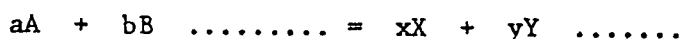


Handling of Experimental Kinetic Data

One of the basic concepts in reaction kinetics is that of the "rate constant". The constant applies to a particular rate expression, and some of the methods adopted for the determination of order and rate constant and so are given in the following pages.

Rate equation

For a chemical reaction represented by

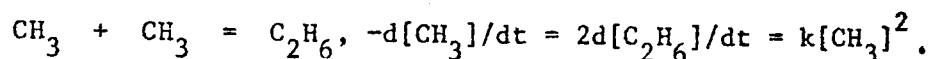


we may write the rate of removal and formation of reactants and products in the form

$$-\frac{1}{a} \frac{d[A]}{dt} = -\frac{1}{b} \frac{d[B]}{dt} = +\frac{1}{x} \frac{d[X]}{dt} = +\frac{1}{y} \frac{d[Y]}{dt} = k[A]^\alpha [B]^\beta .$$

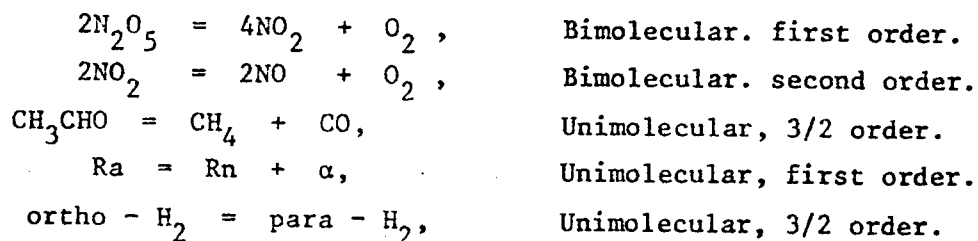
The molecularity of a reaction is defined as $a+b+\dots\dots$, while the order is defined as $\alpha+\beta+\dots\dots$. Molarities and orders may also be defined with respect to particular components (e.g. the order w.r.t. A is α).

Notes: The expression given above defines the rate constant k for a reaction of given stoichiometry. Other definitions are sometimes used, for example, in



It is important to state which component the rate applies to.

Molecularity and order are not always identical, and in general they are the same only for elementary reaction steps. Some examples are given below of molarities and orders:



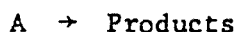
Reaction Variable

It is frequently useful to introduce a reaction variable x , which is the number of equivalents per litre that have reacted in time t . dx/dt is then a convenient expression for the rate of reaction.

Integrated Forms of the Rate Equations

The amount of reactant remaining, or the amount of product formed, after a time t is often the quantity measured experimentally rather than the rate dx/dt . It is therefore necessary to integrate the rate equations. Some examples are given below:

First order reaction



Concentration on a initially, $(a-x)$ after time t . Thus $dx/dt = k_1 (a-x)$, which on integration yields

$$k_1 t = \ln \frac{a}{a-x} \quad (\text{or, } x = a(1 - e^{-k_1 t}))$$

Second order reaction



$dx/dt = k_2 (a-x)(b-x)$, which integrates to

$$\frac{1}{(a-b)} \ln \frac{b(a-x)}{a(b-x)} = k_2 t$$

N.B. For $A=B$, the form $dx/dt = k_2 (a-x)^2$ must be integrated, which gives

$$\frac{x}{a(a-x)} = k_2 t$$

The table on the next page gives the integrated forms of the rate equations for various order reactions involving a single reactant, A.

Fractional Life, τ .

The fractional life, τ , of a reaction is the time taken for the concentration of reactant to reach the specified fraction of its initial concentration. By far the most common fractional life is the "half life", $\tau_{\frac{1}{2}}$, such that $x = \frac{1}{2}a$. Some half lives are given in the table on the next page.

Rate Equations for Single Component Systems

Order	Rate	Integrated Form	Half-Life	Units for k
0th	k_0	$k_0 t = x$	$a/2k_0$	$\text{mole l}^{-1} \text{sec}^{-1}$
1st	$k_1(a-x)$	$k_1 t = \ln \frac{a}{a-x}$	$\ln 2/k_1$	sec^{-1}
2nd	$k_2(a-x)^2$	$k_2 t = \frac{x}{a(a-x)}$	$1/ak_2$	$\text{l mole}^{-1} \text{sec}^{-1}$
3rd	$k_3(a-x)^3$	$k_3 t = \frac{x(2a-x)}{2a^2(a-x)^2}$	$3/2ak_3$	$\text{l}^2 \text{mole}^{-2} \text{sec}^{-1}$
nth	$k_n(a-x)^n$	$k_n t = \frac{1}{(n-1)} \left[\frac{1}{(a-x)^{n-1}} - \frac{1}{a^{n-1}} \right]$	$\frac{2^{n-1} - 1}{(n-1)a^{n-1}k_n}$	$\text{l}^{n-1} \text{mole}^{-(n-1)} \text{sec}^{-1}$

The most important general conclusion to be drawn about half lives is that for any general order of reaction, n,

$$t_{1/2} \propto a^{(1-n)}$$

The proportionality is, in fact, true for any fractional lifetime.

Determination of Order

It is essential to determine the kinetic order of a reaction before rate constants can be evaluated. There are several methods, of which the following are the most important:

- (1) Direct fitting to rate equations
- (2) Method of Initial Rates
- (3) Fractional Life method
- (4) Direct use of rate

(1) A direct fit of experimental concentration measurements to the integrated rate expression. The method is not very satisfactory because the order must be that chosen for one of the plots (i.e. fractional orders would probably not be considered). It may also be difficult to decide which of two plots is better.

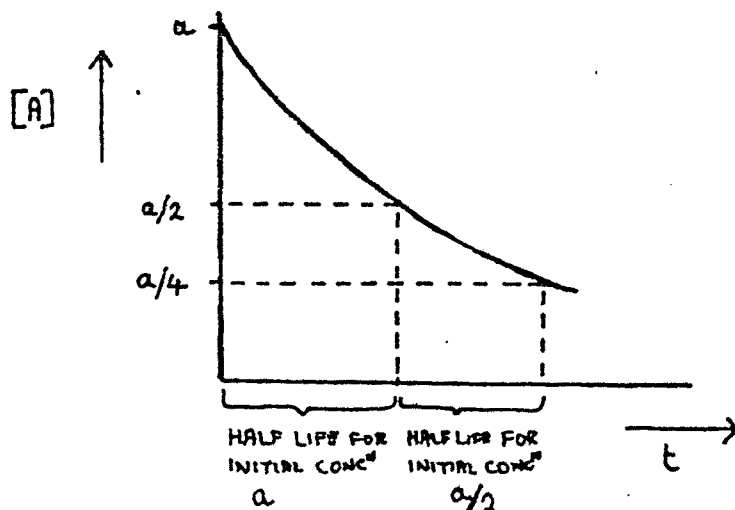
(2) Initial rates: Different initial concentrations are chosen, and the initial rates of reaction are measured:

$$\begin{aligned} (dx/dt)_1 &= k[A]_1^n \\ (dx/dt)_2 &= k[A]_2^n \end{aligned}$$

Dividing and taking logarithms, we have

$$n = \frac{\log(dx/dt)_1 - \log(dx/dt)_2}{\log[A]_1 - \log[A]_2}$$

(3) Fractional life method. The specified fractional life (e.g. half-life) is determined for a number of different initial concentrations, and the relation $\log \tau = \text{constant} + (1 - n) \log a$ is used to determine the order. It is also possible to use the method for single experimental runs. τ is obtained for the starting initial concentration, and then another τ is obtained with the "initial" concentration taken to be the concentration reached after the first τ . The diagram illustrates the method for halflives.



In the actual event, it may be best to use a fractional order of about 0.2, so that no part of the experimental curve is used more than once and so that as many values as possible may be obtained for τ .

(4) Rate Expression may be obtained directly from the rate.

First way of doing this is to draw tangents to the conc.-time graph (or better use a mirror to get the normal to the graph) at a number of different concentrations during the run, and hence obtain the order.

Secondly, the general form of the nth order integrated equation may be rearranged into the form:

$$[(n-1)a^{n-1}k \cdot t] + 1 = \frac{a^{n-1}}{(a-x)^{n-1}} = \left[\frac{a-x}{a} \right]^{1-n} = \left\{ 1 - \frac{x}{a} \right\}^{1-n}$$

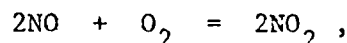
Using the binomial expansion, and neglecting terms in x/a beyond the first, we may write

$$\frac{t}{x/a} = \frac{1}{k \cdot a^{n-1}} + \frac{nt}{2}$$

Thus a plot of $\frac{t}{x/a}$ vs. t should have a slope of $n/2$, and intercept = $\frac{1}{ka^{n-1}}$.

Although the method is in principle only approximate, and depends on having small x/a , it gives remarkably straight lines for values of x/a up to 0.4.

So far we have obtained orders only for systems in which A is the sole reactant. For several reactants it is possible to extend the methods by holding the concentrations of all but one of the reactants constant, and obtain the order for each component separately. Alternatively, can arrange that the reactant concentrations bear a fixed proportion to each other throughout the run (e.g. by putting in the equivalent proportions of the reactant. E.g. in



use partial pressure of NO twice that of O_2 .

For constant proportions, $[\text{B}] = p[\text{A}]$; $[\text{C}] = q[\text{A}]$ say.

The general equation then becomes

$$dx/dt = k p^\beta q^\gamma [\text{A}]^{\alpha+\beta+\gamma} = k''(a-x)^n$$

where $n = \alpha+\beta+\gamma$, the overall order.