

JUDGING THE SPEED OF A REACTION FROM ITS FUNNY-LOOKING RATE CONSTANT

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In his comprehensive, handwritten source book on reactor design, *The Chemical Reactor Omnibook*, Levenspiel^[1] examines the range of practical reaction rates. Astonishingly, it is about a billion-fold (*i.e.*, 10^9), extending from the slowest biochemical reactions in waste water to the most rapid ones in rocket engines.

Our sense of how rapidly reactions occur is intuitive. Without needing numbers, we recognize that algae grow slowly and that fires burn rapidly. Indeed, anyone who has worked with a particular reaction in a chemical plant can usually state whether that reaction occurs quickly, slowly, or something in between. A list of such terms, describing the speed of a number of familiar batch processes, is suggested in Table 1. In the table, I have arbitrarily assigned the rate of quick-setting epoxy as "moderate." Related adjectives have been assigned to describe the speeds of a number of common reactions that are easily recognized as faster or slower. As a result, their meanings have no particular currency beyond the context of this article.

It seems paradoxical that once a reaction rate has been measured and modeled with a power law, the resulting kinetic rate constant often tends to conceal how fast the reaction occurs. Although sensing the speed of a reaction by observing it may be intuitive, deducing that speed from a rate constant is not. Indeed, most students of chemical kinetics cannot easily interpret a rate constant apart from formally integrating the rate equation and examining the time taken for the limiting reactant to approach either zero or its equilibrium concentration.

TABLE 1
Intuitive Classification of Reaction Speeds

Half-Life of Reaction	Example of Batch Process	Adjectives Describing Reaction Rate
months	Growth of new annulus on a tree trunk	extremely slow
days	Fermentation of cabbage to sauerkraut	very slow
hours	Human digestion of a meal	slow
half an hour	Baking a medium-sized potato	moderately slow
a few minutes	Setting of quick epoxy	moderate
half a minute	Dissolving a seltzer tablet in water	moderately rapid
a few seconds	Burning a sheet of newspaper	rapid
deciseconds	Gasoline combustion in a car cylinder (one cycle)	very rapid
milliseconds	Explosion of a cap in a toy pistol	extremely rapid

To a student conducting calculations with a rate constant, the time-honored exhortation to "consider the reasonableness of your figures" sounds ludicrous. Nor do standard textbooks on the subject come to the rescue. Reluctantly, we must conclude that reaction kinetics tends to be one of the least intuitive of scientific subjects; its most basic parameter comes in a wide variety of units, often involving unusual exponents, and its magnitude is usually difficult to grasp. To address this predicament, I always include the following brief topic in my courses in chemical reaction engineering.

To begin, let us consider only constant-volume, power-law kinetic rate expressions—that is to say, only those rate expressions that exhibit an "order" of reaction with respect to one or more concentrations. We start by developing an intuitive interpretation of the speed of a first-order rate constant and then relate first-order rate constants to rate constants of other orders of reaction. Finally, we examine how to estimate the speed of heterogeneous reaction rates from their often peculiar-looking rate constants.

INTERPRETING A FIRST-ORDER RATE CONSTANT

If we consider the first-order rate expression for a reaction $A \rightarrow B$,

$$-\frac{dC_A}{dt} = kC_A \quad (1)$$

which can be rearranged into the form

$$k = -\frac{dC_A}{C_A dt} \approx \frac{-\Delta C_A / C_A}{\Delta t} \quad (2)$$

The final quotient of Eq. (2) may be interpreted to mean that the fractional change in the concentration in a given time is equal to the rate constant of a first-order rate of reaction. Thus, for a first-order constant of 0.1 min^{-1} , the reaction initially consumes reactant at a rate of one-tenth of the concentration per minute.

Because the concentration driving force falls as the reactant disappears, no reaction (except one of zero-order) goes fully to completion. The time at which a reaction is deemed "complete" is therefore arbitrary. Since the notion of completion of reaction still has intuitive appeal, let us consider a reaction when it is "half-complete"—that is, when its concentration has fallen to half of its original value. The rate at this point still reflects its initial value for practical cases, as is discussed below. The "half-life" (the time required for the reaction to reach 50% conversion) is related to the reaction rate constant, the order, and initial concentration, as commonly found in textbooks on reaction kinetics. The half-lives in Table 1 are obtained intuitively by estimating the time at which they are approximately half complete.

For the first-order rate constant above, its half-life is $t_{1/2} = (\ln 2)/0.1$, or about 7 min. Because we are interested in just an approximate value of the half-life, we can simply take the reciprocal of the first-order rate constant. Thus, we obtain $t_{1/2} \approx 1/0.1$, or 10 min. This result indicates that the speed of this reaction is similar to that of fast-setting epoxy.

A first-order rate constant, the numerical value of which is greater than unity, say 42 h^{-1} , is not at first glance easy to interpret as a percentage change in concentration per hour. To consider it as 4200% change per hour obscures its message; what, after all, is the meaning of a percentage change

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greater than 100? But let us choose a smaller time unit with which to express the rate constant as a value less than unity, i.e., 0.012 s^{-1} . Simply interpreted, this constant suggests that the initial rate is rapid—1.2% of the concentration being converted each second. The reciprocal of the rate constant provides a half-life of the order of a minute, so we may regard it as a moderately rapid reaction, according to the terminology of Table 1.

Before we leave the above examples, it is worth emphasizing the well-known point that a first-order rate is unique in being independent of its starting concentration. All other orders of reaction require such information, as will become apparent in the following paragraphs.

INTERPRETING AN n^{th} -ORDER RATE CONSTANT

If we consider the n^{th} -order rate expression for a reaction $A \rightarrow B$,

$$-\frac{dC_A}{dt} = kC_A^n \quad (3)$$

we can rearrange it into the form

$$k = \frac{-dC_A}{(C_A)(C_A^{n-1})(dt)} \approx \frac{-\Delta C_A / C_A}{(\Delta t)(C_A^{n-1})} \quad (4)$$

The final quotient may be interpreted to mean that the fractional change in the concentration in a given time $(-dC_A/C_A)/(dt)$, if divided by C_A^{n-1} , is equal to the rate constant of an n^{th} -order reaction. This C_A^{n-1} needs further interpretation. For purposes of understanding the initial rate of reaction, C_A in C_A^{n-1} should be replaced by some initial value of C_A^0 . Then

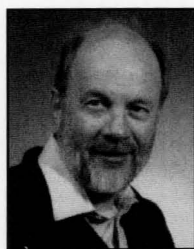
$$k_n \approx \frac{-\Delta C_A / C_A}{(\Delta t)(C_A^0)^{n-1}} = \frac{k_1}{(C_A^0)^{n-1}} \quad (5)$$

where k_1 is the "equivalent" first-order reaction rate constant. Thus

$$k_1 \approx k_n (C_A^0)^{n-1} \quad (6)$$

can be used to recast the n^{th} -order rate constant as an approximately "equivalent" first-order rate constant. Furthermore, the reciprocal of k_1 may be interpreted as the approximate half-life of the reaction

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$$t_{1/2} \approx \frac{1}{k_1} \quad (7)$$

A rigorous expression for the half-life is obtained by setting $C/C^0 = 0.5$ in the integrated reaction rate expression for an n^{th} -order reaction

$$t = \frac{(C/C^0)^{1-n} - 1}{k(n-1)C^{0n-1}} \quad \text{for } n \neq 1 \quad (8)$$

to form

$$t_{1/2} = \frac{(0.5)^{1-n} - 1}{k(n-1)C^{0n-1}} \quad \text{for } n \neq 1 \quad (9)$$

For a second-order reaction, Eq. (7) and Eq. (9) are identities. For the range of practical reaction orders (*i.e.*, $-1 < n < 3$), the half-life approximation of Eq. (7) is of the same order of magnitude as that of the rigorous half-life given in Eq. (9), so it is easier for a quick appraisal to use the approximation.

Let us now consider the approximate speed of the iodine-catalyzed bromination of xylene, the rate constant for which is $0.1 \text{ L}^{1/2}/(\text{mol}^{1/2})(\text{min})$, since the reaction is 3/2-order in bromine concentration. The initial concentration of bromine was 0.3335 mol/L .^[2] An approximate value of the "equivalent" first-order reaction rate constant under these conditions is

$$k_1 \approx k_n (C_A^0)^{n-1} = \frac{0.1 \text{ L}^{1/2}}{(\text{mol}^{1/2} \text{ min})} \left(0.3335 \frac{\text{mol}}{\text{L}} \right)^{1/2} = 0.058 \text{ min}^{-1}$$

Thus, its half-life is approximately a quarter of an hour. A first-order rate constant of this value indicates a reaction of moderate speed, according to the examples in Table 1.

Let us now consider the power-law rate expression for a bimolecular reaction $A + B \rightleftharpoons C$, with an overall power of 2.5, and a rate law

$$\frac{-dC_A}{dt} = k * C_A^2 C_B^{0.5}$$

for which the rate constant k is $0.15 \text{ dm}^{4.5}/(\text{mol}^{1.5} \text{ min})$. The initial concentrations, C_A^0 and C_B^0 , are 0.5 and 0.04 mol/dm^3 , respectively. To estimate the speed of this reaction from its rate constant, we can rearrange it into the form of an "equivalent" first-order reaction as follows:

$$k^* = \frac{-dC_A}{C_A (C_A C_B^{0.5}) dt}$$

and thus the initial rate is approximately

$$\frac{-dC_A}{C_A dt} \approx k^* (C_A^0 C_B^{0.5}) \quad \text{or} \quad k_1$$

Thus, k_1 is calculated to be 0.015 min^{-1} . The reciprocal of k_1

indicates that the half-life of this reaction is approximately an hour, so it must be judged a moderately slow reaction by the terminology of Table 1.

INTERPRETING A HETEROGENEOUS REACTION RATE CONSTANT

The speed of a heterogeneous reaction rate is often hard to judge because of the units accompanying the rate constant. As an example, let us consider the dehydrogenation of ethylbenzene. Wenner and Dybdal^[3] provide an analytical expression for the rate constant of the forward reaction, which is first-order with respect to ethylbenzene partial pressure. At temperature $T_0 = 898 \text{ K}$, the rate constant assumes a value of

$$k = \frac{1.68 (10^{-7}) \text{ kmol}}{\text{s}(\text{kPa}) \text{ kg cat.}}$$

which, clothed in these units, may not be instantly recognizable as a first-order rate constant. For this reaction, the catalyst bulk density is 1440 kg/m^3 of empty reactor. Thus, the equivalent homogeneous rate constant is found by multiplying these two quantities together to obtain

$$k_{\text{homog}} = \frac{2.423 (10^{-4}) \text{ kmol}}{\text{s}(\text{kPa}) \text{ m}^3 \text{ empty bed}}$$

This form is still hard to recognize as a first-order rate constant unless it is further simplified by means of the ideal gas law. By multiplying k_{homog} by the gas constant, $R_g = 8.309 \text{ kPa} \cdot \text{m}^3/(\text{kmol} \cdot \text{K})$, and the feed temperature, T_0 , we obtain the product

$$k'_{\text{homog}} = k_{\text{homog}} R_g T_0$$

which equals 1.81 s^{-1} at 898 K . In this form, the rate constant is clearly recognizable as first-order; thus we can interpret its half-life to be of the order of $1/1.81 \text{ s}$, or about half a second. According to Table 1, the initial dehydrogenation of ethylbenzene would be very rapid. Not surprisingly, a typical empty-tube space-time for a tubular flow reactor under these conditions is of the order of seconds.^[4]

The above approach is one I use to show how to interpret the speed of rate constants of power-law reactions. Its chief benefit is to enable students to estimate whether their reactor calculations are reasonable.

REFERENCES

- Levenspiel, O., *The Chemical Reactor Omnibook*, OSU Book Stores, Inc., Corvallis, OR (1989)
- Neyens, A., in *Cinétique Chimique Appliquée*, Jungers, J.C., et al., Éditions Technip, Paris, France, 88 (1958)
- Wenner, R.R., and F.C. Dybdal, *Chem. Eng. Progr.*, **44**, 275 (1948)
- Smith, J.M., *Chemical Engineering Kinetics*, 3rd ed., McGraw-Hill, New York, NY, Example 13-3 (1981) □