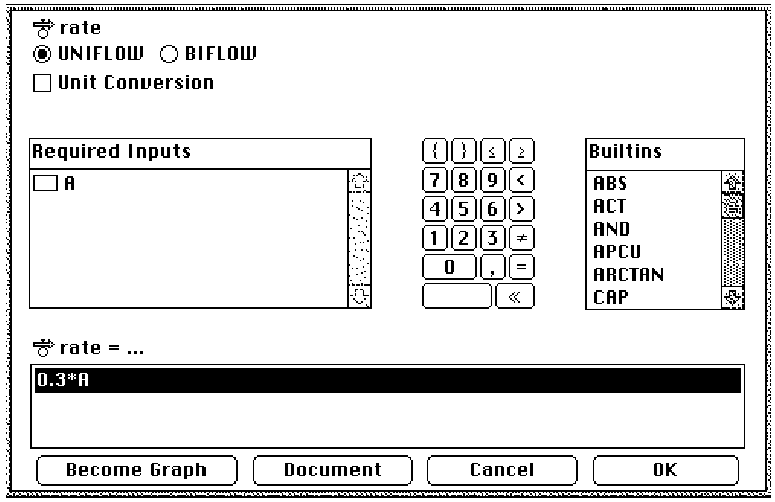
If something goes wrong, you can erase an object by clicking on the dynamite icon () and then clicking on the incorrect object.



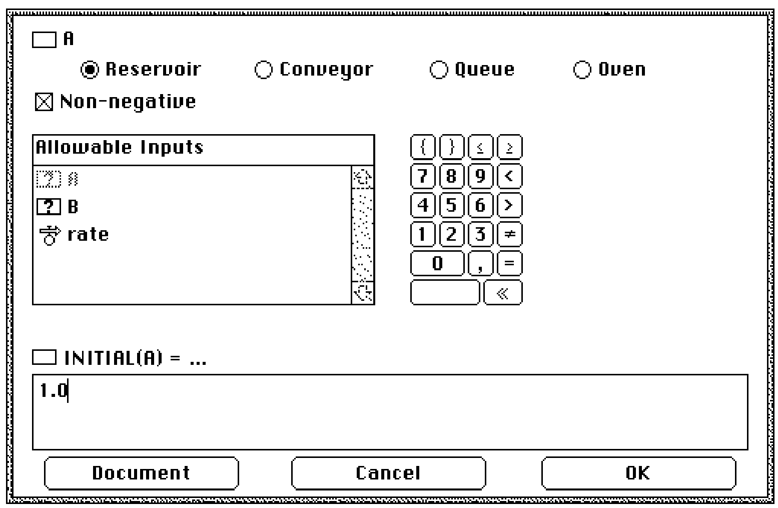
(3) The rate of the reaction (the valve setting) depends on the amount of A present. To set up this dependence, click on the arrow, , then drag the cursor from the middle of the A reservoir to the

circular portion of the valve. You should read an arrow as "depends on". Thus, the rate (the valve setting) "depends on" A.

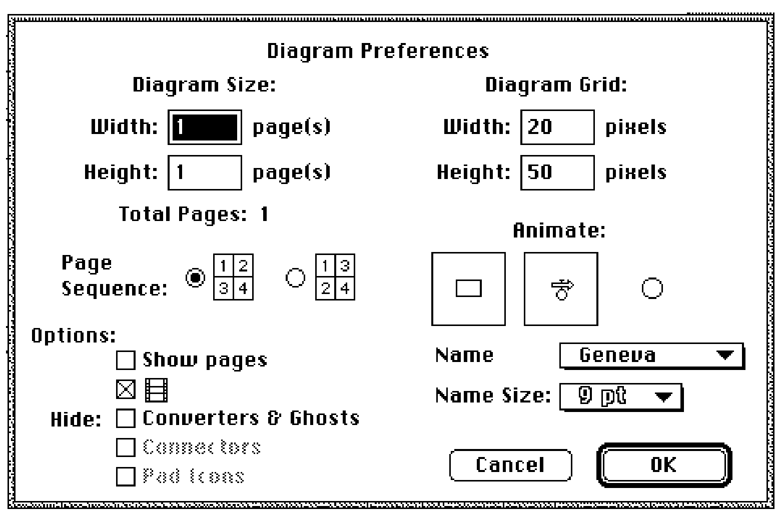
(4) Click on the globe icon in the upper left corner of the window. The globe will change to a χ^2. You can now set up the rate law. Double click on the circular portion of the valve; the circular portion is called the valve controller. A dialog box will appear as shown at right. Type in 0.3*A. Click on OK to get back to the diagram.



(5) The initial conditions must now be set. Double click on the A reservoir and type 1.0. The screen should appear as at right, showing that the initial concentration of A, INITIAL(A), is equal to 1.0. Click on OK. Set the initial concentration of B to zero in an analogous manner.



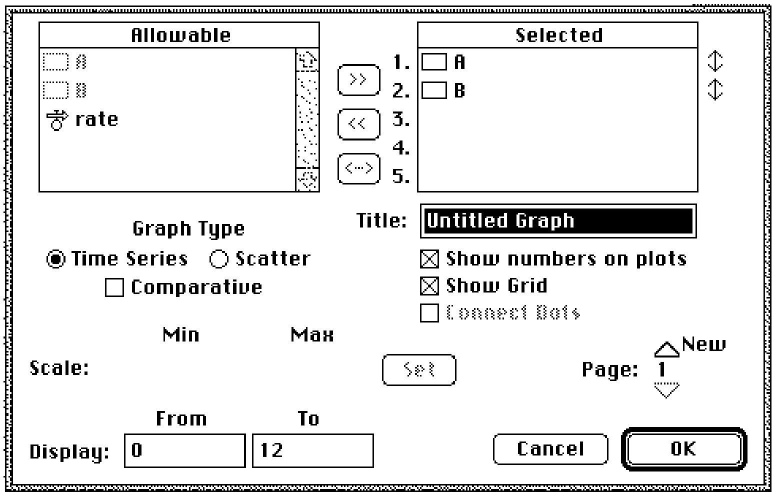
(6) To see the reservoirs fill and empty we must change some preferences: pull down the Edit menu and choose "Diagram Prefs..." Under "Animate" click on the reservoir and pipe icons. The screen will appear as shown at right.



(7)You can now run your model by pulling down the Run menu and selecting Run. If you wish to stop a run before completion, pull down the Run menu and choose Stop.

(8) We now wish to graph the concentrations as a function of time.

Click on the Graph Pad icon, , in the right most group of icons. Then click the mouse under the B reservoir. Double click on the Graph Pad icon after it appears. A dialog box appears, as shown at right. Click on the A reservoir line (the first line) in the "Allowable" scroll box. Click on the ">>" button to select the A variable for plotting. Click on the B reservoir line in the "Allowable" scroll box. Again, click on the ">>" button to select the B variable for plotting. Next click OK. Rerun the model. After the graph is complete, to return to the diagram, click on the "Go-away" box in the upper left-hand corner of the Graph Pad window.



After you finish modifying your model, as requested in the following problems, pull down the File menu and choose Quit.

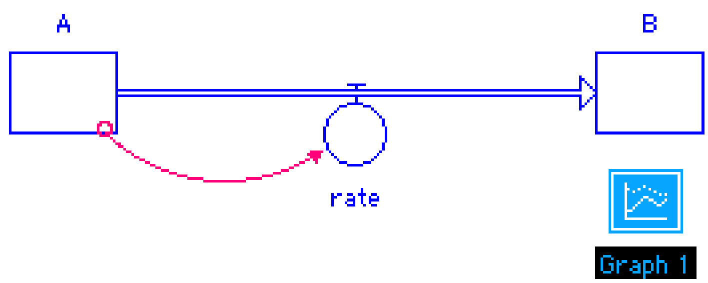


Figure 1. Completed first-order reaction model.

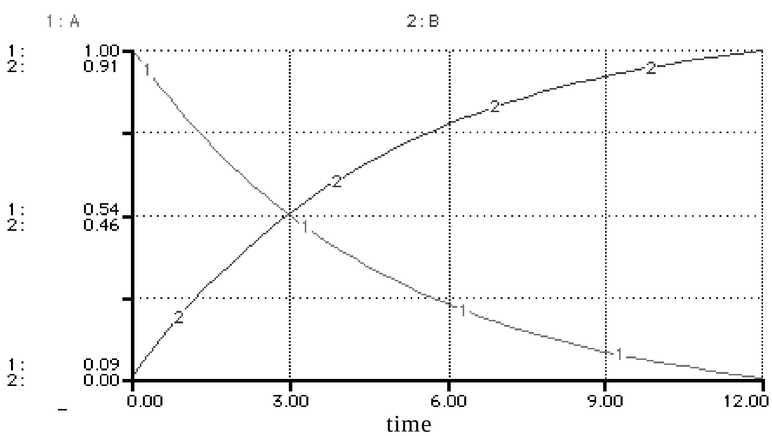
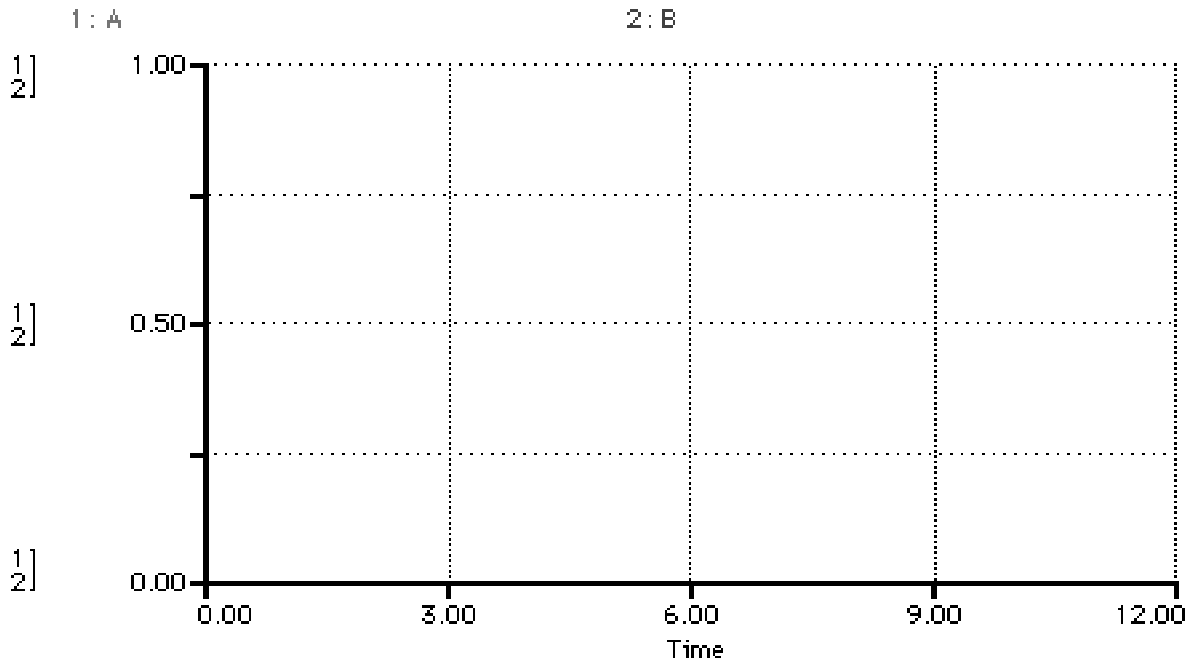


Figure 2. First order results shown for $k_1 = 0.2\ sec^{-1}$.

Stella Study Questions

Chemistry 142 Name ________________________

1) Change the rate constant to 0.8 (sec^{-1}) and rerun the model. Did the reaction run faster or slower? (To change the rate constant, double click on the valve controller and edit the :"rate=" line.) Superimpose the time dependence, for the disappearance of reactants and appearance of products for first order reactions with rate constants of 0.3 sec^{-1} and 0.8 sec^{-1} on the graph below.



2) The purpose of this exercise is to understand the statement:

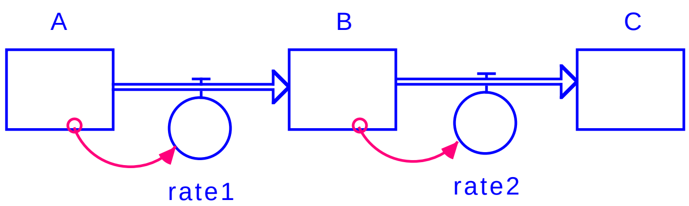
"The slow step is the rate determining step."

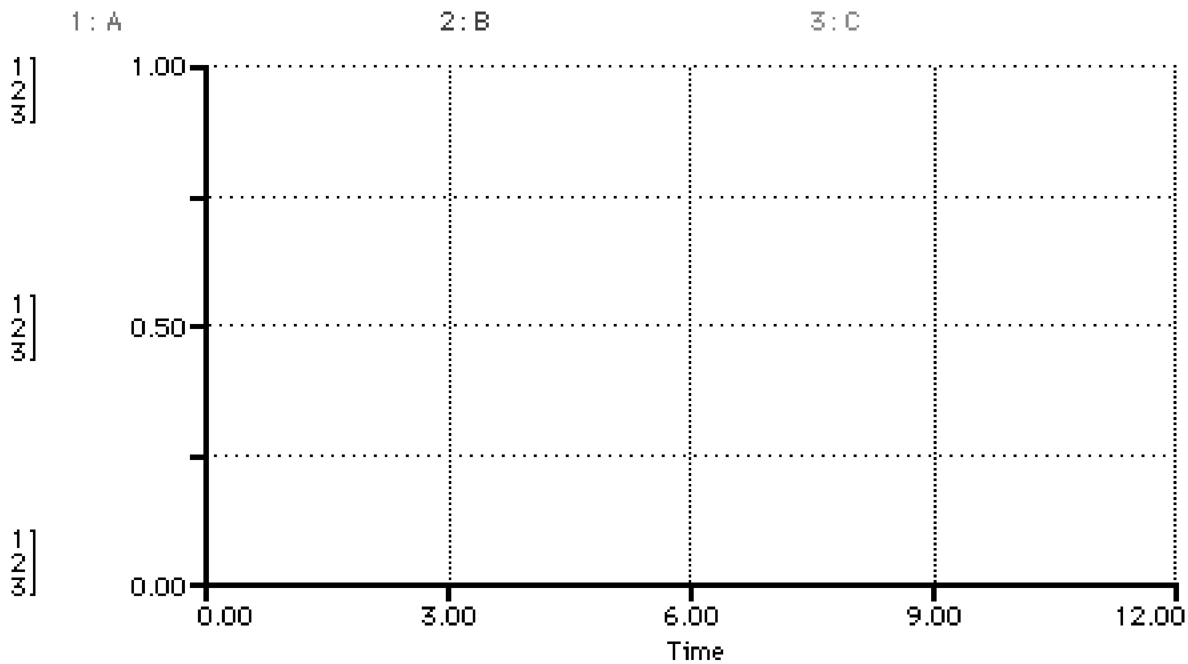
Model a two step mechanism with the following rate laws:

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

$$rate_1 = k_1[A] \qquad\qquad rate_2 = k_2[B]$$

This is called a consecutive reaction. Choose k_1=0.8 and k_2=0.3. Predict the step that will be the rate determining step. Plot the time dependence for A, B, and C. To which curve in question 1 does the disappearance of A correspond, k=0.3 or k=0.8? To which curve in question 1 does the appearance of C correspond? According to the plot, which step is the rate determining step? (To run this model, add a third reservoir and add a second pipe. The first rate law is the same as in problem 1. Add the new rate law for the second valve controller. Remember that the second rate "depends on" B. Don't forget to set initial conditions for C. An example of the model is shown below.


A
B
C
rate1
rate2


1: A
2: B
3: C
1.00
0.50
0.00
0.00
3.00
6.00
9.00
12.00
Time