

## MITOCW | kinetics\_and\_equilibrium

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If you're driving down the highway and want to see how fast you're going, you look down at your speedometer. If you're in a lab and want to see how fast a chemical reaction is going, it's a little more complicated. In this video we'll look at a few factors that influence the speed of chemical reactions.

This video is part of the Equilibrium video series. It is often important to determine whether or not a system is at equilibrium, to do this we must understand how a system's equilibrium state is constrained by its boundary and surroundings.

Hi, my name is George Zaidan and I'm a graduate of the chemistry department here at MIT.

Before watching this video, you should have a basic understanding of chemical equilibrium.

After watching this video, you will be able to: Understand how reaction rate is influenced by reactant concentration Explain how reaction rates change as a system establishes equilibrium, AND Predict relative equilibrium concentrations of reactant and product, based on rates of forward and reverse processes.

Suppose you have this general reaction where A, B, C, and D are molecules and lowercase a, b, c, d are their molar coefficients. As the reaction progresses, A and B will be consumed, and C and D will be formed.

The speed at which any of these four processes happen multiplied by the reciprocal of the appropriate molar coefficient is called the rate of this reaction.

If you want your car to go faster, you step on the gas, but speeding up a chemical reaction is not that simple. There are lots of different factors that affect reaction rate. Three common ones are: the concentration of reactants, the temperature of the reaction mixture and the presence of a catalyst. In this video we'll focus on the effect of concentration on homogenous reactions.

Most chemical reactions are the result of two or more molecules colliding with each other... but not every collision leads to a reaction. The molecules must collide in the proper physical orientation, and they must do so with enough energy to break their bonds.

Imagine a beaker with 100 mL of water, in which you dissolve 106 molecules of reactant A and 106 molecules of reactant B. How likely is the reaction to form C and D? Do a back of the envelope calculation to support your answer. Pause the video.

So let's see. 100 mL of water is 100 grams of water, which is 100 over 18.02, about 5.5 moles of water. That means there are about  $3.3 \times 10^{24}$  molecules of water in the beaker, and only 106 molecules of each reactant...So in any given volume of this solution,  $3.3 \times 10^{24}$  over  $(3.3 \times 10^{24} + 106 + 106)$ , or 99.9999999999999994 %, of molecules are nonreactive water!

Clearly, successful collisions between the reactants would be very rare in this situation.

Intuitively, you would expect that the more concentrated the reactants, the faster the reaction, and this is generally true.

Let's draw a reaction coordinate diagram to better understand our hypothetical reaction.

Let's assume that the reaction is exothermic, in other words, that energy is given off as the reaction progresses, so we draw the curve like this.

The x-axis is the progress of the reaction, and the y-axis is potential energy.

Here are the reactants, and here are the products.

This hump is the activation energy, the point of highest potential energy of the reaction.

Two molecules must collide with at least this amount of energy in order to successfully react.

Do you notice anything about this diagram? There's no indication of directionality; in other words, there's no reason that the reaction couldn't proceed backwards just as well as forwards.

You're probably used to thinking of chemical reactions as processes that happen in only one direction (forward), but most reactions are actually reversible. There are a few exceptions, for example combustion. \*You can't un-burn a match. But most reactions that chemists carry out in the lab or that happen in our bodies are reversible.

Draw your own reaction coordinate diagram and label the forward and reverse reaction paths. Suggest what the relationship might be between the activation energy and the relative rates of the forward and reverse reactions.

Pause the video.

This is the activation energy for the forward reaction. The higher this activation energy, the slower the forward reaction, because the number of reactant molecules with sufficient energy to react when they collide will decrease.

But now let's look at this picture in reverse. The reverse activation energy is not the same as the forward activation energy! In this case, it's higher. So that means that the reverse reaction will be slower than the forward reaction.

If we were to somehow increase the activation energy, both the forward and the reverse rates would slow down, but the relationship between them -- namely that the forward rate is faster than the reverse rate -- would be preserved.

Here are four other diagrams, each for a different hypothetical reaction. Predict the relative rates of the forward and reverse reactions in each of these cases. Pause the video.

In real life chemical processes, the rates of the forward and reverse reactions are often very different. Many of the reactions that you may have previously thought of as "irreversible" actually just have wildly different forward and reverse rates. For example, you've probably seen the dissociation of a strong acid in water written like this.

But really, it's this. In this case, the forward reaction is many orders of magnitude faster than the reverse reaction, so we write it as just the forward reaction.

So far we've seen that concentration and activation energy can each independently affect the rate of a chemical reaction. The higher the concentration of a reactant, the faster the reaction; and the lower the activation energy, the faster the reaction. But there's a twist... Thinking about the hypothetical reaction  $A + B \rightleftharpoons C + D$  yields C and D. Suggest what that twist might be.

Pause the video.

There's no reason that the activation energy of this reaction would change as the reaction progresses. But that's not true for the concentrations: as A and B are converted to C and D, the concentration of all four species change! And as the concentrations change, the reaction rate also changes.

To see if we can understand how the reaction rate changes as the reaction progresses, let's go back to the reaction coordinate diagram. Let's start by considering both the forward and reverse reactions as if they're completely separate.

Here are A and B reacting to form C and D. Let's assume this forward reaction is relatively fast. As more and more A and B get converted to products, their concentrations decrease, and the initially fast reaction rate slows over time. Here are C and D reacting to form A and B. This reaction would be slower than this one, but as C and D react, their concentrations decrease with time and the reaction becomes even slower.

Except that in reality, these aren't two separate reactions. The products of one reaction are the reactants for the other. Let's now consider the forward and reverse reactions at the same time. At the very very beginning, only A and B are present -- no C or D. So the initial rate of the forward reaction will be relatively high, since the concentrations of A and B are high. The reverse reaction can't happen at all yet, because there is no C and D present, so its initial rate is zero.

As the reaction proceeds, two things happen: the concentrations of A and B decrease, and the concentrations of C and D increase. So the forward reaction rate slows, and the reverse reaction rate speeds up. Eventually, we

reach a point where the rates of the forward and reverse reactions are the same: this is the definition of a dynamic chemical equilibrium. When this happens, the concentrations of A, B, C, and D stop changing with time. Be careful not to confuse equilibrium with "no reaction." A and B are still reacting to form C and D; and C and D are still reacting to form A and B. But the rate of formation of products equals the rate of disappearance of reactants and vice versa. That means that the concentrations of A, B, C, and D don't change with time.

Let's go back to our reaction coordinate diagrams for our four hypothetical reactions. We've already worked out the relative rates of the forward and reverse reactions in each case.

Using these relative rates, see if you can predict the relative concentrations of the reactants and products at equilibrium. Pause the video.

-Endo, high  $E_a$ : lots of reactant, not much product -Exo, high  $E_a$ : lots of product, not much reactant -(In both of these cases, the forward rate is the same as the reverse rate...) Same energy, high  $E_a$ : ratio of product/reactant will depend on specific reaction Same energy, low  $E_a$ : ratio of product/reactant will depend on specific reaction Now what's the difference between the last two scenarios? In each case, the forward reaction rate will be the same as the reverse reaction rate. But the rates for this scenario will be much faster than for this one... so equilibrium will be reached much more quickly here than here! The most important thing to understand about reaction rates and equilibrium is that just because the forward and reverse rates are the same DOES NOT mean that the concentrations of the reactants and products are the same.

Some equilibria, like the dissociation of a strong acid in water, strongly favor the products. Others strongly favor the reactants. Many of the reactions that keep us alive are equilibria, and our body goes to a great deal of effort to make sure that the position of equilibrium heavily favors one side or the other.

We hope this video has helped you understand the relationship between reaction rates and equilibrium. We saw that, in general, the rate of a reaction decreases as reactant concentration decreases.

And while we may think of reactions as irreversible, most are actually reversible, it's just that we "see" the faster of the two.

As the forward reaction rate decreases, the reverse reaction rate increases until equilibrium is established. At equilibrium, the rate of the forward reaction equals the rate of the reverse reaction, but this does not imply anything about the equilibrium concentrations of the products and reactants.