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.


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

$$\frac{d[A]}{dt} = -k_1[A], \quad (1)$$

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 $B$,

$$\frac{d[B]}{dt} = k_1[A]. \quad (2)$$

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 $B_0 = [B](0)$. 
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1. Find the function \([A](t)\) which satisfies (1) and which equals \(A_0\) when \(t = 0\).

2. Plug \([A](t)\) into the right side of (2). Find the function \([B](t)\) which solves (2) and which equals \(B_0\) when \(t = 0\).

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

4. Add the two differential equations and use the resulting expression to prove that \([A](t) + [B](t)\) is a constant (i.e. doesn’t depend on \(t\)). Therefore, we must have \([A](t) + [B](t) = A_0 + B_0\). Explain why this just means that the total number of molecules doesn’t change. Check to make sure that the solutions you found satisfy this property (otherwise they aren’t right!).

5. What happens as \(t \to \infty\)?

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


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 6 moles of \(A\) and 3 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

\[
\frac{d[A]}{dt} = -k_1[A] + k_2[B] \quad (3)
\]

\[
\frac{d[B]}{dt} = k_1[A] - k_2[B] \quad (4)
\]

We assume that the initial concentrations are known, \(A_0 = 6\) and \(B_0 = 3\).

1. Explain the meaning of each of the terms in these differential equations.

2. Prove that \([A](t) + [B](t) = A_0 + B_0\). (Hint: what did you do in question 4 of part 1?)
3. We now consider the equations (3) and (4) in the special case when $k_1 = 2$ and $k_2 = 1$:

\[
\begin{align*}
\frac{d[A]}{dt} &= -2[A] + [B] \\
\frac{d[B]}{dt} &= 2[A] - [B].
\end{align*}
\]

Solve the equation in question (2) for $[B](t)$ and substitute the solution into equation (5) to obtain a differential equation which depends only on $[A](t)$. Collect terms and show that the resulting differential equation has the form $y'(t) = ay(t) + b$ where $a$ and $b$ are constants.

4. Solve the initial value problem to find $[A](t)$.

5. Verify that the function $[A](t)$ has the right value at $t = 0$.

6. Use the equation in question 2 to find a formula for $[B](t)$.

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

8. 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.

\[
\begin{align*}
\frac{d[A]}{dt} &= -3[A] + 2[B] \\
\frac{d[B]}{dt} &= 3[A] - 2[B].
\end{align*}
\]

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 equations (7) and (8). Your solution will depend on $A_0$ and $B_0$. What happens to the solutions as $t \to \infty$?

3. Suppose the initial concentrations, $A_0$ and $B_0$, and the rate constants, $k_1$ and $k_2$, are not known. Make conjectures as to what the final concentrations of $A$ and $B$ will be.

The algebra is messy, but it’s possible to show that the solutions to equations (3) and (4) is:

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

(10)

Below, we will show that these solutions do indeed give reasonable values for the final concentrations.

If you’d like to give your algebra skills a good run for their money, try deriving the above solutions yourself.

**Part 3. Equilibrium in the General Case.**

We can gain some insight into reversible chemical reactions by considering the general case with unspecified rate constants and initial conditions. The solutions of (3) and (4) are given above in problem 3 (equations (9) and (10)).

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 (3) and (4) are zero. That is,

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

(11)

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

4. Show that the equilibrium values satisfy the equation

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

(12)

Why does this equation make sense chemically?

5. Explain how you could have computed \( A_\infty \) and \( B_\infty \) by using (11) and (12) 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?