

15.3: Experimental Methods for Determination of Reaction Orders

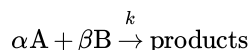
To experimentally measure the reaction rate, we need a method to measure concentration changes with respect to time. The simplest way to determine the reaction rate is to monitor the entire reaction as it proceeds and then plot the resulting data differently until a linear plot is found. A summary of the results obtained in [section 15.1](#) and that is useful for this task is reported in the following table:

	Zeroth-Order	First-Order	Simple Second-Order	Complex Second-Order
Differential Rate Law	$-\frac{d[A]}{dt} = k_0[A]^0 = k_0$	$-\frac{d[A]}{dt} = k_1[A]$	$-\frac{d[A]}{dt} = k_2[A]^2$	$-\frac{d[A]}{dt} = k'_2[A][B]$
Integrated Rate Law	$[A] = [A]_0 - k_0t$	$[A] = [A]_0e^{-k_1t}$	$\frac{1}{[A]} = \frac{1}{[A]_0} + k_2t$	$\frac{[A]}{[B]} = \frac{[A]_0}{[B]_0}e^{([A]_0 - [B]_0)k'_2t}$
Units of k	$\frac{M}{s}$	$\frac{1}{s}$	$\frac{1}{M \cdot s}$	$\frac{1}{M \cdot s}$
Linear Plot vs. t	$[A]$	$\ln[A]$	$\frac{1}{[A]}$	$\ln \frac{[A]_0[B]}{[B]_0[A]}$
Half-life	$t_{1/2} = \frac{[A]_0}{2k_0}$	$t_{1/2} = \frac{\ln 2}{k_1}$	$t_{1/2} = \frac{1}{k_2[A]_0}$	not easily defined

However, this method works only if the reaction has few reactants, and it requires several measurements, each of which might be complicated to make. More useful methods to determine the reaction rate are the *initial rate* and the *isolation* methods that we describe below.

Initial rates method

The *initial rates method* involves measuring the rate of a reaction as soon as it starts before any significant change in the concentrations of the reactants occurs. The initial rate method is practical only if the reaction is reasonably slow, but it can measure the rate unambiguously when more than one reactant is involved. For example, if we have a reaction with the following stoichiometry:



the initial rate method can be used to determine the coefficients of the rate law:

$$\text{Rate} = k[A]^\alpha[B]^\beta \quad (15.3.1)$$

by designing three experiment, where the initial concentrations of A and B are appropriately changed. For example, let's consider the following experimental data from three different experiments:

	$[A]_0$ (M)	$[B]_0$ (M)	initial rate $\left(\frac{M}{s}\right)$
Experiment 1:	0.10	0.10	4.32
Experiment 2:	0.15	0.10	9.70
Experiment 3:	0.10	0.20	4.29

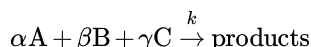
we can calculate α by taking the ratio of the rates measured in experiment 1 and 2:

$$\begin{aligned}\frac{\text{Rate}(1)}{\text{Rate}(2)} &= \frac{k(0.10 \text{ M})^\alpha (0.10 \text{ M})^\beta}{k(0.15 \text{ M})^\alpha (0.10 \text{ M})^\beta} \\ \frac{4.32}{9.70} &= \frac{(0.10 \text{ M})^\alpha}{(0.15 \text{ M})^\alpha} \\ 0.445 &= 0.667^\alpha \rightarrow \ln 0.445 = \alpha \ln 0.667 \\ \alpha &= \frac{-0.81}{-0.405} = 2.\end{aligned}\tag{15.3.2}$$

β can be calculated similarly by taking the ratio between experiments 1 and 3. Alternatively, we can also notice that the reaction rate does not change when the initial concentration $[B]_0$ is doubled, therefore $\beta = 0$.

Isolation method

Another method that is widely used to determine reaction orders is the *isolation method*. This method is performed by using large excess concentrations of all reactants but one. For example, if we have the following reaction with three reagents and unknown rate law:



we can perform three different experiments, in each of which we use an excessive amount of one of the two reagents, such as:

- Experiment 1: $[A]_0 = 1 \text{ M}$, $[B]_0 = 1000 \text{ M}$, $[C]_0 = 1000 \text{ M}$, in which the reaction order with respect to A is measured.
- Experiment 2: $[A]_0 = 1000 \text{ M}$, $[B]_0 = 1 \text{ M}$, $[C]_0 = 1000 \text{ M}$, in which the reaction order with respect to B is measured.
- Experiment 3: $[A]_0 = 1000 \text{ M}$, $[B]_0 = 1000 \text{ M}$, $[C]_0 = 1 \text{ M}$, in which the reaction order with respect to C is measured.

From each experiment we can determine the *pseudo-order* of the reaction with respect to the reagent that is in minority concentration. For example, for the reaction above, we can write the rate law as:

$$\text{Rate} = k[A]^\alpha [B]^\beta [C]^\gamma\tag{15.3.3}$$

and we can write the initial concentrations, $[X]_0$, and the final concentrations, $[X]_f$, of each of the species in experiment 1, as:

$$\begin{aligned}[A]_0 = 1 \text{ M} &\rightarrow [A]_f = 0 \text{ M} && (100\% \text{ change}) \\ [B]_0 = 1000 \text{ M} &\rightarrow [B]_f = 1000 - 1 = 999 \text{ M} \cong [B]_0 && (0.1\% \text{ change}) \\ [C]_0 = 1000 \text{ M} &\rightarrow [C]_f = 1000 - 1 = 999 \text{ M} \cong [C]_0. && (0.1\% \text{ change})\end{aligned}$$

The coefficient α can then be determined by incorporating the concentration of the reactants in excess into the rate constant as:

$$\begin{aligned}\text{rate} &= k[A]^\alpha \underbrace{[B]^\beta [C]^\gamma}_{\text{constant}} \\ &= k'[A]^\alpha\end{aligned}$$

and then determine α by verifying which order the data collected for $[A]$ at various time fit. This can be simply achieved by using the zero-, first-, and second-order kinetic plots, as reported in the table above. We can determine β and γ by repeating the same procedure for the data from the other two experiments. For example, if we find for a specific reaction that $\alpha = 1$, $\beta = 2$, and $\gamma = 0$, we can then say that the reaction is pseudo-order one in A, pseudo-order two in B, and pseudo-order zero in C, with an overall reaction order of three.

This page titled [15.3: Experimental Methods for Determination of Reaction Orders](#) is shared under a [CC BY-SA 4.0](#) license and was authored, remixed, and/or curated by [Roberto Peverati](#) via [source content](#) that was edited to the style and standards of the LibreTexts platform.