

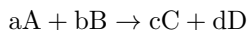
## 1 Reaction kinetics

Not every reaction is the the same: early on, we talked about stoichiometry and how chemical equations give information about what is reacting and in what ratios. We learned how to determine which reactants would be limiting, and which would be in excess. The *rate* of a reaction is the change in concentration as a function of change in time. Reactants are consumed, so their rate is negative, and products are formed, so their rate is positive.

To determine the rate of a reaction experimentally, we simply measure and plot the concentration as a function of time. The *order* of a reaction refers to the relationship between concentration and rate. If the reaction rate is independent of the concentration of a reagent, the reaction is  $0^{th}$  order in that reagent. If the reaction rate doubles when the concentration of a reagent is doubled, the reaction is  $1^{st}$  order in that reagent. Finally, if the reaction rate quadruples when the concentration of a reagent is doubled, the reaction is  $2^{nd}$  order in that reagent. Note that order is defined with respect to a specific reagent (usually for each reactant), not for a reaction as a whole!

When there are multiple reactants, it can be difficult to determine which reactant is causing the rate to change in what way. The best way to isolate the effect of changing concentration is to modulate the concentration of each reactant in turn, while holding the others constant.

Say we have a reaction of the following form:



Conservation of mass allows us to write a generalized rate law, since we know that the rate at which the reactants disappear must equal the rate at which products appear:

$$\text{rate} = -\frac{1}{a} \frac{d[A]}{dt} = -\frac{1}{b} \frac{d[B]}{dt} = \frac{1}{c} \frac{d[C]}{dt} = \frac{1}{d} \frac{d[D]}{dt}$$

Say the dependence of rate on concentration is as follows:

	[A]	[B]	rate
Experiment 1	2 M	1 M	140 mM/s
Experiment 2	2 M	4 M	560 mM/s
Experiment 3	1 M	1 M	35 mM/s

Notice that if we compare Experiments 1 and 2, the concentration of B quadruples, while the concentration of A is kept constant, and the rate also quadruples. This reaction must be first order in B! Comparing Experiments 1 and 3, the concentration of A halves, the concentration of B is constant, and the rate decreases by a factor of 4. Since the reaction increases with the square of the concentration of A, this reaction must be second order in A. The *general* rate law can be expressed as

$$r = k[A]^2[B]$$

Here, the constant  $k$  is called the *rate constant*. The overall order of the reaction is given by the sum of the rates of the individual components. In our example above, the overall reaction rate is 3.

## 2 Rate laws and rate constants

The rate law for a  $0^{th}$  order reaction is

$$r = k[A]^0 = k$$

The units of the rate constant must therefore be units of rate, or M/s. The integrated rate law can be found by integrating the rate law with respect to time, recalling that rate is change in concentration per unit time. For  $0^{th}$  order, the integrated rate law is

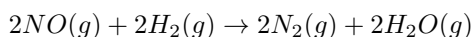
$$[A] = [A]_0 - kt$$

A similar analysis can be performed for first and second order reactions; the characteristics are summarized below:

	$0^{th}$ order	$1^{st}$ order	$2^{nd}$ order
rate law	$r = k$	$r = k[A]$	$r = k[A]^2$
units of k	$M s^{-1}$	$s^{-1}$	$M^{-1} s^{-1}$
integrated rate law	$[A] = [A]_0 - kt$	$\ln[A] = \ln[A]_0 - kt$	$\frac{1}{[A]} = \frac{1}{[A]_0} + kt$

If you've had some diff eq, try to produce the integrated rate laws for each order for the rate laws given! You just need to separate variables and choose appropriate integration limits.

**Example:** You measure the rate at which reactants are consumed for the following reaction. Determine the overall order of the reaction and write the general rate law. What are the units of the rate constant k?



Trial	[NO]	[H <sub>2</sub> ]	rate
1	0.1 M	0.1 M	1.2 mM/s
2	0.1 M	0.2 M	2.4 mM/s
3	0.3 M	0.1 M	10.8 mM/s

Comparing trial 2 to trial 1, the rate doubles while the concentration of H<sub>2</sub> doubles, so the reaction must be first order in [H<sub>2</sub>]. Comparing trial 3 to trial 1, the concentration of NO triples and the rate increases by a factor of 9 (= 3<sup>2</sup>). The reaction must therefore be second order in [NO].

The overall rate law for this reaction is

$$\text{rate} = -\frac{d[NO]}{dt} = -\frac{d[H_2]}{dt} = k[NO]^2[H_2]$$

The overall order of the reaction is the sum of the orders of the constituent reactants: in this case, 2+1=3, so the overall reaction order is 3. Finally, both sides of the rate equation must have the same units: the rate has units of M/s. We must choose the units of k such that the right hand side matches. The concentrations contribute M<sup>3</sup>; therefore, the units of k must be M<sup>-2</sup>s<sup>-1</sup> to match.

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