Chemical Kinetics

 Reaction Rates

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We've talked a little bit already about the driving force for a reaction. For instance, when you have a car there's a driving force for the car to roll downhill. We talked about that in terms of enthalpy changes and changes in internal energy. We are going to talk about that more, but right now what I'd like to do is talk a little bit about kinetics or the rates of reaction.

The first point I want to make is that, in general, the rate of reaction and the driving force are totally disconnected. In other words, you can have a reaction that has a very great driving force for proceeding. For instance, we've looked at the reaction of hydrogen and oxygen to form water. The reaction is very slow as evidenced by the fact that we can put the two gases into a balloon and just float it. Probably, if we left it alone, the hydrogen would diffuse out of the balloon and the balloon would just fall to the floor eventually. So, in other words, hydrogen and oxygen are perfectly happy to be next to each other. Even though there is a great driving force for making water, we have to bring a spark up or something like that in order to get the reaction to go. Well, that idea of the rate at which the reaction proceeds, and in the case of hydrogen and oxygen, just extremely small, is the basis for this subject called kinetics or rates of reaction.

To tie it to your real life, I have several questions that I'd like to pose as “have you ever wondered why?” For instance, have you ever wondered why we paint steel? Particularly, why do we have to paint steel bridges that are over bodies of water? Why is the Golden Gate, well it's not really gold, it's more reddish-brown, but why is it reddish-brown as opposed to the color of steel like silver colored. The answer is that in the presence of all that saltwater steel tends to corrode, it tends to rust. We can slow down the rate of rusting by putting paint on top of the steel. The idea is that we can affect the rate of reaction, in that case, the rate of iron reacting with O₂ in the air to form ferric oxide by putting paint on top. This is a case where we make the reaction go slower.

Similarly, why do we put food into a refrigerator? A refrigerator is probably one of the great inventions that man has come up with. Why is it so important? Well, it turns out that rotten food makes you sick. The longer that we can keep food from spoiling or from rotting; the better it is for you. So, what do we do? It turns out that reactions go slower when you cool them down. That is just a general principle. It is not always true, but it is generally true. You put food in the refrigerator and it doesn’t rot as fast and so you can eat it over the course of a week as opposed to over the course of a day.

We also tend to wrap food in Saran Wrap, plastic wrap. Why do we do that? Well, it turns out that reactions with oxygen in the air are the kinds of reactions that degrade food. We can slow down those reactions by wrapping them in plastic. What about the dates that you've noticed on soda cans, particularly diet soda? When I was a kid, diet soda could add saccharin in it. It was sweetened by saccharin instead of sugar. It turns out that saccharin is perfectly stable. You don’t really have to worry about something happening to the saccharin. In other words, a diet pop that is only sweetened with saccharin, a year later, it probably tastes exactly the same. But one of the new artificial sweeteners, aspartame or NutraSweet, turns out it degrades as time goes by. In other words, it loses its sweetness. It goes to an entirely different molecule. That molecule, the new molecule, happens not to be sweet. You put a date on the can because if you waited a year that can of soda wouldn’t be sweet anymore.

How do you make it last longer? Go back to putting it back in the refrigerator. Remember, putting it in the refrigerator slows down reactions. If you want your diet sodas to keep sweet for a while, or for longer, what you do is you store them at low temperature. If you really want to trash them, store them at high temperature. Leave them in the sunshine or put them inside your car in the sunshine and they are going to taste like crap in no time.

Finally, what about the concern over radioactive waste? Radioactive waste, why is it any more hazardous than any other kind of waste? The answer is because radioactive reactions that give rise to radioactive decay tend to be really slow. Being really slow, it means that something is radioactive today, 10 years from now it is still radioactive, 100 years from now it’s still radioactive, and a million years from now it might still be radioactive. Radioactivity is bad for you. It damages biological tissues. The nature of the problem is that we have it for a long time. The problem just exists for a long time because the reactions are very slow.

Now let’s talk a little more about rates, reactions, and, in particular, the application to chemistry. The next analogy I’d like to make is the idea of when you go on a car trip we talk about rates as well. Not rates of reaction, but rates meaning how far did you go and how long did it take. For instance, you go on a car ride and say it's 200 miles and say it takes four hours. You would say that the average rate for this car trip was 50 mph. You traveled 50 miles in the first hour, 50 miles in the second, 50 in the third, and 50 in the fourth, on average. There’s a difference between that
Let’s take a look at this chemical reaction. It is the reaction of dinitrogen pentoxide, N₂O₅, going to nitrogen dioxide, NO₂, and oxygen, O₂. We plot the concentration of O₂, which is one of the products as a function of time, and it looks something like this. Here’s the data; the data is the red curve at time zero. There is no oxygen because we haven’t really started the reaction. As the reaction proceeds, we make more, more, and more O₂ and eventually we reach some level. What this level is, it’s the maximum amount of O₂ we can make given that we put a certain amount of dinitrogen pentoxide into the pot. Eventually all of that is going to be converted to O₂. So, the concentration of O₂ asymptotically approaches the level that is dictated by the stoichiometric coefficients for the reaction and how much stuff, how much reactant that we originally put in.

Now, let’s define the average rate for a chemical reaction. Instead of how far you’ve gone divided by the amount of time, we are going to define it as the change in concentration of a reactant or product, in this case, product, divided by the change in time. That is, the rate of formation of O₂. Well, what is that? That’s the concentration of O₂ at some time, t₂, minus the concentration of O₂ at some time, t₁, divided by t₂ minus t₁. You need to express this over a particular time frame. In other words, the rate of formation of O₂, between the time t₁ and t₂, is given by this expression. This is, again, what we call the average rate.

So, what do we do? Well, we just note whatever the concentration is at t₂. We note whatever the concentration is at t₁. Then the denominator is just t₂ minus t₁ and it gives an expression that looks like this. The units are in molar per second because the y-axis here is molarity units and the x-axis is time. Since we are taking the ratio, it is molarity per unit time or molar per second.

Now, we could also define something else called the “instantaneous rate.” What is the instantaneous rate when you are going on a car trip? It is exactly what the speedometer happens to read at any given moment. You know that if you traveled 50 miles an hour on average, some of the time you might have been going 75, some of the time you might have been going 30, and some of the time you might have been going 90. The instantaneous rate is how fast the car is going at any given point in time. We define the instantaneous rate at a particular time not over a range of times. From calculus, the instantaneous rate is the limit as the change in time goes to zero of that original function that we had before, the change in concentration of O₂ divided by the change in time. The calculus says that this quantity, as Δt goes to zero, is given by d[O₂]/dt, or the derivative of the concentration of O₂ with respect to time. Well, the derivative is just the slope of a tangent on the curve at any given point. In other words, this quantity d[O₂]/dt is exactly the slope of the purple line that I’ve drawn here, at the point tₐ. If we had some other time, for instance, some time down here, we would draw a different tangent, and the slope of that tangent would be the instantaneous rate at that time.

So, you can see that the instantaneous rates change over the course of the reaction. They get smaller and smaller and smaller and smaller. At the end of the reaction they are zero, because at the end of the reaction we’re not making any more O₂. All the dinitrogen pentoxide is reacted away, we’re not making any more O₂. So, the instantaneous rate goes to zero.

Let’s now use these two ideas, average rate and instantaneous rate, and look at a problem. Let’s look at what the reaction looks like first. The reaction is nitrogen dioxide plus carbon monoxide going to nitric oxide plus carbon dioxide. This is a reaction in which we are going to monitor the rate of production of nitric oxide as a function of time. That looks like this, we plot nitric oxide in molarity units and time. What we are going to do is calculate the average rate, for instance, the average rate between 50 and 150 seconds. Here are the two problems that we are going to work, calculate the average rate between 50 and 150 seconds and also the instantaneous rate at 150 seconds.

Let’s look at the average rate first. The average rate is just the slope of this line that connects the value of the data at 150 seconds and the value of data at 50 seconds. That looks like the concentration of nitric acid at 150 seconds minus the concentration of nitric oxide at 50 seconds divided by 150, which is t₂, and 50, which is t₁, and these are in seconds. We plug in the values. Read them off the plot in the graphic box for the concentration at 150 and a concentration at 50, and then the change in time is 100 seconds. So we get, 1.28 x 10⁻⁵, and again, the units are molar per second for the average rate.
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Computer programs that could do this for you exactly, but this is going to work just great. We are going to draw a
tangent, so in other words, the red line touches the blue line at exactly one point. That one point is at 150 seconds,
and that is what the tangent is. To find the slope of this tangent, all we have to do is find out what the value is of the
tangent at 2 times, say at 200 seconds and at 150 seconds. Then using the graphical way of calculating the slope of
the red line, we’ll get the instantaneous rate.

Again, it is the slope of the tangent that we’ve drawn in, the red line, at 150 seconds. We evaluate the line at two
different points, at 200 seconds, then at 100 seconds, and the change in time is 100 seconds. So the slope of that line
is 7.7 x 10^-5 molar per second. From calculus that’s d[NO]/dt or the derivative of the concentration of [NO] with respect
to time.

Finally, let me point out that the average slope is greater than the instantaneous slope at 150. The average slope
over this time range is greater than, meaning that the slope is larger, than the instantaneous rate. In general, the
instantaneous rate and the average rate are going to get smaller and smaller as the reaction proceeds.

What we are going to see in the next tutorial is that there is a relationship between how fast a particular reaction is
going or what the rate of production of [NO] is and how much of the reactants we have still in the pot. That is really
the crux of what kinetics is all about.