Chemical Thermodynamics, Equilibrium and Kinetics

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Numerical Computation of Chemical Kinetics

Objectives

In this computational lab, experimental chemical kinetics rates will be used to numerically simulate concentrations reaction constituents. The primary learning outcome of this lab is to learn how to numerically solve the time-dependent progress of complex chemical reactions.

1 Introduction

We are going to investigate numerical solutions of complex chemical reactions. Note that for all reactions/processes described here, you can assume the reactions are elementary steps (*i.e.* reaction stoichiometry matches reaction orders). First, we will start with a series of reactions given as

$$A \xrightarrow{k_1} B \xrightarrow{k_2} C, \tag{1}$$

where the first reaction has a rate law given as

$$\text{Rate} = k_1[A], \tag{2}$$

and the second reaction has a rate law given as

$$\text{Rate} = k_2[B]. \tag{3}$$

Both of the steps in the above sequence are first order processes. From class, we know that the time-dependent concentrations of $[A], [B]$, and $[C]$are given as

$$[A] = [A_0]\mathrm{e}^{-k_1 t} \tag{4}$$

$$[B] = \frac{k_1}{k_2 - k_1}\left(\mathrm{e}^{-k_1 t} - \mathrm{e}^{-k_2 t}\right) \tag{5}$$

$$[C] = [A_0] - [A] - [B], \tag{6}$$

assuming $[B_0] = [C_0] = 0$.

Now, suppose we did not konw the formula for $[A]$, but did have an expression for the rate (slope):

$$\frac{d[A]}{dt} = -k_1[A], \tag{7}$$

and also know the initial concentration of $[A]$. In this case, with a small step in time (Δt), the concentration of $[A]$ can be approximated as

$$[A] = [A_0] + \frac{\Delta[A]}{\Delta t} \times \Delta t = [A_0] - k_1[A_0]\Delta t. \tag{8}$$

We can compute $[A]$ at any arbitrary number of time steps as

$$[A]_{tf} = [A]_{ti} - k_1[A]_{ti}\Delta t, \tag{9}$$

where $[A]_{tf}$ and $[A]_{ti}$ are the concentrations at the final and initial times of Δt.

Similarly, $[B]$ can be calculated as

$$[B]_{tf} = [B]_{ti} + k_1[A]_{ti}\Delta t - k_2[B]_{ti}\Delta t, \tag{10}$$

where $[B]$ is gained from the first reaction and lost in the second reaction. Additionally, $[C]$ is given as

$$[C]_{tf} = [C]_{ti} + k_2[B]_{ti}\Delta t, \tag{11}$$

Part A

To investigate the above reaction, load `Kinetics-lab-1.py`, and execute the script.

1. How does it work with what you expect from the analytical solution?
2. Change the rate constants such that either the first or second step is the rate-limiting step. Record your results compared to your expectations from the analytical solutions.
3. Also change Δt and see what happens.
4. What are the shortcomings of this numerical method?

Part B

1. How would things change if you assume (and calculate the concentrations) using the steady state approximation?
2. Investigate how the behavior changes as you alter the values of the rate constants.

Part C

How would things change if the mechanism was

$$A \rightarrow 2B \rightarrow C? \tag{12}$$

Specifically that the second step is a second order process with respect to B.

1. Modify the script to account for this change, and record how the time-dependent concentrations of the reactants and products change.
2. Investigate how the behavior changes as you change the initial concentrations of the components.

Part D

How would things change if the reaction was

$$A + B \rightarrow C? \tag{13}$$

1. Modify the script to account for this change, and record how the time-dependent concentrations of the reactants and products change.
2. Investigate how the behavior changes as you alter the values of the rate constant.

2 An Oscillating Reaction: The Lotka-Volterra mechanism

So far the reactions considered have "normal" kinetics meaning the concentration of reactants falls off monotonically, while the product grows. Intermediate concentrations rise, then fall off smoothly. The Lotka-Volterra mechanism describes an autocatalyic reaction, which can result in exotic kinetic behaviors. Such a system illustrates the principles of complex biological systems, for example, large-scale predator and prey populations. One proposed mechanism is:

$$A + B \xrightarrow{k_1} 2B \tag{14}$$

$$B + C \xrightarrow{k_2} 2C \tag{15}$$

$$C \xrightarrow{k_3} D. \tag{16}$$

One interesting consideration is how the concentrations of the intermediates $[B]$ and $[C]$ change with time. Now, if we apply the steady state approximation, we would assume that these concentrations do not change with time. Numerically, we can investigate the relationship without analytically solving the differential equations.

Part E

1. Write down the differential rate expressions for B and C. Then, open `Kinetics-lab-2.py` and execute the script with $A_0 = 3.0$ M, $B_0 = 0.8$ M, $C_0 = 2.0$ M, $k_1 = 1.0$ M^{-1} s^{-1}, $k_2 = 1.5$ M^{-1} s^{-1}, $k_3 = 1.2$ s^{-1}. What conditions do these rate constants and initial concentrations lead to?

2. Change the initial concentrations of B and C: $B_0 = 0.9$ M, $C_0 = 2.1$ M, and observe how the behavior changed. Does it agree with your expectations?

3. Now, try the following initial conditions: $A_0 = 3.0$ M, $B_0 = 0.85$ M, $C_0 = 3.2$ M, $k_1 = 1.0$ M^{-1} s^{-1}, $k_2 = 1.5$ M^{-1} s^{-1}, $k_3 = 1.2$ s^{-1}.

4. Using the plots you created, estimate the frequency with which the concentrations of B and C change. Are they the same? (Hint: consider what happens to predator populations when their prey start to become scarce because of an increase in predator population).

5. Change the values of the rate constants - how does that impact the situation?

6. Change the initial concentrations - how does this impact the situation? What effect does the food supply have on the situation (e.g. one large pile of food that goes away, constant endless supply of food, or cyclical food cycle).

2.1 Lab Report

The report for this lab will consist of a worksheet-style submission. Answer and discuss the questions posed in this handout. Alternatively, you can use this lab for one of your oral lab reports.