Rate Law

Chemical reactions are happening everywhere around you- literally all the time. So far in AP Chemistry, you've learned about different reaction types, reactants and products, and concentrations. But what about *how fast* these reactions take place? As it turns out, one of the key factors that influence the speed of chemical reactions is the concentration of the reactants. Not only that, but we can mathematically model this to understand how the reaction works on a deeper level. We can do this using something called the **Rate Law**.

> **Definition**
>
> The Rate Law is used to model a reaction's speed based on the concentration of its reactants. It's also sometimes known as the differential rate law.

You'll also come to learn that there's multiple types of Rate Laws (as hinted at in the above definition), and that these are used to categorize reactions based on something called *order*. In this lesson, we'll cover the types of Rate Laws, what order means, and what we can learn from this information.

Overview

- This lesson will help you understand you the fundamental chemistry behind the **Rate Law**.
- We'll start with the basic **Rate Law equation**, and we'll break down what it means.
- We'll then cover what **order** means, and briefly discuss the different types of reaction orders.
- You'll learn that this basic equation is only the first of *two* Rate Laws: **differential and integrated.**
- Lastly, you'll learn a basic method on how to determine reaction order through experimental means using the **Straight Line Test**.

Rate Law Equation

First, let's cover the basic structure of the rate law equation. Let's imagine a basic reaction, where two reactants form the some product. Let's name our two reactants A and B, and imagine our chemical formula to be:
A + B -> C + D.

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

- [A] and [B] represent the **concentrations** of reactants A and B.
- x and y represent the reaction **order** for each reactant *respectively*. (x is [A]'s reaction order, y is [B]'s reaction order, etc.) These are determined **through experiments**.
- k is the rate constant.

StudySmarter

Create the best notes with **StudySmarter.de**

- r is the overall reaction rate.

Analyzing the Equation

Let's break this down step-by-step. This law clearly shows that we can find the overall rate of reaction through considering the concentrations of each reactant, these reactants' "orders," and some experimentally determined rate constant.

Notice how we don't consider the coefficients in our reaction A + B -> C + D. It's implied here that the coefficients for A and B are 1, but what if they were 2? or 4?
What if we had the chemical equation 2A + 4B -> C + D?
If we look at the provided equation, we'll see that the coefficients aren't considered. So for now, we don't need to worry about the coefficients of our reaction.

What about the x and y? These are reaction orders, that also have nothing to do with the coefficients of our chemical reaction, or any sort of related stoichiometry. There's no information that the chemical equation can give you on its own to help you determine these. These have to be found through experiments, and can be calculated if given a proper amount of information.
You'll learn about the types of reaction orders, and briefly how to calculate reactant order later in this lesson.

Lastly, we have to consider k. k is a rate constant that helps to keep the aforementioned variables proportional with the environment that the experiment is taking place in. This typically changes with a given temperature. For example, a problem that provides k would most likely be stated like the following: "In an experiment, it was determined that the reaction constant k is x at y degrees."

Differential Rate Law in Practice

Now that we know what the basic structure of the Rate Law looks like, let's try a simple example.

Practice Problem 1: Write the expression for the following reaction. (Assume that NO is second order and H2 is first order.)
$$2NO_{(g)} + 2H_{2(g)} \rightarrow N_{2(g)} + 2H_2O_{(g)}$$
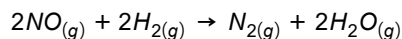
$$r = k[NO]^x[H_2]^y$$
$$x = 2nd\ order,\ y = 1st\ order$$

$$r = k[NO]^2[H_2]^1$$

As you can see, when the order of reactants are provided, the problem is fairly straightforward. Make sure you're comfortable with this form, as it will reappear often.

Reaction Order

Reactant vs Reaction Order

Insofar, we've mentioned the concept of **reaction order** multiple times. But what does that actually mean? In short, the reaction order is the relationship between the concentration of reactants and the actual rate of reaction. A better way of looking at it would be: *"how much does this reactant influence the rate of reaction?"* Obviously, the higher the **reactant order**, the more influence its concentration has on the speed of the reaction.

> **Definition**
>
> Each reactant order represents the proportion of influence that reactant's concentration has on the overall rate of reaction.

Let's refer back to our Practice Problem 1. Would increasing the concentration of NO or H_2 have more of an influence on the overall rate of reaction? Of course, the answer would be NO, because of its higher reactant order.

We've talked about reactant order, but what about the overall reaction order? If we know the Rate Law for a certain reaction, how can we find what order the reaction is?

> **Definition**
>
> The overall rate of reaction can be found by summing the reactant orders.

Simple enough, right? We can find the overall rate of reaction by adding up the orders of each of our reactions. So, referring back to our trusty Practice Problem 1, what would the *reactant* orders and *reaction* order be? NO's reactant order is 2, H_2's reactant order is 1, and the overall reaction order is 3. But why do we go through this process of categorizing reactions into overall orders?

Integrated Rate Law

Before, we mentioned the **integrated rate law**. What's that about? As it turns out, if we integrate the rate law, we can extract information that will help us to analyze experimental plots. This is why overall reactions are categorized into order: we can quickly deduce a good bit of information about a reaction through only a little experimental data.

The integrated rate law is dependent on the order of the rate law being analyzed. This means that there's a different integrated rate law for zero order reactions, first order reactions, second order reactions, and so on. In AP Chemistry, you will only be dealing with these scenarios.

Let's keep things simple and assume that we only care about the concentration of a single reactant. Let's call this reactant A. Because we want to analyze the rate of change in this reactant, we want to consider the initial concentration, and current concentration in question. Let's integrate the Rate Law for each order.

Reaction Order	Rate Law (Differential)	Integrated Rate Law
0	$r = k[A]^0 = k$	$[A] = [A]_0 - kt$
1	$r = k[A]$	$[A] = [A]_0 e^{-kt}$
2	$r = k[A]^2$	$[A] = [A]_0 / (1 - kt[A]_0)$

Deep dive

If you are curious on how the Integrated Rate Law is found from the rate law, a simple mathematical proof is given below for *first order reactions*. This won't be necessary to memorize.

The differential rate law can be rewritten as

$$r = k[A] = \frac{-d[A]}{dt}$$

This means that

$$k[A] = \frac{-d[A]}{dt}$$

We can separate variables

$$-kdt = \frac{d[A]}{[A]}$$

And now integrate to get our Law

$$[A]_0 e^{-kt} = [A]$$

First, let's graph what these integrated rate laws would look like on their own.

Integrated Rate Law reaction order graphs.

These are what zero order, first order, and second order reactions would look like if you had gathered data, used the integrated rate law, and thrown it into a graphing calculator. Notice that the slope of each of these graphs is the rate constant, k. But first and second order look awfully similar, and maybe we want to be extra careful. How can we determine what order a reaction is through experimental data?

Straight Line Test

The answer to this is by trying to set the equation up in a way so that [A] and t plot along a straight line.

Reaction Order	Integrated Rate Law	Straight Line Test
0	$[A] = [A]_0 - kt$	[A] vs t (yields -k)
1	$[A] = [A]_0 e^{-kt}$	ln[A] vs t (yields -k)
2	$[A] = [A]_0 / (1 - kt[A]_0)$	1/[A] vs t (yields k)

Now let's see what we get if we plot according to the Straight Line Test.

Straight Line Test examples for the Integrated Rate Law.

Now here's where the kicker comes in. The Straight Line Test will only work for the order that the reaction actually is. That means that if we have a first order reaction and we try to graph it for ln[A] vs t on our graphing calculator, we'll get a straight line. But if we try to graph that same reaction for [A] vs t or 1/[A] vs t, we won't get a straight line. This means that the Straight Line Test can be used to identify which order a reaction is. Note that second order reactions will give you a straight line with a positive slope k, while zero and first order reactions will yield a negative straight line -k.

Integrated Rate Law in Practice

Let's try to work through an example of the Straight Line Test together.

Practice Problem 2: You are given a table of data that corresponds the concentration of reactant A over time. You remember that the Straight Line Test can help you determine reaction order, so you plot [A], ln[A], and 1/[A] against time on your graphing calculator. What is the reaction order?
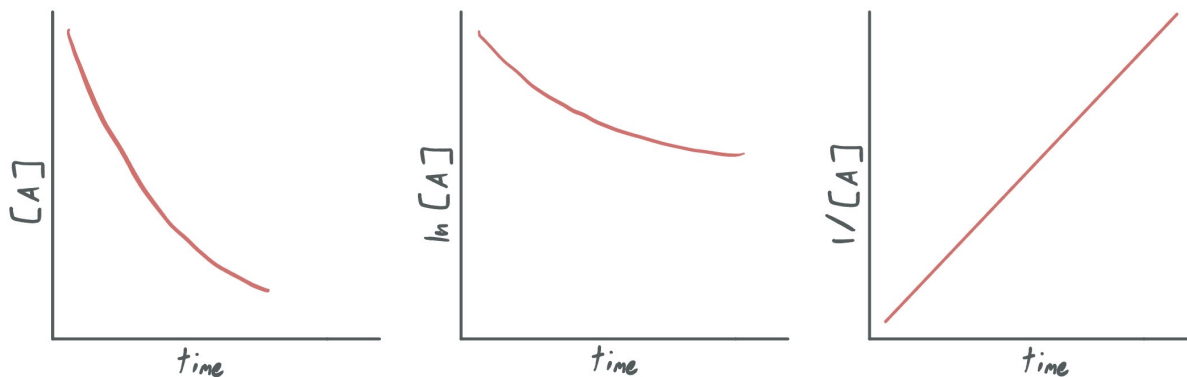
Practice Problem for applying the Straight Line Test.

Therefore, we know that this reaction is x order, because that order is the only one that passes the Straight Line Test.

Rate Law - Key takeaways

- The Rate Law models a reaction's speed based on the concentration of its reactants. It consists of a rate constant, the concentration of reactants, and reactant orders.
- Reactants have individual orders, and overall reactions also have orders. The overall reaction order is the sum of the reactant orders.
- The Integrated Rate Law can be used to determine reaction order through experimental data.
- AP Chemistry primarily deals with zero, first, and second order reactions. Zero and first order reactions will yield a negative slope straight line on the Straight Line Test, while second order reactions will yield a positive slope straight line.
- This slope is representative of the rate constant, k.