

# Simulations of Chemical Kinetics

A Tutorial to be Used With the Weber Labs Web-Based Kinetics Simulations

(see <https://jila.colorado.edu/files/HomeAnimation.html>)

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## Overview

This tutorial is meant to guide faculty and students through the exploration of the Chemical Kinetics Simulation Web Page (see URL above). In the simulation experiments below, we will refer to the numerical parameters as follows:

Concentration of a substance A:	$[A]$
Initial concentration of A:	$[A]_i$
Rate constants:	$k$ , with the appropriate indexes
Time step size:	$\Delta t$
Number of simulation steps:	$N$

## Learning Goals:

After reading the manual of the simulation package (see link in the upper right corner of the simulation landing page, URL above) and going through this tutorial, students should be able to

- describe the time-dependence of concentrations in simple chemical kinetics;
- qualitatively predict how changing the rate constants influences the time dependence of concentrations in simple chemical kinetics without resorting to calculations;
- distinguish between the parameters that describe the physicochemical models involved here and those that merely determine how the simulation runs its calculations;
- evaluate whether a set of simulation parameters for the time evolution of a system are meaningful, given the physicochemical model for the system;

## 1. Simulation Experiments on First-Order Kinetics: $A \rightleftharpoons B$

- a.) Start with the pre-set parameters ( $k_1 = 0.5 \text{ s}^{-1}$ ;  $k_{-1} = 0.3 \text{ s}^{-1}$ ;  $\Delta t = 0.01 \text{ s}$ ;  $N = 100$ ), and check the boxes for showing the concentrations of A and B. Describe what you see in the graphs.
- b.) Without changing the parameters, predict (or guess) what will happen as time progresses further. Will the concentrations become the same at some time? Will they change monotonically in time (i.e., will one always increase, the other always decrease as time increases), or will there be maxima and minima of the concentrations as a function of time? What do you think is the behavior as  $t \rightarrow \infty$ ? Now change the time step size to  $\Delta t = 0.1 \text{ s}$  to check your predictions.
- c.) Change the initial concentration of B to  $[B]_i = 1 \text{ M}$ . Describe in one sentence what happens.
- d.) Now activate the cursor by checking the cursor box. The top row is the time, the two lower rows display the concentrations of A and B. Set  $[A]_i = 1 \text{ M}$ ,  $[B]_i = 0$ ;  $k_1 = 0.5 \text{ s}^{-1}$ ,  $k_{-1} = 0$ ,  $\Delta t = 0.1 \text{ s}$ , and  $N = 100$ . Observe what happens in the graphs. Has the reaction reached equilibrium yet at the end of the time window shown in the graph? How can you tell from the numbers for [A] and [B]?
- e.) Set  $[A]_i = 1 \text{ M}$ ,  $[B]_i = 0$ ;  $k_1 = k_{-1} = 0.5 \text{ s}^{-1}$ ,  $\Delta t = 0.1 \text{ s}$ , and  $N = 100$ . You will be able to see the concentrations approaching steady values, indicating that the simulated reaction reaches equilibrium conditions. Compare these values with the equilibrium constant  $K$  that you can calculate from the values of  $k_1$  and  $k_{-1}$ . Pick other values for the rate constants and compare again with  $K$ .
- f.) To get an intuition for how the output of a simulation depends on the numerical parameters of the simulation itself (as opposed to the physical parameters of the reaction), we will now look at the time step size,  $\Delta t$ , and the number of steps,  $N$ . Set  $k_1 = k_{-1} = 0.10.1 \text{ s}^{-1}$ ,  $\Delta t = 1 \text{ s}$ , and  $N = 50$ . Now increase both rates in steps of  $0.1 \text{ s}^{-1}$ . Describe qualitatively the changes you see. At what value do you clearly stop getting meaningful results? Why do you think that happens? What can you do to make the simulation meaningful again, keeping the same rates?
- g.) With  $k_1 = 0.5 \text{ s}^{-1}$ ,  $k_{-1} = 0.3 \text{ s}^{-1}$ ,  $\Delta t = 0.02 \text{ s}$ , and  $N = 100$ , you can see that you certainly don't see the concentrations reach equilibrium. Now increase the number of steps,  $N$ , in increments of 100 steps. How many do you need to reach equilibrium within the accuracy of the simulation? Can you formulate a relationship between  $\Delta t$ ,  $N$ , and the order of magnitude of the rate constants for what is needed to reach equilibrium? Test your hypothesis with other values of  $k_1$  and  $k_{-1}$ , including those where the forward and back reaction rate constants are different by a factor of 10 or more, keeping in mind that the simulation needs to have sufficiently small time steps to be meaningful.
- h.) Feel free to play with the simulation, changing whatever parameters you like. The simulation becomes slow if you ask it for too many time steps.
- i.) With  $k = 0.5 \text{ s}^{-1}$  and  $k_{-1} = 0$ , use the cursor to "measure" the half-life of A.
- j.) Again using the cursor and with the settings like in (i), "measure" the concentration of A every 0.1 s. Compare the results with the integrated rate law.

## 2. Simulation Experiments on Second-Order Kinetics:

### 2.1. $2A \rightleftharpoons B$

- What are the reaction orders of the forward and backward reaction, judging from the units of  $k_1$  and  $k_{-1}$ ?
- Use the method of initial rates to confirm your result from part (a). Use  $\Delta t = 0.1$  s,  $k_1 = 0.5 \text{ M}^{-1}\text{s}^{-1}$ , and  $k_{-1} = 0.3 \text{ s}^{-1}$ . For the forward reaction, this is easiest if  $[B]_i = 0$ . Start with  $[A]_i = 0.1$  M, and increase it in steps of 0.1 M to 0.4 M. Use 0.1 s for the time interval in the “measurement” of the initial rate. Repeat the simulation using 1 s as the time interval, and discuss any differences you may find. Use a similar strategy to “measure” the order of the back reaction.
- With  $[B]_i = 0$ ,  $\Delta t = 1$  s,  $k_1 = 0.1 \text{ M}^{-1}\text{s}^{-1}$ , and  $k_{-1} = 0$ , vary  $[A]_i$ . Describe your observation how the shape of the curve of  $[A]$  behaves as you perform these different simulations. Now repeat the experiment, but with  $[A]_i = 0$ ,  $\Delta t = 1$  s,  $k_1 = 0$ , and  $k_{-1} = 0.1 \text{ s}^{-1}$ , varying  $[B]_i$ . What is different, and why?
- The concentrations must behave accordingly. Set the  $[A]_i = 1 \text{ mol}\cdot\text{L}^{-1}$ ,  $[B]_i = 0$ ,  $\Delta t = 1$  s,  $k_1 = 0.1 \text{ M}^{-1}\text{s}^{-1}$ , and  $k_{-1} = 0.1 \text{ s}^{-1}$ . Calculate the equilibrium constant  $K$  based on these settings. Use the final concentrations for A and B (3 significant figures) to determine the equilibrium constant  $K$ . Do the predicted and simulated values for  $K$  agree? If not, why not? What do you need to do to get them to agree?
- With  $k = 0.5 \text{ s}^{-1}$  and  $k_{-1} = 0$ , use the cursor to “measure” the half-life of A.
- Again using the cursor and with the settings like in (e), “measure” the concentration of A every 0.1 s. Compare the results with the integrated rate law.

### 2.2. $A + B \rightleftharpoons C$

- What are the reaction orders of the forward and backward reaction, judging from the units of  $k_1$  and  $k_{-1}$ ? What order is the forward reaction in A and B, respectively?
- Use the method of initial rates, similar to part (b), to confirm your answer from part (g). Consider the right starting point for the initial concentrations of A and B for determining each reaction order.
- Again using the cursor and with the settings like in (e), “measure” the concentration of A every 0.1 s, using initial concentrations. Compare the results with the integrated rate law.

### 3. Simulation Experiments on Sequential Reactions: $A \rightleftharpoons B \rightleftharpoons C$

- a.) Allow only forward reactions. Start with  $k_1 = k_2 = 0.1 \text{ s}^{-1}$ ,  $k_{-1} = k_{-2} = 0$ ,  $\Delta t = 0.1 \text{ s}$ , and  $N = 500$ , with nothing but  $1 \text{ mol}\cdot\text{L}^{-1}$  of A present at the beginning of the simulation. Describe the time dependent behavior of all concentrations.
- b.) Start with the same settings as in part (a). At what time is the intermediate concentration [B] at its maximum? Now vary  $k_1$  in steps of  $0.1 \text{ s}^{-1}$  until you get to  $k_1 = 1.0 \text{ s}^{-1}$ . Make a table containing  $k_1$  and  $t_{B,\text{max}}$ . Use the integrated rate law for [B] to calculate the maximum concentration of B in time. Compare your result with the simulated results from part (b) and plot  $t_{B,\text{max}}$  against  $k_1$  for  $k_1 > 0.1 \text{ s}^{-1}$ . Note: The data point from the integrated rate law for  $k_A = 0.1 \text{ s}^{-1}$  is tricky!
- c.) Start with the same settings as in part (a). Now vary  $k_2$ , increasing it in steps of 0.1 until you get to  $k_2 = 1.0 \text{ s}^{-1}$ . Describe the time dependent behavior of all concentrations. What is the role of the intermediate B as  $k_2$  grows to become much larger than  $k_1$ ? If you go to very large ratios for  $k_2/k_1$ , what other simulation does the result remind of (try  $k_1 = 0.1 \text{ s}^{-1}$ ;  $k_2 = 5 \text{ s}^{-1}$ )? Explain why this situation ( $k_2 \gg k_1$ ) is called “steady state approximation”.
- d.) Let’s introduce back reactions, starting with the same settings as in part (a), but  $k_1 = k_{-1} = 0.1 \text{ s}^{-1}$ ,  $k_2 = 0.001 \text{ s}^{-1}$ ,  $k_{-2} = 0$ . Explain why this situation is called “pre-equilibrium”.
- e.) What initial concentrations and rate constants do you need to create a situation where the roles of A and C are exactly reversed from part (a)? Use screen shots to prove that you were able to do that.
- f.) Playing with the different rate constants of the system, formulate a general rule for the rate constants to make one of the three substances the most abundant species at equilibrium, regardless of initial concentrations. None of the rate constants must be zero.

Stay tuned for tutorial parts on parallel reactions, Lindemann-Hinshelwood kinetics, Michaelis-Menten kinetics, and a catalytic cycle.