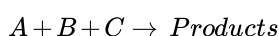


5.10: Rate Laws by the Study of Initial Rates

In concept, the most straightforward way to measure reaction rate directly is to measure the change in the concentration of one reagent in a short time interval immediately following initiation of the reaction. The initial concentrations are known from the way the reaction mixture is prepared. If necessary, the initial mixture can be prepared so that known concentrations of products or reaction intermediates are present. The initial reaction rate is approximated as the measured concentration change divided by the elapsed time. The accuracy of initial-rate measurements is often poor. This can result from concentration variations associated with initiation of the reaction; the actual mixing process is not instantaneous and significant reaction can occur before the mixture becomes truly homogeneous. Measuring small changes in concentration with sufficient accuracy can also be difficult.

Enzymes are naturally occurring catalysts for biochemical reactions. In the study of enzyme-catalyzed reactions, it is usually possible to select the enzyme concentration and other reaction conditions so that the initial rate can be measured with adequate accuracy. For such studies, initial-rate measurements are used extensively. For other types of reactions, the method of initial rates is usually less effective than alternative methods.

To illustrate the application of the method, suppose we have a reaction



and that we are able to measure small changes in $[A]$ with good accuracy. We seek a rate law of the form

$$-\frac{d[A]}{dt} = f([A], [B], [C])$$

For any given experiment we approximate $d[A]/dt$ by $\Delta[A]/\Delta t$, and approximate the average concentrations of the reagents over the interval Δt by their initial values: $[A] = [A]_0$, $[B] = [B]_0$, and $[C] = [C]_0$. By carrying out an number of such experiments with suitably chosen initial concentrations, we can determine the functional form of the rate law and evaluate the rate constants that appear in it.

Table 5.10.1: Hypothetical reaction rate data

$\Delta[A]/\Delta t \text{ M}$	$\Delta t, \text{s}^{-1}$	$[A]_0$	$[B]_0$	$[C]_0$
-2×10^{-7}	1000	0.010	0.010	0.010
-4×10^{-7}	500	0.010	0.010	0.020
-2×10^{-7}	1000	0.010	0.020	0.010
-8×10^{-7}	2500	0.020	0.010	0.010

Table 5.10.1 presents data for a hypothetical reaction that serve to illustrate the basic concept. We suppose that initial rates have been determined for four different combinations of initial concentrations. Comparison of the first and second experiments indicates that doubling $[C]$ doubles the reaction rate, indicating that the rate depends on $[C]$ to the first power. Comparison of the first and third experiments indicates that doubling $[B]$ leaves the reaction rate unchanged, implying that the rate is independent of $[B]$. Comparison of the first and fourth experiments indicates that doubling $[A]$ increases the reaction rate by a factor of four, implying that the rate is proportional to the second power of $[A]$. We infer that the rate law is

$$-\frac{d[A]}{dt} = k[A]^2[B]^0[C]^1$$

Given the form of the rate law, an estimate of the value of the rate constant, k , can be obtained from the data for each experiment. For this illustration, we calculate $k = 0.20 \text{ M s}^{-1}$ from each of the experiments.

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