

Chapter 17: Kinetics



If you want chemical reactions to proceed quickly, you can add a catalyst or increase the temperature. However, people wishing to make their brains work more quickly sometimes resort to using crystal meth. This is, it should be noted, a bad idea.

[http://commons.wikimedia.org/wiki/File:Illegales_Methlab_\(USA\).jpg](http://commons.wikimedia.org/wiki/File:Illegales_Methlab_(USA).jpg)

Section 17.1: A Brief Intro to the Basics of Chemical Kinetics

Because most textbooks make this a hard concept, let's break kinetics down into terms that are easier to understand. To put it simply, **kinetics** is the study of how fast a chemical reaction will make products from reagents.

To put this another way, kinetics is the study of chemical reaction rates. In turn, **reaction rates** are measured by how the concentration of the reactant changes over time.¹ Because I know you all love equations, let's put this into equation form:

$$\text{rate} = \frac{\text{change in concentration during the reaction}}{\text{the amount of time the reaction was proceeding}} = \frac{\Delta M}{\text{sec}}$$

Important features of this equation:

- ΔM means “change in molarity of the solution” over the course of the reaction. This is always treated as a positive value, even though the final molarity will be less than the initial molarity.
- “sec” refers to the reaction time in seconds. Even if the reaction takes hours upon hours to perform, we still do this in seconds. Go figure.
- The units of reaction rate are either M/sec or mol/L·sec. They mean the same thing, so don't sweat it too much.

Using this equation, we can see that if a reagent decreases in concentration from 1.00 M to 0.30 M in a period of 3600 sec, the rate of the reaction will be $0.70 \text{ M}/3600 \text{ sec} = 1.9 \times 10^{-4} \text{ M/sec}$ or $1.9 \times 10^{-4} \text{ mol/L}\cdot\text{sec}$ (units depending on the person who's grading your paper).

Who cares, anyway?



Figure 17.1: You should care! For example, let's say that you're a secret agent flying deep into Russian airspace to bomb Moscow, and your airplane is about to crash. Being the good secret agent you are, you take the poison pill they gave you so that you wouldn't give up national secrets only to find that your airplane doesn't crash after all and that you can just fly it home. In this situation, wouldn't it be nice, if you had the antidote, to find a way to make the antidote react more quickly with the poison so you won't die? This is just one of the many real-world applications of chemical kinetics.

<http://commons.wikimedia.org/wiki/File:AtomicWar0401.jpg>

¹ For gases, the concentration is measured in terms of partial pressures.

Section 17.2: Why Are Reaction Rates the Way They Are?

Some reactions are fast and some reactions are slow. Fast reactions include acid-base reactions while many organic reactions are painfully, boringly slow. Why the big difference?

Well, I'm glad you asked.² Reaction rates can be described by something known as **collision theory**, which states that reagent particles have to bash into each other in just the right way if they're going to react. If they bash together in a different way, or don't bash together at all, no reaction.³

Collision theory tells us that there are two big factors that affect reaction rates. Let's take a look:

1. The orientation in which the particles hit each other: Think of a pen – you can cram the cap and the pen together as hard as you want, but if they're not aimed in the right way, the cap will never, ever fit onto the pen. The same thing happens with molecules; if the parts of the molecules that want to react aren't aimed up with one another, the molecules won't react with each other.

Digging Deeper Into Stuff

*Once the particles in the compound hit each other in the right orientation, they may or may not actually continue the reaction. The way that the products look when they've half-reacted with each other is known as the **transition state**. To go back to the pen example, the transition state is achieved when the cap is halfway on the pen, but not all the way there. At this exact point, the cap is neither on the pen nor off the pen – it's somewhere in the middle. Incidentally, the transition state of a reaction is sometimes called the activated complex, but that's not technically true according to IUPAC standards, so don't use it.*

2. The energy with which the particles collide. Again, using our pen example, imagine a two month old baby putting a cap directly on a pen. Though the cap may be properly aimed with respect to the pen, the child simply won't have enough energy to actually get the cap to stick in place. Likewise, if two molecules collide in exactly the right orientation to react, no reaction will occur unless they have enough energy to get the bonds to rearrange themselves. The minimum amount of energy to make a reaction take place is known as the **activation energy** (E_a).

² Actually, I could care less that you asked.

³ This is not unlike the situation with my former neighbors, who I hated a whole lot. You see, if I never bumped into the neighbors when unloading groceries from my car, then there would be no problem. However, if I bumped into one of those jerks when I was heading out to work, we'd usually react to one another (i.e. make rude hand gestures, mutter rude comments, and so forth). This all stemmed from one time when we asked them if they wanted to go out and do something during the weekend, and they said that they couldn't because they were busy. No problem, right? Anyway, when we looked out our window that night, we found that they were just hanging around the house and hadn't gone anywhere. I think this slight might have been related to an earlier occasion when I made fun of the guy's name (he was named "Stephen", and I said that it sounded pretentious given that my son's name is Steve) and he took it the wrong way. Seriously, it's not like I killed their dog or something.

Because we like to make graphs, let's make a graph that shows how the reaction $A + B \rightarrow C + D$ occurs, from an energetic standpoint:

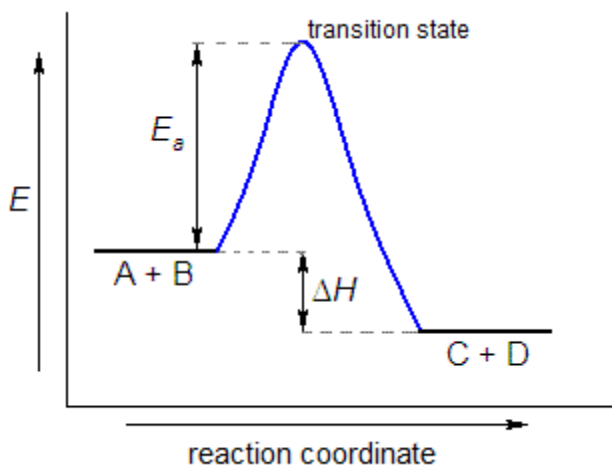


Figure 17.2: This chart is an energy diagram showing the how $A + B$ (the reagents) require energy (the activation energy, E_a) to react, and then decrease in energy until the products $C + D$ have lower energy than the reactants (i.e. the heat of reaction, ΔH is negative). For endothermic reactions, the line showing $C + D$ is higher than that for $A + B$.

http://upload.wikimedia.org/wikipedia/commons/e/eb/Coordena_da_reaccion.GIF

One thing that should be mentioned is that thermodynamics and kinetics are entirely different things and have nothing to do with each other. Thermodynamics tells us whether or not a reaction will be spontaneous, while kinetics tells us how fast the reaction will occur. For example, thermodynamics tells us that ΔG for the combustion of gasoline is very negative, but kinetics tells us that gasoline simply doesn't burn when combined with oxygen at room temperature.

To put this another way, thermodynamics refers to the ΔH term in the energy diagram above, while kinetics deals with the E_a term. *The size of the activation energy of a reaction is the only thing that determines reaction rates.* The heat of reaction is irrelevant in finding reaction rates.⁴

Section 17.3: Making Stuff React Faster

If you're interested enough in a chemical reaction to try and perform it, you're probably also interested enough in it to make it occur quickly. The following things are factors that affect the rates of chemical reactions:

- The higher the concentration of the reagents, the faster the reaction will occur.⁵ Using our knowledge of collision theory, it makes sense that if we have more collisions between the reactants, we'll have more chances for the reagents to hit in the right orientation.
- The higher the surface area of the reagents, the faster the reaction will occur. More surface area = more reagent particles that can be exposed to the other reagent. And, as mentioned above, more collisions between reagents = faster reaction rates.

⁴ Seriously, keep this distinction in mind. Heats of reaction and free energy values have absolutely, positively, nothing to do with reaction rates. The only thing that has anything to do with reaction rates is the activation energy for the reaction.

⁵ For gaseous reactions, replace "concentration" with "partial pressure."

- The higher the temperature, the faster the reaction will occur. Because two reagent molecules need a minimum amount of activation energy to undergo the reaction, it's a lot more likely that they'll have this minimum energy at higher temperatures than at low temperatures.
- The presence of a catalyst will speed up a chemical reaction. **Catalysts** are materials that combine the reagent particles in just the right way that they can react. For example, I can try and put a basketball inside my house by bouncing it really hard against the wall – eventually, if I give it enough time, it will go through the wall and enter my house. However, if I pick up the ball and place it into the house, I've acted as a catalyst in that; a) the process happened more quickly; b) the way in which the ball enters the house is different; and c) less energy was required to make the process occur. Examples of catalysts in the real world include enzymes (which allow biochemical reactions to occur) and catalytic converters in cars that convert carbon monoxide into carbon dioxide.^{6,7}

Labs You Can Do At Home

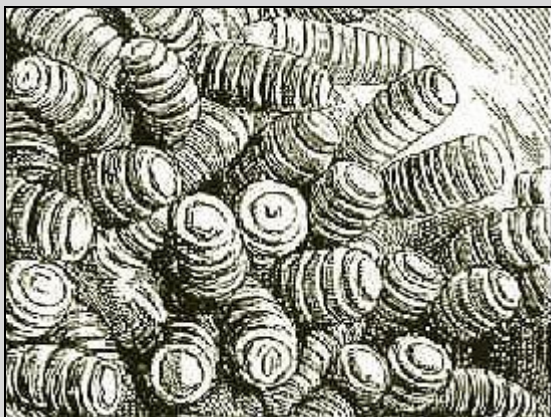


Figure 17.3: Place one piece of raw steak in the freezer and another on your kitchen counter. Record the decomposition of each piece of steak over a period of six weeks, comparing and contrasting this process for each piece of steak. Which steak decomposed more quickly? Why do you think this is?

http://commons.wikimedia.org/wiki/File:Gasterophilus_intestinalis_Oestre.jpg {{PD-1923}}

Section 17.4: Rate Laws

Now that we know what affects reaction rates, let's figure out some equations that describe mathematically how fast a reaction occurs. These equations that describe the kinetics of chemical reactions are called **rate laws**.

Rate laws for the chemical reaction $aA + bB \rightarrow cC + dD$ have the general form:

$$\text{rate} = k[A]^x[B]^y$$

⁶ In contrast to catalysts, inhibitors are compounds that slow chemical reactions by orienting the reactants in the *wrong* direction to react.

⁷ Enzymes are homogeneous catalysts because they are in the same state as the reaction they're catalyzing. The example of catalytic converters involves heterogeneous catalysts because the catalyst is a solid metal and the process being catalyzed involves gaseous reagents.

where k is called the **rate constant**, $[A]$ and $[B]$ are the molarities of A and B, respectively, x is the order of compound A, y is the order of compound B, and $(x+y)$ is the overall reaction order. That said, what do these terms mean?

- The **rate constant** of a reaction is a general term that describes how easily the reactants combine with one another. A high rate constant denotes a fast reaction while a low rate constant denotes a slow reaction.
- The molarities of each compound are, well, the molarities of each compound. As always, for reactions in the gas phase, these are replaced with partial pressures.
- The **order** of each reagent, x and y , describe how the reaction rate depends on the concentration of each reagent. These values, when combined with experimental data, can be used to figure out the specific mechanism (i.e. the way in which the reagents combine to form product) for the reaction.
- The **reaction order** is equal to $x + y$, and isn't really good for all that much, as far as I can tell.

Unrelated Uses of the Word "Order"



Figure 17.4: These animals all belong to the biological order carnivora. This, apparently, is a real thing.

http://commons.wikimedia.org/wiki/File:Order_Carnivora.jpg

Figuring out the rate laws depends mainly on finding the order of each of the reagents.⁸ This is done by using experimental data that shows the dependence of the overall reaction rate on the concentration of the reactants.

Here's how this works: For the reaction $aA + bB \rightarrow cC + dD$, we get the general rate law:

$$\text{rate} = k[A]^x[B]^y$$

⁸ We don't need to find the order of the products because the products have nothing to do with the rate of the forward reaction. At least, not for an irreversible reaction like we're assuming these are. For reversible reactions, you'll have to check out the equilibrium chapter, which is coming up.

To find x and y, let's look at some experimental data:

	[A]	[B]	rate (M/s)
Experiment 1	0.200 M	0.200 M	3.00×10^{-4}
Experiment 2	0.200 M	0.400 M	6.00×10^{-4}
Experiment 3	0.400 M	0.400 M	6.00×10^{-4}

Figure 17.5: A bunch of imaginary kinetic data.

We can figure out the rate law of this reaction from the data given using the following awesome rules:

- If you double the concentration of the reactant and the rate of the reaction remains unchanged, the reaction is zeroth order in that compound. In other words, the exponent is zero and you can totally ignore that compound in the rate law.
- If you double the concentration of the reactant and the rate of the reaction doubles, the reaction is first order in that compound.
- If you double the concentration of the reactant and the rate of the reaction is squared, the reaction is second order in that compound.
- If you say that a reaction is third order or higher, you're probably wrong. So knock it off.

In our case, we can see that, comparing experiment 1 to experiment 2, [A] has stayed the same while [B] doubled. Since the reaction rate doubled, the reaction is first order in B. When comparing experiment 2 to experiment 3, we can see that [A] doubled while [B] remained the same. Since the reaction rate didn't change, this means that the reaction order of A is 0.⁹ This gives us an overall rate law of:

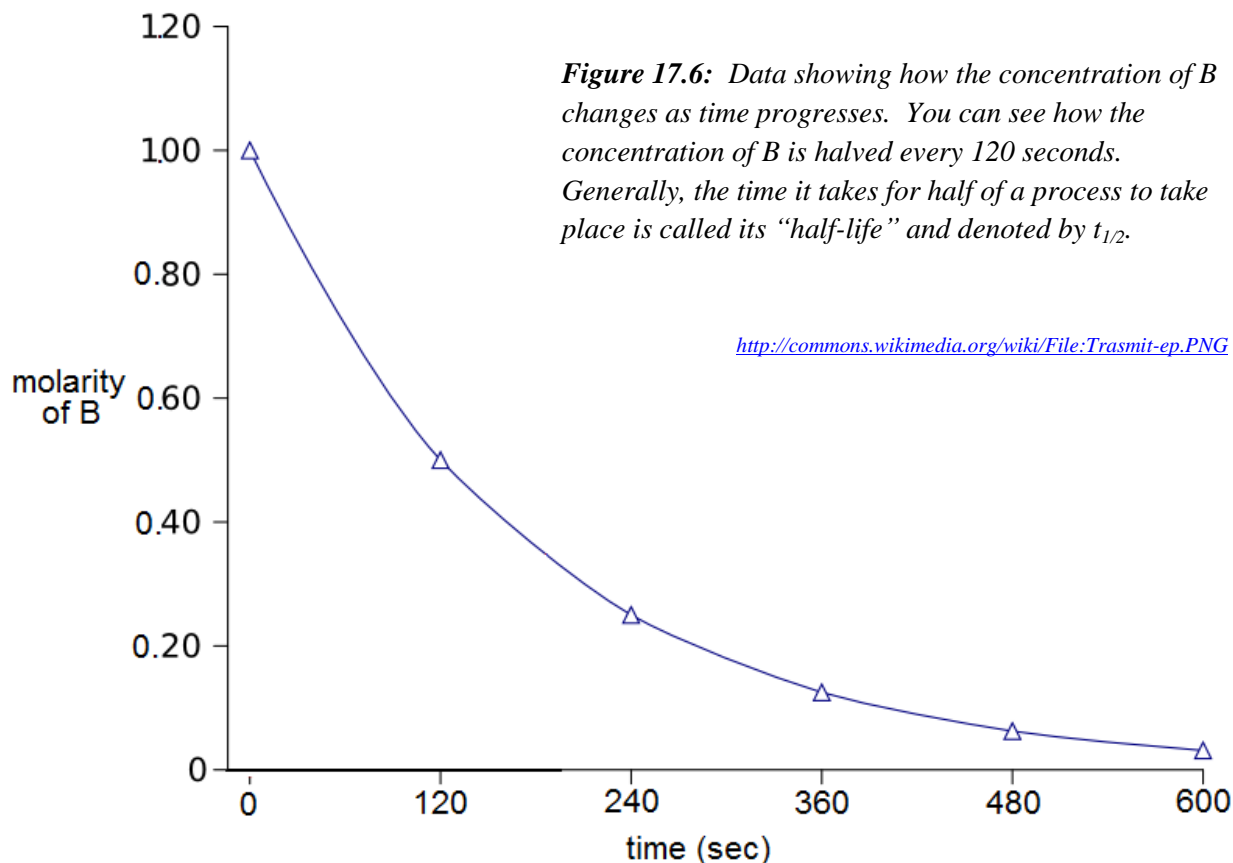
$$\text{rate} = k[\text{B}]$$

Some Handy Information

You may or may not be asking yourself what happens if the kinetic data in the problems you're given shows something other than a doubling of the concentration of each reactant. Fortunately, you won't run into this problem, as nobody ever does this when writing problems for a quiz or test. You see, in most places, the state education standards require that you teach this material, not that you actually give realistic examples of the material. You might argue that this is bad teaching practice, but you've got to admit that it's awfully convenient for you, the student.

⁹ The reason we didn't compare experiment 1 to experiment 3 is that the concentration of both reactants were doubled at the same time, making it difficult to figure out which one was responsible for the increase in reaction rate. When examining kinetic data, always compare two trials in which the concentration of only one of the reagents is changed.

Let's examine a chemical reaction with the rate law we found above: $\text{rate} = k[\text{B}]$. As we can see, this rate law shows that, as the concentration of B decreases, the rate of the reaction will also decrease. In other words, as time passes, the reaction will slow down because there won't be as much of compound B to react. If we felt like it¹⁰, we could graph this relationship like this:



To figure out what the rate of this reaction is at any given time, you can do one of two things. The first is to use a bunch of really bad-ass equations, and the second is to just find the slope of the tangent line of the curve at the time you're interested in knowing the reaction rate.¹¹ This is a lot easier.

For example, if we want to find the rate of this reaction at $t = 120$ sec, we can just draw the tangent line to the curve at 120 seconds and find its slope. Because I want to make you do at least *some* of the work, I'll let you figure this out yourself.¹²

If you are, for some reason, given a rate constant, reactant concentrations, and the rate law, you can just use the rate equation to find the instantaneous reaction rate. However, if anybody actually had all of this information, they'd probably just do the problem themselves.

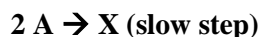
¹⁰ And we do.

¹¹ In case you don't know anything about tangent lines, you can either visit the Wikipedia page at <http://en.wikipedia.org/wiki/Tangent> or you can go ask your math teacher.

¹² Time to check your work: The answer is 0.003 M/s, or at least that's what I found it to be when I found the slope of the line. Your answer may vary slightly, depending on your interpretation of the tangent line.

Section 17.5: Reaction Mechanisms

Though some chemical reactions take place in one step, others require a bunch of different steps to take place before the reaction goes to completion. Let's imagine the reaction $A + B \rightarrow C$ which takes place via the following two steps:



Giving the final equation of $2 A + X + B \rightarrow X + C$, which reduces to $A + B \rightarrow C$. What will the rate law for this reaction be?

Well, as it turns out, the rate of any chemical reaction is determined by only one step: The slowest one (which is also known as the **rate-determining step**). This can be illustrated using a real-life example:¹³

Let's say that I've caught a squirrel in my back yard and want to hit it with a baseball bat. Well, I don't have a baseball bat in my house,¹⁴ so I've got to go to Target to buy one.¹⁵ Because it's a couple of miles down the street, I've got to go through three traffic lights, including one that takes forever to turn because the traffic engineers are morons. Then I go inside and find the baseball bats and wait in line while the *one checker on duty* takes 45 minutes to get everybody through the line. After that, I go up to the counter, where the checker realizes that, all of a sudden, she's forgotten how to process credit card payments, and then the manager comes over and helps her out. As I leave, store security stops me because my wife put one of those theft-prevention tags in the lining of my coat as a joke. I finally get in my car, drive home, nearly avoid hitting the neighbor's cat (which is always hanging around on my driveway, for some reason) and finally enter my home. I walk through the living room and the living room to the backyard, where I smack the squirrel with the bat.

If I wanted to save a lot of time, I could have just written the preceding paragraph in the form of a **reaction mechanism** (which is just a fancy way of saying "the method by which something gets done.") Let's do that now:

Decide to hit the squirrel with a baseball bat (fast)

Go to Target and buy a bat (slow)

Hit the squirrel with the bat (fast)

Overall, the rate at which the squirrel gets hit with the bat depends only on the rate-determining step (i.e. the time it takes for me to buy the bat). Compared to the amount of time it takes for me to do this, the other steps take no time at all. If I were to write a rate equation for this whole process, it would only involve one step – the bat-buying step.

¹³ Please don't send me letters complaining about how awful I am. It's just a joke.

¹⁴ I don't believe in exercise, as anything involving sweat just *can't* be good for you.

¹⁵ "Target: Your squirrel-smacking superstore since 1962."

Likewise, let's use the same thinking when talking about the reaction at the top of the page. Given that the slow step is $2 A \rightarrow X$, we can say that the rate equation for the whole process reflects the combination of two molecules of A, giving us an overall rate equation of:

$$\text{rate} = k[A]^2$$

This equation, incidentally, reflects the fact that two molecules of A have to combine with each other simultaneously in this step.

But what about X? Because compound X is formed in the first step and consumed in the second step, it is referred to as an **intermediate** in this process. Neither A nor B is an intermediate because they are not formed during any step of the process, and C is not an intermediate because it is the ultimate product of the reaction.

The Wonders of Nature



***Figure 17.7:** Squirrels are one of the many awesome things you can see if you go outside and look at the many Wonders of Nature. They're easy to squish with baseball bats, though. It is thought that, given the current direction of their evolution, that they will be able to withstand the collision of even the hardest Louisville Slugger in the next 5-10 million years.*

http://commons.wikimedia.org/wiki/File:Hylopetes_nigripes.jpg