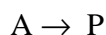


First Order Rate Laws and the Kinetics Mechanism Simulation Program

The “Kinetics Mechanism Simulation” program (kine) is useful for building models in a wide variety of areas, including population dynamics, chemistry, administrative science, biology, economics, and psychology. We will use the program to build a model of a first-order reaction with stoichiometry:



We will use a first-order rate constant $k_1=0.05 \text{ sec}^{-1}$ and an initial concentration of A of 1.0 M. The concentrations of A and P will be represented as beakers that fill and empty. The program assumes that the entered reactions are steps in the mechanism of the reaction. Because the reactions are elementary reactions in the mechanism, the rate law for each step can be determined from the stoichiometry:

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

The units are not specified in the program. However, the units must be consistent for the time, the concentrations, and the rate constants. For example, if the time is in units of minutes and the concentrations are in units of M, then the rate constants for first-order reactions will be in units of minutes^{-1} and the rate constants for second order reactions will be in units of $\text{M}^{-1} \text{ minutes}^{-1}$.

To build your model, do the following steps. The Web page for the program can be accessed from the course homepage.

- (1) The default screen starts with A as a reactant. Pull down the first product menu and choose “P.”



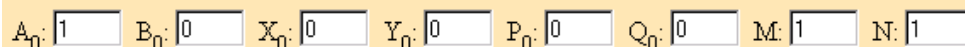
- (2) We will use the default rate constant for the forward reaction and the default value of zero for the reverse reaction.

If something goes wrong, you can erase everything and start over by clicking on “Clear.”



- (3) The initial conditions must now be set. We will use the default value of 1. We will assume the units are molar, M.


Initial Conditions:



(M and N are constant concentration reservoirs, such as a background gas, the vessel walls, or a constant flow source.)

- (4) We will also use the default Maximum time setting of 150 and 750 time steps. Now click on “Initialize” and then click repeatedly on “Step.” The beakers should empty and fill. The tabulated values for the concentrations will appear in the “Tabulation Window.” You can cut and paste these values into EXCEL for fancy plotting or for curve fitting.

- (5) We now wish to graph the concentrations as a function of time. Choose the variables to plot as A and P.



Click on "Run Full." A new plot window should now be displayed with the time course for your reaction. Sketch the curve on the graph axes given in Question 1 in the following homework sheet. After viewing, click this window away by clicking in the go-away box (the box in the upper right side of the graph window for Windows systems and the box in the upper left side of the graph window for Macs).

Homework:

1) Change the rate constant to 0.2 and rerun the model. Did the reaction run faster or slower? Superimpose the time dependence for the disappearance of reactants and appearance of products for your first order reactions with rate constants of 0.05 sec^{-1} and 0.2 sec^{-1} on the graph below.



Consecutive Reactions

A consecutive reaction follows a two-step mechanism where an intermediate from the first step is consumed in the second step. If we assume that both steps are first order, we find the following rate laws:

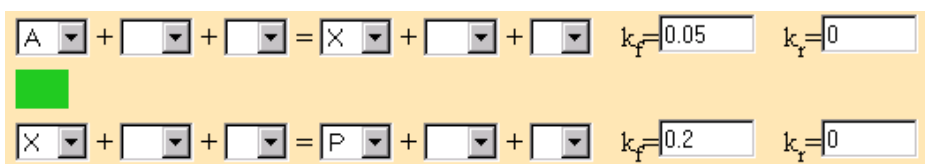


In determining the overall rate law for the reaction, we use the rule that:

"The slow step is the rate determining step."

The following project demonstrates what this rule means. First we will build the mechanism with the first step having the smaller rate constant. That is, the first step will be the slow step. In your homework you will choose the opposite; the second step will have the smaller rate constant.

The First Step as the Slow Step: Choose $k_1=0.05$ and $k_2=0.2$. Predict the step that will be the rate determining step. The mechanism will look like:



Plot the time dependence for A, X, and P. Your results should appear as in Figure 1. To which curve in Homework question 1, above, does the disappearance of A correspond, $k=0.05$ or $k=0.2$?

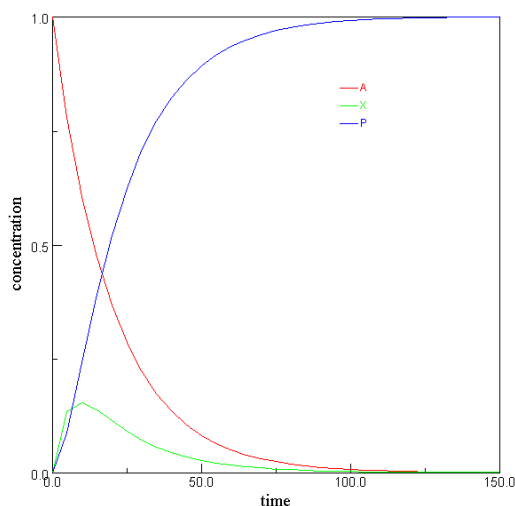


Figure 1. $k_1=0.05$, $k_2=0.2$

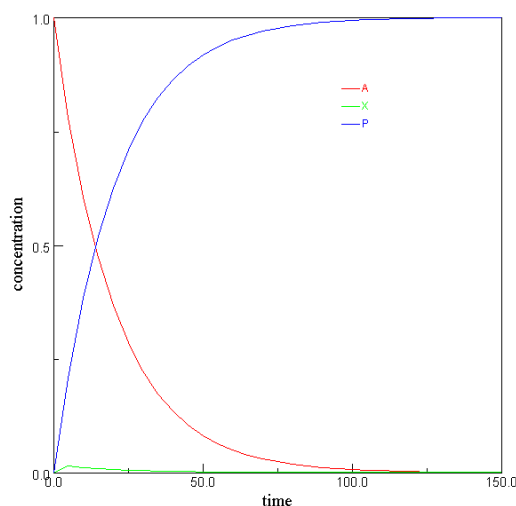


Figure 2. $k_1=0.05$, $k_2=2.0$

The disappearance of A in Figure 1 corresponds to the simple first-order reaction with the slower rate constant, $k=0.05$. To which curve in question 1 does the appearance of P correspond? From Figure 1 we see that the appearance of P corresponds, once again to the first-order reaction with the slower rate constant. In other words the slow step is the rate determining step. The rate law for the overall process can then be written:

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

or

$$\text{rate} = k_1[A]$$

We can approach this issue in another way. If the first step is the rate determining step, then we should be able to change k_2 and the rate of disappearance of A and the rate of appearance of P shouldn't change. Try this idea out: change k_2 to 2.0. What do you see? Your results should appear as in Figure 2. Notice that the curves for A and P hardly change at all, even though we increased k_2 by a factor of 10! The size of k_2 doesn't have an effect on the overall rate of the reaction. What does change in going from $k_2 = 0.2$ to 2.0?

Notice that the concentration of the intermediate, X, is very sensitive to the size of the second rate constant. When the k_2 value was increased from 0.2 to 2 the concentration of the intermediate doesn't build up as much. As the intermediate becomes more reactive, k_2 becomes larger. If the intermediate is more reactive, it doesn't last as long and the concentration doesn't build up.

Homework:

2) The Second Step as the Slow Step: Choose $k_1 = 0.2$ and $k_2 = 0.05$. Predict the step that will be the rate determining step. Plot the time dependence for A, X, and P. To which curve in question 1 does the disappearance of A correspond, $k = 0.05$ or $k = 0.2$? To which curve in question 1 does the appearance of P correspond? According to the plot, which step is the rate determining step? An example of the model is shown below.

+ + = + + $k_f = 0.2$ $k_r = 0$

+ + = + + $k_f = 0.05$ $k_r = 0$

You can sketch your results below.



Kinetics Mechanism Simulation Study Questions – Handin Sheet

Name _____

Use this sheet to report your results from homework questions 1 and 2, above:

1) In question 1, did the reaction run faster or slower for $k = 0.2$?

Superimpose the time dependence, for the disappearance of reactants and appearance of products for first order reactions with rate constants of 0.05 sec^{-1} and 0.2 sec^{-1} on the graph below. In other words, please redraw your graphs from question 1, above:



2) In question 2, with the second step as the slow step, to which curve in question 1 does the disappearance of A correspond, $k=0.05$ or $k=0.2$?

To which curve in question 1 does the appearance of P correspond?

According to your plot, which step is the rate determining step?

Please redraw your graphs from question 2, above:

