Chemical Rates

**Purpose**  The purpose of this project is to show how the techniques of calculus are used in the study of chemical reactions.

**Preview**  The concentrations of chemicals involved in reactions satisfy differential equations. We shall see that in simple cases the differential equations are ones that we have already studied. By solving the differential equations, we can predict the concentrations at future times.

**Part 1: A simple first-order reaction**

Consider a chemical reaction in which molecules of chemical species $A$ are turned into molecules of species $B$. This reaction is symbolized by the diagram

$$A \rightarrow B$$

Let $[A](t)$ and $[B](t)$ denote the concentrations of the two chemical species at time $t$. Concentration is measured in moles per unit volume where one mole has $6.02 \times 10^{23}$ molecules. By tradition, the concentration of a chemical is denoted by square brackets around the chemical name. Of course, when we write $[A](t)$ and $[B](t)$ we are assuming that some time units (seconds, minutes, or hours) have also been chosen.

**What Do We Expect to Happen?**  Spend a few minutes discussing what you expect to happen in the long-run as the reaction proceeds. If, say, we start with 6 moles of $A$ and 2 moles of $B$, what will be the concentrations of $A$ and $B$ at the end of the reaction? Do you expect the reaction to happen faster at the beginning or toward the end? Draw conjectural graphs of $[A](t)$ and $[B](t)$ using your answers to these questions.

**A Mathematical Model**  Since $[A](t)$ is a function denoting the concentration of $A$ at time $t$,

$$\frac{d[A]}{dt}$$

is the rate of change of concentration per unit time. We make the assumption (this is a special case of the Law of Mass Action) that this rate is proportional to the concentration of $A$. If we denote the constant of proportionality by $k_1 > 0$, then

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

where we use the minus sign because the concentration of $A$ is decreasing. Since the rate of loss of concentration of $A$ is the gain of concentration of $B$,

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

The reaction is called “first order” because the rate depends on the first power of the concentration $[A]$. We suppose that the concentrations of the two chemical species at time $t = 0$, namely $[A](0)$ and $[B](0)$, are known. To simplify notation, we will write $A_0 = [A](0)$ and $B_0 = [B](0)$.
1. Solve the first differential equation above to find the function \([A](t)\). Make sure your solution equals \(A_0\) when \(t = 0\)!

2. Plug \([A](t)\) into the right side of the second differential equation above. You should get a differential equation that you can solve using just antidifferentiation! Solve it to find the function \([B](t)\) given that \([B](0) = B_0\).

3. Assuming that \(A_0 = 6\), \(B_0 = 2\), and \(k_1 = 2\), sketch graphs of \([A](t)\) and \([B](t)\).

4. What happens to \([A](t)\) and \([B](t)\) as \(t \to \infty\)? Do your conjectures fit in with the mathematical model you just derived? Explain carefully. If not, go back and rethink those assumptions!

5. (a) Add the two differential equations for \([A](t)\) and \([B](t)\):

\[
\frac{d[A]}{dt} + \frac{d[B]}{dt} = \quad =
\]

(b) Use this to show that \([A](t) + [B](t)\) is a constant (i.e. doesn’t depend on \(t\)).

(c) Given \([A](0) + [B](0) = A_0 + B_0\), what is the value of that constant?

(d) Check to make sure that the solutions you found for \([A](t)\) and \([B](t)\) satisfy this property (otherwise they aren’t right!).

Part 2: A reversible reaction

Suppose now that the molecules of species \(B\) can also change back into molecules of species \(A\) at a rate proportional to the concentration of \(B\) (with constant of proportionality \(k_2\)). This is symbolized by

\[
A \rightleftharpoons B
\]

What Do We Expect to Happen? Spend a few minutes discussing what you expect to happen in the long-run as the reaction proceeds. How does this differ from the case you previously discussed and modeled? (There is one very crucial difference. What is that difference?)

1. Suppose \(A\) changes into \(B\) twice as fast as \(B\) changes into \(A\). Suppose also that we start with 7 moles of \(A\) and 2 moles of \(B\). What do you think the final concentrations of \(A\) and \(B\) will be? Explain!

2. Will the reactions proceed faster at the beginning or toward the end?

3. Draw conjectural graphs of \([A](t)\) and \([B](t)\).

A Second Mathematical Model In this case the differential equations satisfied by \([A](t)\) and \([B](t)\) are

\[
\frac{d[A]}{dt} = -k_1[A] + k_2[B]
\]

\[
\frac{d[B]}{dt} = k_1[A] - k_2[B]
\]

We assume that the initial concentrations are known, \(A_0 = 7\) and \(B_0 = 2\).
1. Explain the meaning of each of the terms in these differential equations.

2. Prove that \([A](t) + [B](t) = A_0 + B_0 = 9\) moles. (Hint: See Question 5 of part 1.)

3. We now consider these equations in the the special case when \(k_1 = 2\) and \(k_2 = 1\):

   \[
   \frac{d[A]}{dt} = -2[A] + [B],
   \]
   \[
   \frac{d[B]}{dt} = 2[A] - [B].
   \]

   (a) Rearrange the equation in Question 2: \([B](t) = \) 
   
   (b) Substitute this into the first of the two equations above: \(\frac{d[A]}{dt} = \) (You should obtain a differential equation which depends only on \([A](t)\).)
   
   (c) Collect like terms. You should see that \(\frac{d[A]}{dt}\) is a linear function of \([A]\): \(\frac{d[A]}{dt} = \) 

4. Solve this differential equation with initial value \(A[0] = 7\) moles to find \([A](t)\).

5. Use Question 3a to find a formula for \([B](t)\).

6. Show that as \(t \to \infty\) the solutions, \([A](t)\) and \([B](t)\) approach limiting values.

7. Do your conjectures fit in with the mathematical model you just derived? Explain carefully. If not, go back and rethink those assumptions!

Practice Problems

1. Consider the following model of a chemical reaction. First, make conjectures regarding how it proceeds, then solve.

   \[
   \frac{d[A]}{dt} = -3[A] + 2[B],
   \]
   \[
   \frac{d[B]}{dt} = 3[A] - 2[B].
   \]

   if \(A_0 = 1\) and \(B_0 = 4\). What happens to the solutions as \(t \to \infty\)?

2. Suppose the initial concentrations, \(A_0\) and \(B_0\), are not known. Make conjectures as to what the final concentrations of \(A\) and \(B\) will be, in terms of \(A_0\) and \(B_0\). Now solve the equations above. Your solution will depend on \(A_0\) and \(B_0\). What happens to the solutions as \(t \to \infty\)?
Part 3: The General Case

The algebra is messy, but it’s possible to show that the solutions to the equations

\[
\frac{d[A]}{dt} = -k_1[A] + k_2[B]
\]
\[
\frac{d[B]}{dt} = k_1[A] - k_2[B]
\]

with initial values \([A](0) = A_0\) and \([B](0) = B_0\) is:

\[
[A](t) = \frac{k_1 A_0 - k_2 B_0}{k_1 + k_2} e^{-(k_1 + k_2)t} + \frac{k_2}{k_1 + k_2} (A_0 + B_0)
\]
\[
[B](t) = -\frac{k_1 A_0 - k_2 B_0}{k_1 + k_2} e^{-(k_1 + k_2)t} + \frac{k_1}{k_1 + k_2} (A_0 + B_0).
\]

If you’d like to give your algebra skills a good run for their money, try deriving the above solutions yourself. Below, we will show that these solutions do indeed give reasonable values for the final concentrations. We can gain some insight into reversible chemical reactions by considering the general case with unspecified rate constants and initial conditions.

1. Show that as \(t \to \infty\) the solutions of the reversible reaction, \([A](t)\) and \([B](t)\), approach limiting values. We will denote these limiting values by \(A_\infty\) and \(B_\infty\), respectively.

2. Find formulas for \(A_\infty\) and \(B_\infty\). Show that \(A_\infty\) and \(B_\infty\) depend only on the ratio of the rate constants \(k_1\) and \(k_2\) and on the sum of the initial concentrations.

3. Show that if we replace \(A(t)\) by \(A_\infty\) and \(B(t)\) by \(B_\infty\), then the right hand sides of the differential equations above are zero. That is,

\[-k_1 A_\infty + k_2 B_\infty = 0.\]

Why do you think that \(A_\infty\) and \(B_\infty\) are called “equilibrium values”?

4. Show that the equilibrium values satisfy the equation

\[A_\infty + B_\infty = A_0 + B_0.\]

Why does this equation make sense chemically?

5. Explain how you could have computed \(A_\infty\) and \(B_\infty\) by using these last two equations instead of solving the differential equations and taking the limit as \(t \to \infty\).

6. Choose initial conditions \(A_0 = 10\) and \(B_0 = 2\). Draw graphs of the solution curves in each of the following cases:

   (a) \(k_1 = 1, k_2 = 2\).
   (b) \(k_1 = 10, k_2 = 20\).
   (c) \(k_1 = .1, k_2 = .2\).

What is the effect of the size of the rate constants on the solution curves?