

Deriving the Integrated Rate Laws for First-Order and Second-Order Reactions

The experimentally determined differential rate laws, which have the general form $Rate = k[A]^m[B]^n \dots$, show the relationships between concentrations and $Rate$. These are inherently differential equations, because the $Rate$ is always defined as a change in concentration with time; i.e., the first derivative of concentration with respect to time. If a differential rate law equation is integrated between appropriate limits, the resulting integrated rate law equation shows the dependence of concentration on time. The order of the differential rate equation, of course, determines the form of the integrated equation. In the cases of first- and second-order reactions, the two unique forms of the integrated rate law expression yield different straight-line equations, the slopes of which can be used to calculate the rate constant, k , for the reaction. Determining k from plots of the integrated rate law expressions is better than using just one pair of concentration and $Rate$ values, because the plot tends to average out all the experimental errors.

First-Order integrated Rate Law

For a reaction, $A \rightarrow \text{products}$, which is first-order in A , we can write

$$Rate = \frac{-d[A]}{dt} = k[A] \quad (1)$$

We can rearrange equation (1) with the stipulation $[A] \neq 0$ as follows:

$$\frac{-d[A]}{[A]} = k dt \quad (2)$$

Suppose we consider the change in concentration of A from its initial value $[A]_0$ at time $t_0 = 0$ to its value $[A]$ at some later time t . Integrating equation (2) between the limits $[A]_0$ and $[A]$ on the left and between the limits $t_0 = 0$ and t on the right gives

$$-\int_{[A]_0}^{[A]} \frac{d[A]}{[A]} = k \int_{t_0 = 0}^t dt \quad (3)$$

Solving the integrals on both sides gives

$$-\ln\left(\frac{[A]}{[A]_0}\right) = kt \quad (4)$$

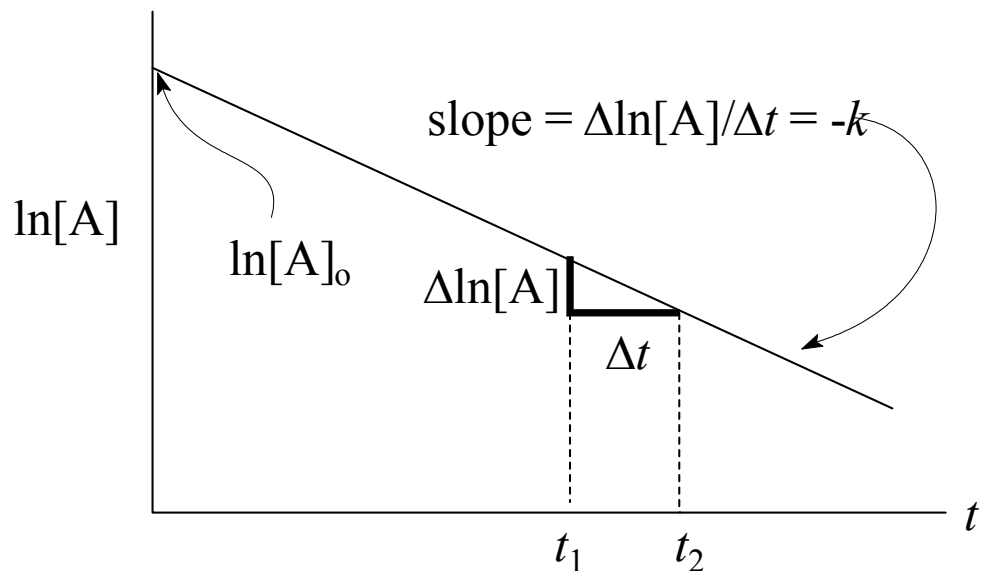
which may be rewritten as

$$\ln\left(\frac{[A]}{[A]_0}\right) = -kt \quad (5)$$

If we expand equation (5) we see that this is a straight-line equation of the form $y = mx + b$

$$\ln[A] = -kt + \ln[A]_0 \quad (6)$$

in which $\ln[A]$ is the y variable, t is the x variable, $-k$ is the slope (m), and $\ln[A]_0$ is the y intercept (b). Thus, if we plot the natural logarithm of $[A]$ versus t for a first-order reaction we should get a straight line whose slope is $-k$ and whose intercept is $\ln[A]_0$.



Obtaining a straight-line plot of this type from a set of kinetic data is proof of first-order kinetics. Moreover, obtaining the value of k from the slope is better than obtaining by solving the differential rate law for one pair of observed rate and concentration values, because experimental error is more likely to be averaged out.

Second-Order Integrated Rate Law

For a reaction, $A \rightarrow \text{products}$, which is first-order in A , we can write

$$\text{Rate} = \frac{-d[A]}{dt} = k[A]^2 \quad (7)$$

We can rearrange equation (7) with the stipulation $[A] \neq 0$ as follows:

$$\frac{-d[A]}{[A]^2} = k dt \quad (8)$$

As with the first-order case, let us consider the change in concentration of A from its initial value $[A]_0$ at time $t_0 = 0$ to its value $[A]$ at some later time t . Integrating equation (8) between the limits $[A]_0$ and $[A]$ on the left and between the limits $t_0 = 0$ and t on the right gives

$$-\int_{[A]_0}^{[A]} \frac{d[A]}{[A]^2} = k \int_{t_0=0}^t dt \quad (9)$$

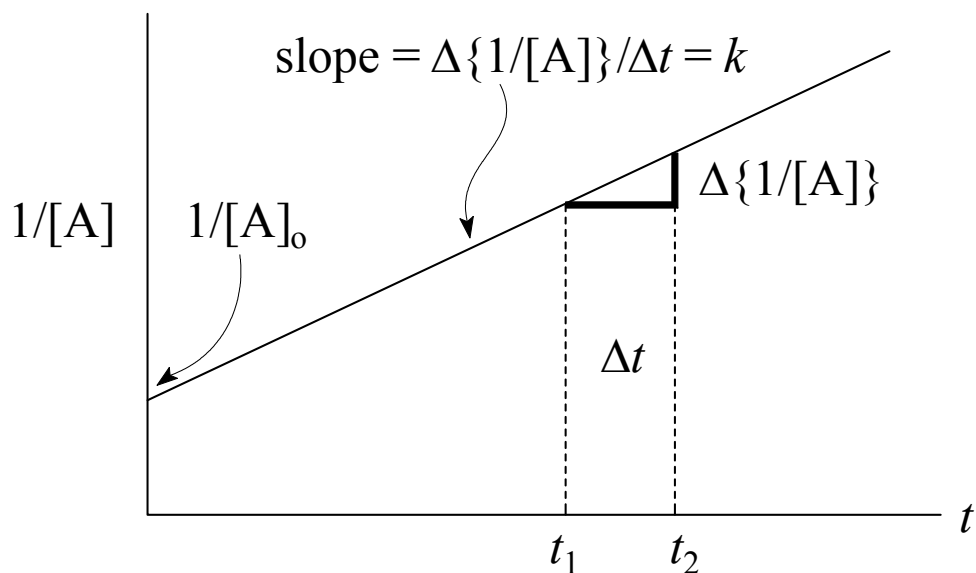
Solving the integrals on both sides gives

$$\frac{1}{[A]} - \frac{1}{[A]_0} = kt \quad (10)$$

Rearranging equation (10) as follows

$$\frac{1}{[A]} = kt + \frac{1}{[A]_0} \quad (11)$$

gives a straight-line equation of the form $y = mx + b$ in which $1/[A]$ is the y variable, t is the x variable, k is the slope (m), and $1/[A]_0$ is the y intercept (b). Thus, if we plot the reciprocal of $[A]$ versus t for a second-order reaction we should get a straight line whose slope is k and whose intercept is $1/[A]_0$.



As with the first-order plot, the linearity of a plot of $1/[A]$ vs. t can be taken as proof of second-order dependency of the *Rate* on $[A]$. Likewise, using the straight-line slope as a method for determining k is experimentally preferable to using data for a single pair of observed rate and concentration data.