

2.2: The Rate Law Takes Different Forms

Sometimes it is useful to think of the rate law in different ways.

First Order Rate Law

For a first order reaction, we have seen the following rate law:

$$\text{Rate} = \frac{d[P]}{dt} = k[R] \quad (2.2.1)$$

In this case, R is a reactant and P is the product. This rate law indicates that as reactant concentration increases, the rate of formation of the product increases proportionally. On the other hand, the concentration of reactant will decrease as it is converted into product, so we could also describe the rate of reactant consumption by the same rate law.

$$\text{Rate} = \frac{-d[R]}{dt} = k[R] \quad (2.2.2)$$

Sometimes, it can be useful to look at that rate law a different way. If we use a little algebra on the original rate law, we can cross-multiply and get an equivalent expression:

$$d[R] = -k[R]dt \quad (2.2.3)$$

or, going one step further,

$$\frac{d[R]}{[R]} = -kdt \quad (2.2.4)$$

What we are doing here is separating out these two differential terms so that we can integrate the expression. Instead of looking at what is happening in, for example, an infinitesimal unit of time, we are going to step back and see what happens in a much larger block of time.

$$\int \frac{d[R]}{[R]} = \int -kdt \quad (2.2.5)$$

We can pull any constants in front of the integral.

$$\int \frac{d[R]}{[R]} = -k \int dt \quad (2.2.6)$$

We can integrate the two halves of the equation separately. The right hand side is simple. The integral of dt is just t, time. It is the elapsed time from the start of the experiment until the current time.

$$\int \frac{d[R]}{[R]} = -k(t - t_0) \quad (2.2.7)$$

Or if the experiment started at $t = 0$

$$\int \frac{d[R]}{[R]} = -kt \quad (2.2.8)$$

The left side is not very complicated either; the integral of $1/x \, dx$ is $\ln(x)$, the natural log. Again, it would be the current value of $\ln(x)$ minus the value of $\ln(x)$ at the beginning of the experiment.

$$\ln([R]) - \ln([R]_0) = -kt \quad (2.2.9)$$

Or, using the rules of logarithms,

$$\ln\left(\frac{[R]}{[R]_0}\right) = -kt \quad (2.2.10)$$

This is called the integrated form of the rate law. The form we started with is called the differential form of the rate law. Both are useful. The reason people use an integrated form is to easily plot linear relationships. In this form, if we plot $\ln([R]/[R]_0)$ on the y

axis and time on the x axis, and the reaction is first order, we will get a straight line. The slope will be $-k$. This is an easy way to find a rate constant.

Another useful outcome of the integrated form of the rate law is the relationship between "half life" and the rate constant. Half life is the time it takes for a first order reaction to be 50% complete; half the reactants have been converted to product. In other words, the ratio $[R]/[R]_0 = 0.5$. At that point,

$$\ln(0.5) = -kt_{\frac{1}{2}} \quad (2.2.11)$$

In which $t_{1/2}$ just refers to the half life, the time to get to 50% completion of the reaction.

Once again, the rules of logarithms can help simplify things.

$$-\ln(0.5) = \ln(2) \quad (2.2.12)$$

so

$$\ln(2) = kt_{\frac{1}{2}} \quad (2.2.13)$$

$$0.693 = kt_{\frac{1}{2}} \quad (2.2.14)$$

or

$$t_{\frac{1}{2}} = \frac{0.693}{k} \quad (2.2.15)$$

So if we know the half life, we can easily calculate the rate constant, and vice versa.

Second Order Rate Law

We can take a similar approach for a rate law that is second order in reactant. The integrated rate law provides a different treatment that can be useful.

$$\text{Rate} = \frac{-d[R]}{dt} = k[R]^2 \quad (2.2.16)$$

Cross-multiplying allows us to separate the two differential terms.

$$\frac{d[R]}{[R]^2} = -kdt \quad (2.2.17)$$

We can integrate each side. This time, we have the integral of $1/x^2$, or x^{-2} , which is just $1/x$, or x^{-1} .

$$\int \frac{d[R]}{[R]^2} = -k \int dt \quad (2.2.18)$$

$$\frac{1}{[R]} - \frac{1}{[R_0]} = -kt \quad (2.2.19)$$

Like the integrated form of the first order rate law, the integrated form of the second order rate law allows concentration data to be plotted against time, giving a linear relation. This time, the reciprocal of the reactant concentration is plotted, $1/[R]$. The slope once again provides the rate constant via $-k$. The y intercept is the reciprocal of the starting concentration of reactant.

This page titled [2.2: The Rate Law Takes Different Forms](#) is shared under a [CC BY-NC 3.0](#) license and was authored, remixed, and/or curated by [Chris Schaller](#) via [source content](#) that was edited to the style and standards of the LibreTexts platform.