
2.1 Objectives

After completing this module, a student should be able to:

- Describe the conditions under which computer models may not be completely reliable.
- Compare and contrast two different types of modeling: agent-based and dynamic systems modeling.

2.2 Definitions

- Agent-based modeling
- Bimolecular
- Concentration
- Dynamic systems modeling
- Equilibrium
- Kinetics
- Rates
- Reaction
- Unimolecular

2.3 Motivation

Often in science, we investigate and explore processes that change over time. This module will introduce two classes of computational science for how you can use computers to model these processes: *agent-based* and *dynamic systems*. We will use the area of chemical reaction kinetics to explore these two classes.

First, we will work with two models from NetLogo, a program that uses agent-based modeling. Agent-based modeling simulates autonomous agents that act and are acted upon, to view the impact on the whole system. In our examples, NetLogo will show a graph of the change in a reaction over time along with visual representations of individual molecules and their changes and interactions during the course of the reaction.

Next, we will investigate two models with the Vensim Personal Learning Edition (PLE) software, a program that utilizes dynamic systems modeling. Vensim allows the user to model a chemical reaction from the perspective of the chemical equations and the mathematical model of the reaction dynamics. The model will provide predictive information about the change in a reaction over time.

2.4 Introduction

Before we delve into the models, a brief review of chemical reaction kinetics is needed. Say we understand that when we combine two molecules in a beaker, a reaction will take place as described by the following chemical equation:



where A, B, and C represent three different chemical molecules and the double arrow represents that the equation is reversible – that is, the chemical reaction can go both ways, forward from A+B to C, and in reverse from C to A+B. By convention, the left side components are called the reactants, with the right side components called the products. The reaction will reach a dynamic equilibrium, meaning there will be a stable number of A, B, and C molecules all in the beaker at the same time. (That does not mean the reactions cease, just that there is a balance between C being produced and being used.)

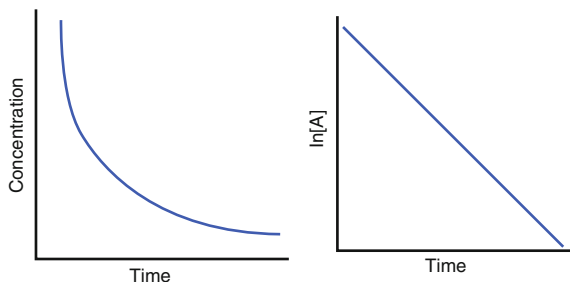
Note that Eq. (2.1) does not provide any information about the rate at which the reaction will take place, nor what the equilibrium conditions may be. To understand that, a reaction rate needs to be determined. The following shows a hypothetical relationship between concentration and time that could have been determined from an experiment (by putting the reactants A and B together in a beaker and measuring the concentration of A over time as the reaction takes place).

Since the $\ln[A]$ plot in Fig. 2.1 shows a straight line (linear) relationship, we would call this a first-order reaction. The slope of that line would be equal to k , the reaction rate coefficient. Mathematically:

$$\text{Rate} = -\frac{d[A]}{dt} = k[A] \quad (2.2)$$

$$[A] = [A]_0 e^{-kt} \quad (2.3)$$

Fig. 2.1 Reactant concentrations vs time (From <http://chemwiki.ucdavis.edu/>)



where $[A]$ is the concentration at some time, and $[A]_0$ is the initial concentration. Equation (2.3) is considered the rate law for the reaction going in the forward direction. A similar rate law could be experimentally determined for the reverse reaction.

The forward and reverse reaction rate coefficients can then be used in models to represent the chemical reaction over time.

Answer It!

Q02.01: What is a reversible reaction?

Q02.02: What is a reaction rate?

Q02.03: What occurs at equilibrium in a reversible reaction?

2.5 Agent-Based Chemical Kinetics

Open up the NetLogo model of Simple Kinetics 1 using NetLogo Web which can be found at <http://www.netlogoweb.org/launch#http://www.netlogoweb.org/assets/modelslib/Sample%20Models/Chemistry%20&%20Physics/Chemical%20Reactions/Simple%20Kinetics%201.nlogo>

The *Model Info* tab contains the description of the simulation and provides some basic information about the kinetics of a simple reversible reaction.

Choose the values of the rate constants, k_u and k_b with appropriate sliders. Rate constant k_b controls the rate of the reaction by which two green molecules turn bimolecularly into a single red molecule. Similarly the constant k_u controls the rate of the reaction, by which a red molecule turns unimolecularly into two green molecules.

You also need to set the initial number of molecules (*number* slider). You are allowed to choose anything from 0 to 100. Start with a reasonable number of around 100.

Having chosen values for the rate constants and initial molecules, click *SETUP* to clear the world and create an initial number of green molecules. (Note: this model only starts with green molecules, but one could program it to also start with some red molecules.) Click *Go* to start the simulation. You will see molecules floating

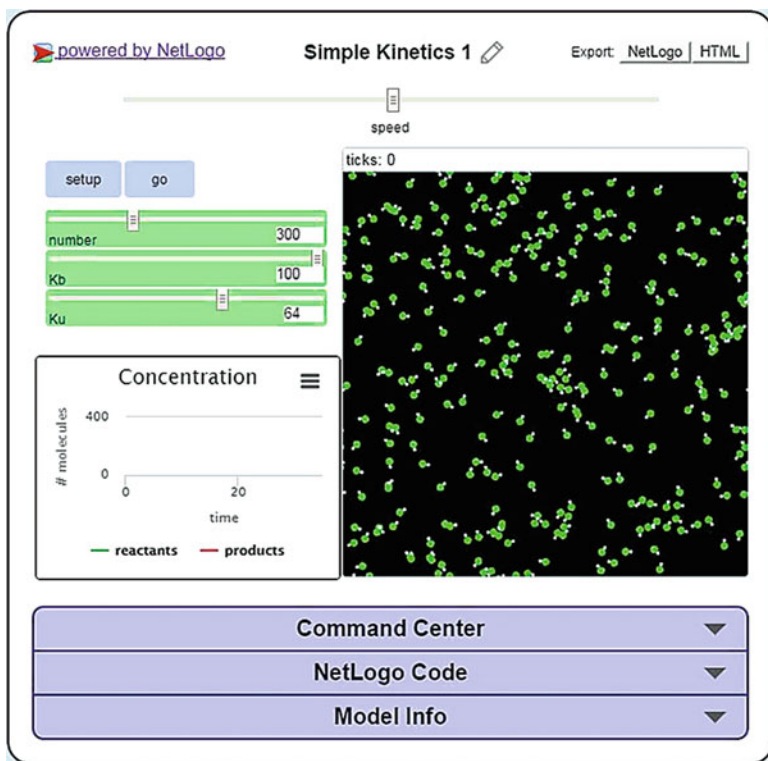


Fig. 2.2 NetLogo Web – Simple Kinetics 1 model (Screen capture from www.netlogoweb.org)

around the box and changing color. Pay attention to the plot of the concentrations. You can press *Go* a second time to stop the simulation. When you have seen what happens, try changing the sliders to different values, press *setup* and *go*, and observe what happens (Fig. 2.2).

Answer It!

- Q02.04: What is the chemical reaction equation for this model? (In a form similar to Eq. (2.1).)
- Q02.05: What variable name does the model use for the forward reaction rate coefficient?
- Q02.06: What variable name does the model use for the reverse reaction rate coefficient?
- Q02.07: What is the Principle of Stationary Concentrations? (See the Model Info tab.)
- Q02.08: Do the plots soon reach stationary concentrations when running the model?

- Q02.09: How does changing the concentrations of reactants and products (numbers of molecules) in the system affect the equilibrium?
- Q02.10: Does it take more or less time to reach a stationary state under various conditions?
- Q02.11: How do the stationary concentrations depend on the values of k_u and k_b ?
- Q02.12: You can change k_u and k_b while the model is running. See if you can predict what the stationary concentrations will be with various combinations of k_u and k_b . What were some of your predictions, and did you get what you expected?
- Q02.13: What happens if you choose k_u , k_b , or both to be 0?

The way the Simple Kinetics 1 model is currently designed, it is a reasonable simulation for behavior of chemical reactions. However, can we always depend on our computer models? Try selecting 1 for the number of molecules (press *Setup* after you do this), then run the simulation. What happens? What happens to the molecules and the graph? What does this tell us about the reliability of computer simulations?

Now open up the NetLogo model of Simple Kinetics 2 using NetLogo Web: <http://www.netlogoweb.org/launch#http://www.netlogoweb.org/assets/modelslib/Sample%20Models/Chemistry%20&%20Physics/Chemical%20Reactions/Simple%20Kinetics%202.nlogo> This is a model that is very similar to Simple Kinetics 1, but with some important differences/additions as we shall discuss. As before, choose the values of k_u and k_b with appropriate sliders. You will not be able to choose as large a number for k_u as you did for the previous simulation.

What separates Simple Kinetics 2 from Simple Kinetics 1 are the features that have been added to simulate experimental changes other than rate constants: initial numbers of molecules, temperature of the reaction, and volume (the reaction box is shown with yellow walls that can vary in thickness).

Temperature changes have a unique effect on equilibrium compared with the other variables. You can observe this effect by toggling the *temp-effect* button on or off and using the slider to set the temperature of the reaction in Celsius. The initial number of molecules and the volume of the reaction also affects the concentration of the reactants and products (Fig. 2.3).

Start with the default *edge-size* and be sure that *temp-effect* is set to *off*. Click *SETUP* to clear the world and create an initial number of green molecules. Click *GO* to start the simulation. You should observe similar results to those you observed with Simple Kinetics 1.

Run the simulation several times, using the sliders and buttons to observe how initial numbers of molecules and reaction volume vary the concentration and affect the equilibrium. Then use the slider to observe how temperature affects the equilibrium. Finally, vary both concentration and temperature to see if your observed effects are impacted by some sort of interaction.

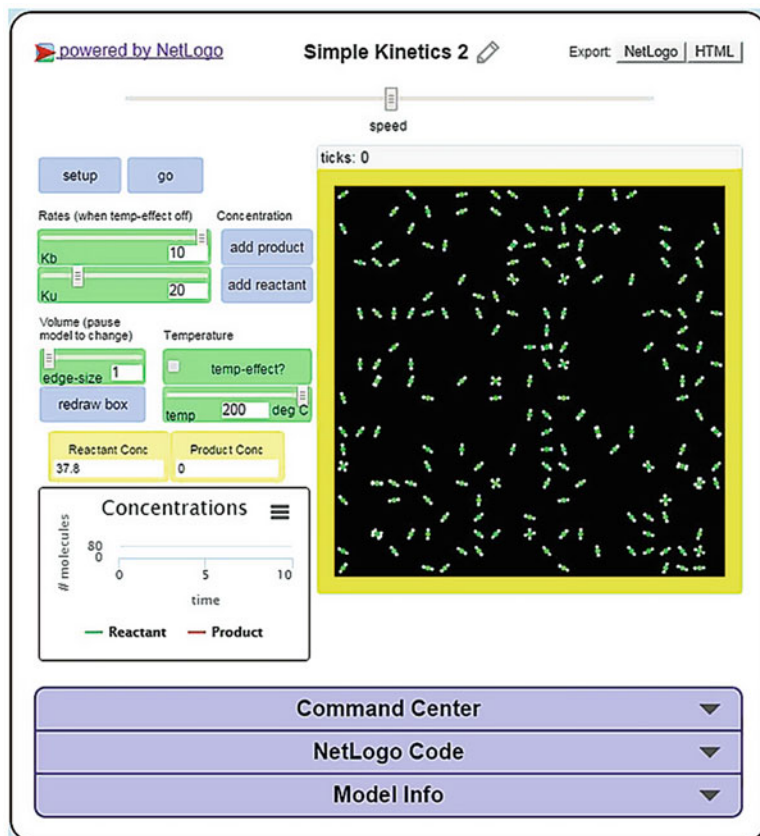


Fig. 2.3 NetLogo Web – Simple Kinetics 2 model (Screen capture from www.netlogoweb.org)

Answer It!

- Q02.14: If you could alter this model so that you can simulate what happens to the reaction at 1000° Celsius, do you think it would make much difference to the time at which equilibrium is achieved? Why? (Hint: Extrapolate your observations from increasing the temperature.) Why might the result not be consistent with your observations with the current model?
- Q02.15: Click on the *NetLogo Code* tab and find the portion of the program where the temperature effect is simulated. What equation is used to calculate this effect?
- Q02.16: When reading the information in the paragraph about the temperature effect calculation, can you see something that indicates that there may be a difference between the model and a real-world experiment?

Q02.17: What do your above observations mean for the reliability of this computer model? What might we need to be aware of when dealing with computer simulations?

Discuss It!

At an atomic level, chemical reactions take place during collisions of molecules. From your experimenting and examination of the code for the NetLogo models you just used, do you think the models are simulating the reactions from collisions? If not, why do you think the molecules were shown during the simulation? Would it be possible (or practical) to simulate chemical reactions at the atomic collision level?

2.6 Systems Dynamics Chemical Kinetics

The systems dynamics approach to modeling is based on a feedback loop or causal loop of organizing a system. The Vensim Personal Learning Edition (PLE) software is an icon-based systems dynamics modeling package that is available for free (<http://www.Vensim.com>). It uses a tank and flow representation of causal loops which can be used to model a chemical reaction based on mathematical equations. This model can provide predictive information about the change in a reaction over time.

Recall our original first-order chemical reaction Eq. (2.2), slightly rewritten:

$$[A_{t_2}] = [A_{t_1}] (1 - k\Delta t) \quad (2.4)$$

Therefore we can compute the concentration at time t_2 if we know the rate coefficient k , the concentration $[A]$ at the initial time (t_1). Similarly, for the next time, t_3 , we need to know the concentration and time at t_2 . This type of equation is a feedback loop since we need to feed the answer at t_2 back into the equation to get our answer for t_3 , and so on.

2.6.1 Simple First Order Reaction

Consider a first order reaction similar to the one you worked with in Netlogo. A first order reaction is one in which there is a linear relationship between the concentration of single reactant and the rate of reaction. The following are examples of first order reactions.



You can see from the above reactions that the number of molecules on the reactant side of the equation (one in Eq. (2.5), two in Eq. (2.6)) does not necessarily indicate the order of the reaction. A simple first order reaction can be indicated with the following simple chemical equation.



One can use differential rate equations to describe the progress of this reaction toward completion as the concentration of A, [A] decreased, and the concentration of B, [B] increases. The rate at which this reaction occurs can be expressed as the change in concentration (quantity) of each substance in the reaction with respect to time.

$$\frac{dA}{dt} = -k_1 A \quad \frac{dB}{dt} = k_1 A \quad (2.8)$$

To model a reaction with Vensim, we must build the system and program the equations. For a first order reaction, we will use tanks to represent the concentrations of our reactants and products, and a flow “valve” to represent the rate of change (Eq. 2.8). The resulting Vensim model is shown in Figs 2.4, 2.5 and 2.6.

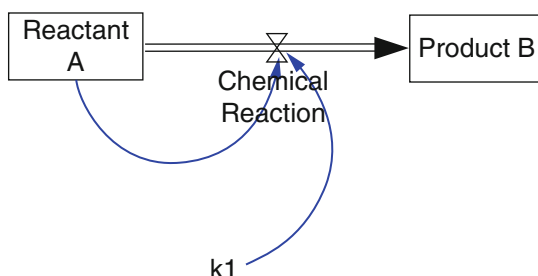
Answer It!

Create the first order chemical reaction simulation in Vensim. Use 1000 for the initial value of Reactant A, 0 for the initial value of Reactant B, and a value of 1 for k_1 . The Chemical Reaction equation will be the multiplication of k_1 and Reactant A. The time step should be .0625, with a Final Time of 10 (seconds). Use the RK4 integration type. Graph the values of Reactant A and Product B.

Q02.18: What is the sum of A and B at any given time?

Q02.19: Thinking back to the original reaction that you are modeling and the starting conditions for the chemicals (A and B), can you explain why the sum of A and B at any given time equals this value?

Fig. 2.4 First order reaction in Vensim



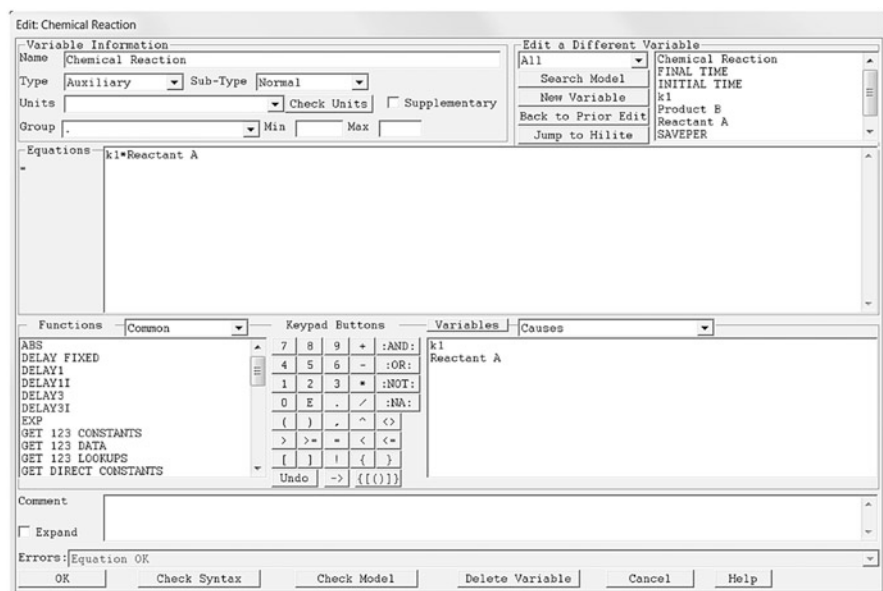


Fig. 2.5 Reaction rate equations in Vensim

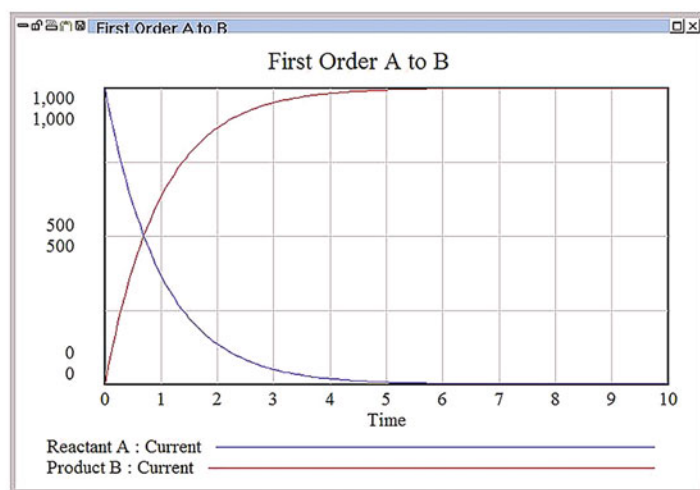


Fig. 2.6 Example output from first order reaction simulation

- Q02.20: At what approximate time does $A = B$ (50% completion)? Why might this point in the reaction be important for this reaction?
- Q02.21: How would the graph change if $k_1 = 2$? You can check your answer by clicking the *Equation* button. Click on k_1 in the model. To the right of

the equation sign in the dialogue box, change 1 to 2 and click *OK*. Run the model again and display the graph.

Q02.22: How does the graph change? Is this consistent with what you would expect, given the equation that you are using for the rate of this reaction?

2.6.2 Reversible First Order Reactions

A reversible reaction is one in which the reaction moves in both the forward and reverse directions. It is designated with a double-headed arrow and indicates an equilibrium (see definitions). A reversible first order reaction is one in which both the forward and reverse directions are first order. An example reaction would be the dissociation of a proton from a weak acid such as hydrofluoric acid.



As mentioned before in the discussion of the simple first order reaction, the number of particles on either side of the equation does not necessarily indicate the order of the reaction.

The following equation is the simplest general representation of a reversible first order reaction.



The differential rate equations are:

$$\frac{dA}{dt} = -k_1 A + k_2 B \quad \frac{dB}{dt} = k_1 A - k_2 B \quad (2.11)$$

Answer It!

Build the model as shown in Fig. 2.7 by using the instructions that are given previously. 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 and B change with time

Q02.23: What is the sum of A and B at any given time?

Q02.24: How will the graph change if $k_1 = 2$ and $k_2 = 1$? Change the model and see.

Q02.25: Once equilibrium is established, is the ratio B/A the same as k_1/k_2 ?

Q02.26: Try several different numbers for A , B , k_1 , and k_2 . Were you able to find values that gave graphical results that seem incorrect compared those that you saw previously? If so, what were those values? Under what conditions do you think this type of model would be unreliable?

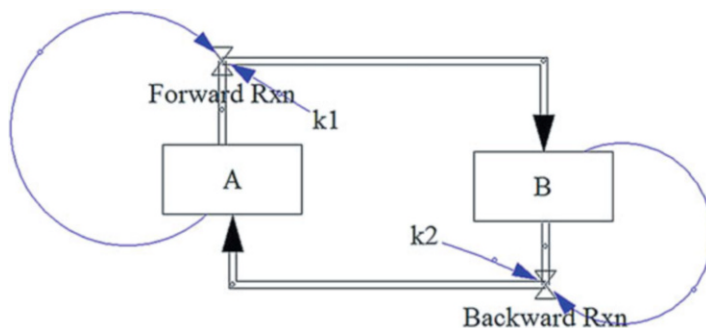


Fig. 2.7 Reversible first order reaction simulation in Vensim

Discuss It!

Which of the two classes of simulations (agent based or system dynamics) did you find easiest to implement to represent a first order chemical reaction? Which one was (potentially) more flexible to accommodate additional controls?

2.7 Computing Questions

- How reliable were the simulations you used/developed? Why?
- How valid were the simulations you used/developed? Why?
- How did you verify the simulations you used/developed?
- What were the possible sources of errors in your simulation(s)?
- Did your simulation(s) alleviate measure/time/cost and/or ethical issues? If so, how?

2.8 Related Modules

- Module 1: Introduction to Computational Science. Simulations are introduced.

Acknowledgement The original version of this module was developed by Dr. Willa Harper.

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