Rate Constant

In the previous lesson on the Rate Law, we talked about what the Rate Law is, how there are different reaction orders, and different types of rate laws that can tell us different characteristics about a system. However, how do chemists actually determine the rate constant for a reaction in the real world? Moreover, how could you repeat the same process they follow? That's what we'll cover in this lesson on the rate constant.

Overview

- First, we'll go through a quick review of the rate law and what the rate constant is.
- Then, we'll cover a few examples on how to calculate the rate constant from the rate law.
- Next, we'll learn the different units that are used for the rate constant.
- After that, we'll go over more difficult problems such as finding the rate constant of the rate determining step, or finding the rate constant from a table.

Review of the Rate Law

First, recall that the rate law is a mathematical model that describes how quickly a reaction takes place. The rate law is modeled like such:

$$r = k[A]^x[B]^y$$

Where A and B are reactants, x and y are their respective reactant orders, k is the rate constant, and R is the overall reaction rate. Also recall that there are reaction orders, which is the sum of reactant orders. Reaction orders help to standardize different reaction rates, so that if one were to say "this reaction is first order," we would know how time compares to reactant concentration.

We talked about this concept in the aforementioned lesson: zero order reactions have concentration directly proportional to time, while first order time is directly proportional to the natural log of the concentration, and second order time is directly proportional to the reciprocal of the concentration. To understand this concept better, we discussed the straight line test, which is a simple test that can be done to prove which order an unknown reaction is.

Most important to this lesson, we've learned that the rate constant is what ties our entire rate law together. Without the rate constant, our concentrations wouldn't describe the sum of its parts. But in formal terms, what is the rate constant?

The rate constant, k, is the unique, experimentally determined constant that connects the concentrations of the reactants to the overall rate of reaction.

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When we say unique and experimentally determined, we mean that for each different reaction, there is a different rate constant. This rate constant must be found through experimentation, which typically involves multiple trials.

💡 We'll show you how to find the rate constant through one of these experiments later in this lesson!
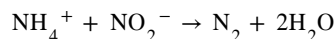
But now that we've covered what we've learned in the previous lesson on the Rate Law, let's try a few basic examples before we step into more complicated scenarios.

Rate Constant from the Rate Law

Let's try to find the unique rate law for these reactions given that we already know the Rate Law. Try to solve these on your own before checking the answers below. Again, if you need a reminder on how to approach these types of problems, consult our lesson on the Rate Law for more detail.

> **Example**
>
> **Practice Problem 1:** Write the rate law expression for the following reaction. (Assume that NH_4^+ is first order, and NO_2^- is also first order).
>
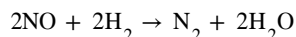> $$NH_4^+ + NO_2^- \rightarrow N_2 + 2H_2O$$
>
> Solution:
>
> $r = k[A]^x[B]^y$
> $r = k[NH_4^+][NO_2^-]$
>
> This problem is pretty straightforward. We're only considering the reactants for [A] and [B], and because both are first order, we only have an exponent of one for each.

Now, let's try to up the complexity by actually solving for the rate constant.

> **Example**
>
> **Practice Problem 2:** Write the rate law expression for the following reaction. (Assume that NO is second order, and hydrogen gas is first order). Then find the rate constant. Also report the overall reaction order.
>
> $$2NO + 2H_2 \rightarrow N_2 + 2H_2O$$
>
> Solution:

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$$r = k[A]^x[B]^y$$
$$r = k[NO]^2[H_2]$$

Remember that the reaction order is the sum of the reactant orders. If NO is second order and hydrogen gas is first order, then the overall reaction is third order.

As you can see, these problems are fairly straightforward: write an expression that accurately describes the reaction, and then solve for k, the rate constant. However, notice the different units in each problem. If each concentration has the unit mol/L, and we're adding different exponents together, this means that the units our rate constants in Practice Problem 1 and 2 are different. What's going on with that? As it turns out, because reactions can have different overall orders, rate constants can have different units as well.

Reporting the Rate Constant in Units

Recall that the purpose of the rate constant is to convert the actual concentrations of our reactants into an overall rate. While this is nice, not all reactions can just be converted "one-to-one" with simple units. Remember that concentration is measured in moles per liter. We also know that reaction rate is measured in molarity (mole per liter) per second. Therefore, let's see how the rate constant does this with Practice Problem 2.

$$r = k[NO]^2[H_2]$$
$$\frac{M}{s} = k(M)^2(M)$$
$$\frac{M}{s} = k(M)^3$$
$$\frac{1}{M^2 * s} = k$$

As you can see, the rate constant converts whatever units the equation is in to M/s. If we were using a second order reaction, the rate constant would be 1/M*s. This is because there is one less M to cancel out. By this logic, the rate constant would be reported in the following units:

Now that we understand how to determine the rate constant from the rate law formula, and what units to report that constant in, let's walk through some more complicated examples.
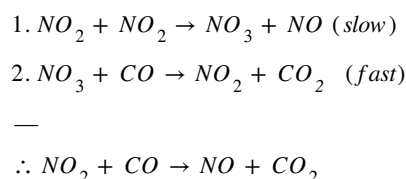
Determining the Rate Constant in Complex Examples

There are two different scenarios that you are most likely to encounter during the AP Chemistry exam when it comes to determining the rate constant: a multi-step problem, or an experimental problem. Let's walk through how to solve each of

them.

Solving a Multiple Step Problem

Sometimes analyzing a chemical equation doesn't tell the full story. As you should be aware of, final chemical equations are usually the overall chemical equations. This means that there may be more than one step that produces the overall equation. For example, take the following overall chemical equation, where each step is fully written out, including how fast each step relatively occurs.

$$1.\ NO_2 + NO_2 \rightarrow NO_3 + NO\ (slow)$$
$$2.\ NO_3 + CO \rightarrow NO_2 + CO_2\ \ (fast)$$
$$\underline{\qquad}$$
$$\therefore\ NO_2 + CO \rightarrow NO + CO_2$$

As you can see, the overall chemical equation is found by cancelling out the common reactants and products. This applies to the entire system of chemical equations. (For example, the NO_2 in the reactants of Step 1 cancels the NO_2 in the products of Step 2, which is why NO_2 doesn't appear in the products of the overall reaction.) But how would you figure out what the rate law is for a problem like this? Take a second to think about what determines how fast this reaction occurs.

Intuitively, the overall reaction is only as fast as its slowest step. This means that the overall rate law for this reaction would be its slowest step, which would be Step 1. This also means that Step 1 would be the **Rate Determining Step**. As for solving the rate constant, we now just follow the same process we have before. We set up a rate law equation using the rate determining step, and solve for k.

Solving an Experimental Problem

As mentioned earlier in this lesson, chemists have to experimentally determine a chemical equation's unique rate law. But how do they do this? As it turns out, the AP test has problems that are just like this. For example, let's say that we have hydrogen gas reacting with nitric oxide. We want to determine the rate law and rate constant from the following experimental data. How would we do this?

$$2NO + 2H_2 \rightarrow N_2 + 2H_2O$$
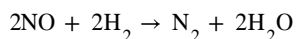
Experiment	[NO]	[H_2]	Initial Rate (M/s)
1	$5.0 * 10^{-3}$	$2.0 * 10^{-3}$	$1.3 * 10^{-5}$
2	$10.0 * 10^{-3}$	$2.0 * 10^{-3}$	$5.0 * 10^{-5}$
3	$10.0 * 10^{-3}$	$4.0 * 10^{-3}$	$10.0 * 10^{-5}$

The point of this exercise is to first determine the rate law. Recall that the rate law provides us with different reactant concentrations, as well as the orders for each reactant. This means that for each experiment, we could technically write out a "rate law" for each, which looks something like this:

$$r = k[NO]^x[H_2]^y$$

$$(1.3 * 10^{-5}) = k(5.0 * 10^{-3})^x(2.0 * 10^{-3})^y$$

$$(5.0 * 10^{-5}) = k(10.0 * 10^{-3})^x(2.0 * 10^{-3})^y$$

$$(10.0 * 10^{-5}) = k(10.0 * 10^{-3})^x(4.0 * 10^{-3})^y$$

Notice how we have every component we need with the exception of the reactant orders and rate constant. For now, let's ignore the latter and figure out how to solve the reactant orders. To do this, we can divide different experimental rate laws based on complimentary common concentrations. For example, let's say we wanted to figure out the reactant order x for NO. We see that in Experiments 1 and 2, H_2 (the reactant not in question) has the same concentration. Therefore, let's divide Experiment 2's rate law by Experiment 1's rate law, solve for x, and see what happens.

$$\frac{k(10.0 * 10^{-3})^x(2.0 * 10^{-3})^y}{k(5.0 * 10^{-3})^x(2.0 * 10^{-3})^y} = \frac{(5.0 * 10^{-5})}{(1.3 * 10^{-5})}$$

$$\therefore \quad \frac{(10.0 * 10^{-3})^x}{(5.0 * 10^{-3})^x} = \frac{(5.0 * 10^{-5})}{(1.3 * 10^{-5})}$$

$$\therefore \quad 2^x = 3.85$$

$$\therefore \quad x \approx 2$$

This means that NO's reactant order is 2. Let's repeat the same process for H_2. Which two Experiments can we use?

$$\frac{k(10.0 * 10^{-3})^x(4.0 * 10^{-3})^y}{k(10.0 * 10^{-3})^x(2.0 * 10^{-3})^y} = \frac{(10.0 * 10^{-5})}{(5.0 * 10^{-5})}$$

$$\therefore \quad \frac{(4.0 * 10^{-3})^y}{(2.0 * 10^{-3})^y} = \frac{(10.0 * 10^{-5})}{(5.0 * 10^{-5})}$$

$$\therefore \quad 2^y = 2$$

$$\therefore \quad y = 1$$

Experiments 3 and 2 allow for the same algorithm to be used. From this, we can determine that H_2's reactant order is 1. Now, we know that the overall rate law for this reaction is:

$$r = k[NO]^2[H_2]$$

Lastly, we can determine the rate constant k by following the same process as before: taking the data of an experiment, filling in the proper reactant orders, and solving for k. For the example below, I used Experiment 3's data. However, you should get the same rate constant despite which experimental data you use.

$$k(10.0 * 10^{-3})^2(4.0 * 10^{-3}) = (10.0 * 10^{-5})$$

$$\therefore \quad k = 250 \, \frac{1}{M^2s}$$

$$\therefore \quad r = (250)[NO]^2[H_2]$$

Hopefully, walking through these difficult problems step-by-step helps you to feel more confident when approaching these questions. It's important to remember to take your time with these sorts of problems, and to always double check your

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work.

Rate Constant - Key takeaways

- We first went through a quick review of the rate law and what the rate constant is.
- Then, we covered a few examples on how to calculate the rate constant from the rate law.
- Afterwards, we learned the different units that are used for the rate constant.
- Lastly, we went over more difficult problems such as finding the rate constant of the rate determining step, or finding the rate constant from a table.

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