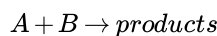# 11.3: Rate Laws

A rate law is any mathematical relationship that relates the concentration of a reactant or product in a chemical reaction to time. Rate laws can be expressed in either derivative (or ratio, for finite time intervals) or integrated form. One of the more common general forms a rate law for the reaction

$$A + B \rightarrow products$$

may take is

$$\text{rate} = k[A]^\alpha [B]^\beta$$

where k, α, and β are experimentally determined values. However, a rate law can take many different forms, some of which can be quite intricate and complex. The powers α and β need not be integers. For example

$$\text{rate} = k[A]^\alpha [B]^{1/2} \tag{11.3.1}$$

is a rate law that is observed for some reactions. Sometimes, the concentrations of products must be included.

$$\text{rate} = \frac{k[A]^{1/2}[B]}{[P]}$$

In some cases, the concentration for a catalyst or enzyme is important. For example, many enzyme mitigated reactions in biological systems follow the Michaelis-Menten rate law, which is of the form

$$\text{rate} = \frac{V_{max}[S]}{K_m + [S]}$$

where V_{max} and K_M are factors that are determined experimentally, and $[S]$ is the concentration of the substrate in the reaction.

Order

For those cases where the rate law can be expressed in the form

$$\text{rate} = k[A]^\alpha [B]^\beta [C]^\gamma$$

where A, B, and C are reactants (or products or catalysts, etc.) involved in the reaction, the reaction is said to be of α order in A, β order in B, and γ order in C. The reaction is said to be $\alpha + \beta + \gamma$ order overall. Some examples are shown in the following table:

Table 11.3.1: Example Rate Laws

Rate law	Order with respect to A	Order with respect to B	Order with respect to C	Overall order
$\text{rate} = k$	0	0	0	0
$\text{rate} = k[A]$	0	0	0	1
$\text{rate} = k[A]^2$	0	0	0	2
$\text{rate} = k[A][B]$	0	1	0	2
$\text{rate} = k[A]^2[B]$	0	1	0	3
$\text{rate} = k[A][B][C]$	0	1	1	3

Reaction orders can also be fractional such as for Equation 11.3.1 which is 1st order in A, and half order in B. The order can also be negative such as
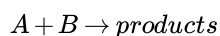
$$\text{rate} = k\frac{[A]}{[B]}$$

which is 1st order in A, and -1 order in B. In this case, an build-up of the concentration of B will retard (slow) the reaction.

In all cases, the order of the reaction with respect to a specific reactant or product (or catalyst, or whatever) must be determined experimentally. As a general rule, the stoichiometry cannot be used to predict the form of the rate law. However, the rate law can be used to gain some insight into the possible pathways by which the reaction can proceed. That is the topic of Chapter 12. For now we will focus on three useful methods that are commonly used in chemistry to determine the rate law for a reaction from experimental data.

Empirical Methods

Perhaps the simplest of the methods to be used are the empirical methods, which rely on the qualitative interpretation of a graphical representation of the concentration vs time profile. In these methods, some function of concentration is plotted as a function of time, and the result is examined for a linear relationship. For the following examples, consider a reaction of the form

$$A + B \rightarrow products$$

in which A is one of the reactants. In order to employ these empirical methods, one must generate the forms of the integrated rate laws.

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