

Chemical Rates

Purpose The purpose of this lab 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



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 6.02×10^{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 $B_0 = [B](0)$.

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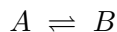
1. Solve the first differential equation above to find the function $[A](t)$. Make sure your solution equals A_0 when $t = 0$!
2. Plug $[A](t)$ into the right side of the second differential equation above. You should get a differential equation that you can solve using just antidifferentiation! Solve 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 $t \rightarrow \infty$? 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 $[B](t)$:

$$\frac{d[A]}{dt} + \frac{d[B]}{dt} = \underline{\hspace{2cm}} = \underline{\hspace{2cm}}$$

- (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



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?)

- 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!
- Will the reactions proceed faster at the beginning or toward the end?
- 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

$$\begin{aligned}\frac{d[A]}{dt} &= -k_1[A] + k_2[B] \\ \frac{d[B]}{dt} &= k_1[A] - k_2[B]\end{aligned}$$

We assume that the initial concentrations are known, $A_0 = 7$ and $B_0 = 2$.

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6. Explain the meaning of each of the terms in these differential equations.
7. Prove that $[A](t) + [B](t) = A_0 + B_0 = 9$ moles. (Hint: See Question 5 of part 1.)
8. We now consider these equations in the special case when $k_1 = 2$ and $k_2 = 1$:

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

- (a) Rearrange the equation in Question (7): $[B](t) = \underline{\hspace{2cm}}$
 - (b) Substitute this into the first of the two equations above: $\frac{d[A]}{dt} = \underline{\hspace{2cm}}$ (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 $[A]$: $\frac{d[A]}{dt} = \underline{\hspace{2cm}}$.
9. Solve this differential equation with initial value $A[0] = 7$ moles to find $[A](t)$.
 10. Use Question **8(a)** to find a formula for $[B](t)$.
 11. Show that as $t \rightarrow \infty$ the solutions, $[A](t)$ and $[B](t)$ approach limiting values.
 12. Draw graphs of the solutions. Do your conjectures fit in with the mathematical model you just derived? Explain carefully. If not, go back and rethink those assumptions!

Practice Problems

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

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

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

14. Suppose that we still have $k_1 = 3$ and $k_2 = 2$, but that 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 $t \rightarrow \infty$?

Report: The General Case

In general, we have the equations

$$\begin{aligned}\frac{d[A]}{dt} &= -k_1[A] + k_2[B], [A](0) = A_0 \\ \frac{d[B]}{dt} &= k_1[A] - k_2[B], [B](0) = B_0\end{aligned}$$

In this report, you will show that we can derive the final concentrations algebraically without solving the equations.

Denote the final concentrations of the reactants by A_∞ and B_∞ respectively.

- Why must it be true that $A_\infty + B_\infty = A_0 + B_0$?
 - Recalling that A_∞ and B_∞ are the *equilibrium values* of $[A](t)$ and $[B](t)$ respectively, explain why it must be true that $-k_1A_\infty + k_2B_\infty = 0$.
- If $A_0 = 10$ moles/litre, $B_0 = 2$ moles/litre, $k_1 = 1$, and $k_2 = 2$, find A_∞ and B_∞ without solving the differential equations. (Hint: use the equations from Question 1!)
 - At beginning of an experiment, we measure $A_0 = 10$ moles/litre and $B_0 = 5$ moles/litre. After a long time, we measure again and find that the concentration of A is 3 moles/litre and the concentration of B is 12 moles/litre. Can you find k_1 and k_2 ? If not, can you find $\frac{k_1}{k_2}$? What does this ratio tell you?

The algebra is messy, but it is possible to show that the solutions to the general system of DEs at the top of the page is:

$$\begin{aligned}[A](t) &= \frac{k_1A_0 - k_2B_0}{k_1 + k_2} e^{-(k_1+k_2)t} + \frac{k_2}{k_1 + k_2} (A_0 + B_0) \\ [B](t) &= -\frac{k_1A_0 - k_2B_0}{k_1 + k_2} e^{-(k_1+k_2)t} + \frac{k_1}{k_1 + k_2} (A_0 + B_0).\end{aligned}$$

If you'd like to give your algebra skills a good run for their money, try deriving the above solutions yourself. (This is not required for the report!)

- For initial conditions $A_0 = 10$ moles/litre and $B_0 = 2$ moles/litre, write down equations for $[A](t)$ and $[B](t)$ using these general solutions, then draw their graphs in each of the following cases (I suggest using the same domain $-0 \leq t \leq 3$ works well.): (a) $k_1 = 1$, $k_2 = 2$; (b) $k_1 = 10$, $k_2 = 20$; (c) $k_1 = 0.1$, $k_2 = 0.2$.

The final concentrations of reactants is the same in all these cases. What is the difference between them? What is the effect of the *size* of the rate constants on the solution curves (as opposed to their *ratio* - compare Question 2(b))?