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SIMPLIFIED HALF-LIFE METHODS FOR THE ANALYSIS OF KINETIC DATA

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September 1988

Research Institute for Advanced Computer Science
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RIACS Technical Report 88.24

NASA Cooperative Agreement Number NCC 2-387

(NASA-CR-185407) SIMPLIFIED HALF-LIFE
METHODS FOR THE ANALYSIS OF KINETIC DATA
{Research Inst. for Advanced Computer
Science) 8 p

N89-26418

CSCL 09B

Unclas

G3/61 0217900

RIACS

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The analysis of reaction rate data has as its goal the determination of the order rate constant which characterize the data. We will consider here chemical reactions with one reactant and present simplified methods for accomplishing this goal. The approaches presented involve the use of half lives or other fractional lives. These methods are particularly useful for the more elementary discussions of kinetics found in general and physical chemistry courses.

Work reported herein was supported in part by Cooperative Agreement NCC 2-387 between the National Aeronautics and Space Administration (NASA) and the Universities Space Research Association (USRA).

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This paper has been submitted to the *Journal of Chemical Education*

SIMPLIFIED HALF-LIFE METHODS FOR THE ANALYSIS OF KINETIC DATA

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The analysis of reaction rate data has as its goal the determination of the order and rate constant which characterize the data. We will consider here chemical reactions with one reactant and present simplified methods for accomplishing this goal. The approaches presented involve the use of half lives or other fractional lives. These methods are particularly useful for the more elementary discussions of kinetics found in general and physical chemistry courses.

The entire discussion will be based on the n th-order reaction $aA \rightarrow$ products, where A is the single reactant and a is its stoichiometric coefficient. The rate law for the reaction is then

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

where $[A]$ is the molarity of A and k is the reaction rate constant. The solution to this differential equation, for $n \neq 1$ is

$$\frac{1}{[A]^{n-1}} = \frac{1}{[A]_0^{n-1}} + (n-1)akt \quad (2)$$

where $[A]_0$ is the value of $[A]$ at time $t = 0$. When $n = 1$

$$\ln([A]/M) = \ln([A]_0/M) - akt \quad (3)$$

is the solution to eq 1, where M is the abbreviation for the molarity unit,

i.e., $1 \text{ M} = 1 \text{ mol dm}^{-3}$.

As a consequence of the form of eqs 2 and 3, students are often directed toward a trial-and-error procedure involving the plotting of various functions of $[A]$ (those found on the left-hand sides of eqs 2 and 3) against time, followed by use of the most linear plot to identify the order and determine the rate constant. Table 1 shows the appropriate plots required for several of the more common reaction orders. Although this time-honored procedure is excellent when sufficient time is available (such as in homework or laboratory situations), students do get anxious about whether they will have adequate time to apply the procedure (several plots may be required) during an examination.

Half-life methods provide a means of obtaining n and k without using a trial-and-error plotting procedure. If the time in eq 2 is taken to be the half-life, $t_{1/2}$, and the molarity is $[A] = [A]_0/2$, then the resulting equation can be rearranged to yield, for $n \neq 1$

$$t_{1/2} = \frac{(\frac{1}{2})^{1-n} - 1}{(n-1)ak} [A]_0^{1-n} \quad (4)$$

Similar substitutions in eq 3 yield, for $n = 1$

$$t_{1/2} = \frac{\ln 2}{ak} = \text{constant} \quad (5)$$

Eq 4 shows how the reaction order determines the dependence of the half life on the initial molarity. Eq 5 indicates that only for a first-order reaction is the half life a constant independent of $[A]_0$.

According to eq 4, a log-log plot of $t_{1/2}$ versus $[A]_0$ is linear and has a slope of $(1 - n)$, and thus the reaction order can be obtained from the slope. When $n = 1$ the slope is zero, which is consistent with both eqs 4 and 5. Although k can be obtained from the intercept of this log-log plot, it will have a value consistent with the above value of n , which in general is not exactly the integer or half-integer expected from theory. For this reason it is often recommended that the original $[A]$ versus t data be plotted using the appropriate function of $[A]$ from Table 1, or that k be calculated from eq 4 using the theoretically acceptable value of n .

Thus, ordinary half-life methods can require as many as three plots to obtain the values of n and k :

- (1) a plot of $[A]$ versus t in order to obtain a table of $t_{1/2}$ versus $[A]_0$ values,
- (2) a log-log plot of $t_{1/2}$ versus $[A]_0$, which is used to determine n , and
- (3) a plot of the function of $[A]$ versus t in order to obtain a value of k which is consistent with the nearest integer or half-integer value of n (k is then obtained from the slope), or, alternatively,
- (3') a redrawing of the linear log-log plot imposing the theoretical value of n (k is then obtained from the intercept).

Although this procedure is not trial-and-error, it is nonetheless quite lengthy, and is also not practical for examinations of ordinary length.

In situations where student time is limited and taking full statistical advantage of the reaction rate data is not essential, the half-life method can be considerably simplified and shortened. The first simplification is to select only two half lives and two initial molarities, rather than the usual choice of many more. Suppose that the two half lives, $t_{1/2}'$ and $t_{1/2}''$, are measured from the two initial molarities $[A]_0'$ and $[A]_0''$. If eq 4 is written for both of these half lives and the two equations are divided, then the result is

$$t_{1/2}'' / t_{1/2}' = ([A]_0'' / [A]_0')^{1-n} \quad (6)$$

Then the reaction order can be obtained, when $n \neq 1$, by solving eq 6 for n

$$n = 1 - \frac{\ln(t_{1/2}'' / t_{1/2}')}{\ln([A]_0'' / [A]_0')} \quad (7)$$

Once n is found in this fashion from the two half lives and their starting molarities, k can be obtained from either half life and starting molarity by solving eq 4, yielding

$$k = \frac{(1/2)^{1-n} - 1}{(n-1)at_{1/2}} [A]_0^{1-n} \quad (8)$$

using again the nearest theoretically acceptable value of n . If $n = 1$, then eq 6 indicates that $t_{1/2}'' / t_{1/2}' = 1$, which again shows that the half life is a

constant for a first-order reaction, consistent with eq 5.

Half-life methods can be further simplified if the two half lives are successive, i.e., if the second half life begins where the first half life ends. In this case $[A]_0' = [A]_0$ and $[A]_0'' = [A]_0/2$. Substituting these relationships into eq 6 gives, for $n = 1$,

$$t_{1/2}''/t_{1/2}' = (1/2)^{1-n} = 2^{n-1} \quad (9)$$

Table 2 shows the ratios of successive half lives for the common reaction orders, and can be used to select the theoretical reaction order which best fits the rate data. Alternatively, eq 9 can be solved for n giving

$$n = 1 + \frac{\ln(t_{1/2}''/t_{1/2}')}{\ln 2} \quad (10)$$

After determining n from Table 2 or eq 10, k can again be found as indicated in eq 8.

Analyzing rate data with successive half lives requires that the course of a reaction be followed for at least two half lives, i.e., from a molarity of $[A]_0$ to $[A]_0/4$. If rate data is not available for this long a period of time, then a pair of shorter fractional lives can be employed. A fractional life, t_α , is defined as the time required for $[A]$ to decrease from $[A]_0$ to $\alpha[A]_0$, where $\alpha < 1$. Thus, a fraction larger than $1/2$ yields a fractional life shorter than a half life. Substituting $[A] = \alpha[A]_0$ and $t = t_\alpha$ into eq 2 gives, after rearrangement, for $n \neq 1$

$$t_\alpha = \frac{\alpha^{1-n} - 1}{(n-1)ak} [A]_0^{1-n} \quad (11)$$

which is a generalization of eq 4. As was the case with eq 4, this equation is ordinarily used to find n from a log-log plot of t_α versus $[A]_0$. However, a much simpler procedure is again available where the equation is used for two successive fractional lives, t_α' and t_α'' , which begin at $[A]_0$ and $\alpha[A]_0$, respectively. Dividing the resulting two equations gives the generalization of eq 9, namely

$$\frac{t_\alpha''}{t_\alpha'} = \alpha^{1-n} \quad (12)$$

Solving eq 12 for n provides

$$n = 1 - \frac{\ln(t_{\alpha}''/t_{\alpha}')}{\ln \alpha} \quad (13)$$

As with the use of half lives, the value of k can be found from the theoretical value of n and eq 11.

In summary then, successive half lives or fractional lives provide a rapid and simple way of determining reaction order. The method is especially well suited to examination situations where concepts may be more important than extracting the best possible values of n and k from a set of reaction rate data. The approach is not intended to replace the more accurate, traditional methods which are summarized in the early part of this paper and which are to be preferred when time is available for their use.

Table 1. Plots for the Determination of Reaction Order and Rate Constant		
n	linear plot	slope
0	[A] vs. t	$-ak$
1/2	[A] ^{1/2} vs. t	$-ak/2$
1	ln ([A]/M) vs. t	$-ak$
3/2	[A] ^{-1/2} vs. t	$ak/2$
2	[A] ⁻¹ vs. t	ak

**Table 2. Ratios of
Successive Half Lives**

n	$n - 1$	$t_{1/2}'' / t_{1/2}'$
0	-1	$0.500 = 2^{-1}$
1/2	-1/2	$0.707 = 2^{-1/2}$
1	0	$1.000 = 2^0$
3/2	1/2	$1.414 = 2^{1/2}$
2	1	$2.000 = 2^1$