

Solving Simple Kinetics without Integrals

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S Supporting Information

ABSTRACT: The solution of simple kinetic equations is analyzed without referencing any topic from differential equations or integral calculus. Guided by the physical meaning of the rate equation, a systematic procedure is used to generate an approximate solution that converges uniformly to the exact solution in the case of zero, first, and second order kinetics. The approximate solution is shown to have unequivocally the same form as the exact solution, except for an effective parametric rate constant that turns into the actual rate constant of the process at the appropriate limit. The use of simple algebraic methods makes the analysis elementary and its generalization to processes with fractional order kinetics straightforward. We discuss the educational value of this approach while highlighting its use for introducing chemical kinetics and related topics to high school and first-year students. Furthermore, instructors and students already familiar with the main results derived here will also benefit from this presentation as it offers a different perspective on the solution of routinely found differential equations.

KEYWORDS: First-Year Undergraduate/General, Kinetics, Physical Chemistry

INTRODUCTION

Chemistry education aimed at high school and first-year students presents unique challenges for instructors. The complexity of chemical processes is usually of such a sophisticated nature that detailed and convincing arguments have to be very often relegated or postponed to junior and senior years of college. An understanding of several areas of physical chemistry, for example, usually requires several semesters of calculus and some knowledge of matrix algebra, differential equations, and complex analysis.^{1–3} Yet, mathematical skills and logical thinking have been found to be among the most significant factors affecting college chemistry performance.^{4,5}

Chemical kinetics, in particular, deals with the problem of the evolution in time of the concentration of a reactant (or product), and this is typically described in terms of an ordinary differential equation.^{1–3} The most commonly found kinetic equations in a chemistry curriculum of high school and first year of college have the form^{6,7}

$$\frac{\Delta[A]}{\Delta t} = -k[A]^\alpha \quad (1)$$

where k is the rate constant of the process. The parameter α in this equation is called *the order of the reaction*, and in the simplest scenarios it could be zero, one, or two. Reactions are then said to be of zero order ($\alpha = 0$), first order ($\alpha = 1$), or second order ($\alpha = 2$). Some reactions however can exhibit a fractional order kinetics, for example, the thermal decomposition or pyrolysis of acetaldehyde is known to have $\alpha = 3/2$ under certain circumstances, indicative of a complex reaction mechanism associated with this process.^{2,8}

The bracket notation $[A]$ on the right-hand side of eq 1 represents the concentration of reactant A as a function of time, and it is a shorthand version of the perhaps more appropriate notation $[A]_t$. The specific form in which the concentration of reactant A depends on time is called *the solution* of the given

equation namely, $[A]$ (or $[A]_t$). The symbol $\Delta[A]$ on the left hand side of the equation above expresses the change of concentration exhibited by reactant A with time, i.e.,

$$\Delta[A] = [A]_{t_2} - [A]_{t_1} \quad (2)$$

Meanwhile, $\Delta t = t_2 - t_1$ represents the time interval during which this concentration change takes place. When the time interval Δt approaches zero, the finite difference relation in eq 2 above formally becomes a so-called *ordinary differential equation*.

While this description can be intuitively motivated, the typical solution of the ensuing differential equation is not a trivial exercise for someone with less than two semesters of college calculus and some exposure to differential equations. Indeed, separation of variables, integration on both sides, and the theorem of existence and uniqueness of the solution of a differential equation, while standard topics in junior and senior years of college,^{1–3} are well beyond the comprehension of nearly all high school and first-year students.

Therefore, in this work, we set the goal of analyzing the solution of kinetic equations with the form specified by eq 1 for zero, first, and second order without referencing any topic from differential equations or the process of integration. We discuss a systematic procedure that allows one to generate a discrete (and generally approximate) version of the solution and investigate analytically its uniform convergence to the exact solution. The overall strategy therefore consists of transforming the original difference problem stated in eq 1 into a limiting exercise that requires simple algebraic manipulations. The scheme discussed here is similar in spirit to the approach used in numerical analysis when solving ordinary differential equations in a computer.^{9,10} It is however different in practice

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because it does not rely on analyzing explicitly the limit when the integration time step goes to zero as the route for convergence to the exact solution. Instead, the approach considered here is based on introducing a different parametrization amenable to straightforward analytical manipulations. In this context, as the given parameter approaches infinity, the concentration change ($\Delta[A]$) and the time interval (Δt) go simultaneously to zero as the exact analytic solution is found. (It is worth noting that the generalization of this protocol to arbitrary fractional orders is straightforward and is presented in the [Supporting Information](#) where the connection to the results obtained for the simplest cases is explained.)

The focus and relevance of the present discussion is 2-fold. On the one hand, it suggests a strategy to rigorously introduce, at an elementary level, important results regarding kinetic processes that are of paramount significance in chemistry, biochemistry, physics, and engineering. This can be particularly impactful when employed at educational stages earlier than the ones at which these topics are routinely presented under current academic programs. High school and first-year students in various disciplines, in particular, could benefit in notable ways from this overall approach.

On the other hand, for instructors and students already familiar with the results considered in this work, the discussion herein will allow them to analyze and view the results from a different perspective. This might, in turn, further enrich their understanding, as well as the implications that derive from the contrast between the arguments ordinarily given in this context and the ones presented here. Students interested in the use of numerical procedures for the solution of differential equations and related matters may find this discussion specially convenient as it connects, albeit in an elementary fashion, with their everyday handling of numerical routines.

The paper is organized as follows. A detailed analysis of an approximate solution to first order kinetics and its convergence to the exact solution is first presented. This is followed by the solution of the zero and second order kinetics processes according to the same protocol, respectively. Finally, some general conclusions are given regarding the overall strategy.

FIRST ORDER KINETICS

Approximate Solution

The equation we must solve, corresponding to a process with first order kinetics, is

$$\frac{\Delta[A]}{\Delta t} = -k[A] \quad (3)$$

as it results from eq 1 for the case when the parameter α equals 1. The rate expression in eq 3 indicates that the rate of change of the concentration is proportional to the concentration itself. The negative sign indicates that, as time progresses ($\Delta t > 0$), the changes in the concentration must be negative ($\Delta[A] < 0$), implying that the concentration must decrease with time. Let us then rewrite this equation as

$$\Delta t = -\frac{1}{k[A]} \Delta[A] \quad (4)$$

In this form, we will be able to estimate the amount of time (Δt) required for the concentration to change from its initial value, which from now on will be denoted by $[A]_0$, to some smaller value to be specified below.

Consider as Step 1 the time interval Δt in which the concentration changes from $[A]_0$ to $[A]_0/2$. The change in concentration is clearly given by

$$\Delta[A] = \frac{[A]_0}{2} - [A]_0 = -\frac{[A]_0}{2} \quad (5)$$

We then estimate the value of the concentration by its midpoint and find

$$[A] = \frac{1}{2} \left([A]_0 + \frac{[A]_0}{2} \right) = \frac{3}{4} [A]_0 \quad (6)$$

Placing these two results in eq 4 we estimate the time interval to be

$$\Delta t = -\frac{1}{k(3[A]_0/4)} \left(-\frac{[A]_0}{2} \right) = \frac{2}{3k} \quad (7)$$

Consider now as Step 2 the time interval Δt in which the concentration changes from $[A]_0/2$ to $[A]_0/4$. It is straightforward to verify that the change in concentration is $-[A]_0/4$ and the midpoint value is $3[A]_0/8$. The time interval is therefore estimated as

$$\Delta t = -\frac{1}{k(3[A]_0/8)} \left(-\frac{[A]_0}{4} \right) = \frac{2}{3k} \quad (8)$$

and is obviously the same than the one calculated in Step 1.

If one repeats this process a third time, while going from $[A]_0/4$ to $[A]_0/8$ one would find once again that the time interval is also $\Delta t = 2/3k$. The results obtained up to Step n are collected in Table 1. The main feature is that the time interval Δt remains constant in each step.

Table 1. First Order Kinetics

Step No.	Δt	$[A]_{\text{initial}}$	$[A]_{\text{final}}$
1	$\frac{2}{3k}$	$[A]_0$	$\frac{[A]_0}{2}$
2	$\frac{2}{3k}$	$\frac{[A]_0}{2}$	$\frac{[A]_0}{4}$
3	$\frac{2}{3k}$	$\frac{[A]_0}{4}$	$\frac{[A]_0}{8}$
\vdots	\vdots	\vdots	\vdots
n	$\frac{2}{3k}$	$\frac{[A]_0}{2^{n-1}}$	$\frac{[A]_0}{2^n}$

The results of Table 1 are represented graphically in Figure 1 and compared with the exact solution (discussed below). Although all computed values fall slightly below the exact result, it is clear from this graph that the protocol outlined here allows us to anticipate, rather accurately, the general behavior of the concentration as a function of time. Our plan now is to bring the points closer together, and find the exact solution of the problem in the limit in which the points are infinitely close.

The Exact Solution as a Limit

Before continuing forward, it is useful to recall the following limit:^{11–14}

$$\lim_{M \rightarrow \infty} \left(1 - \frac{1}{M} \right)^M = e^{-1} = \frac{1}{2.7182\dots} \quad (9)$$

This limit plays a major role in the analysis below, and it is further discussed in an elementary manner in the [Supporting Information](#) (section A).

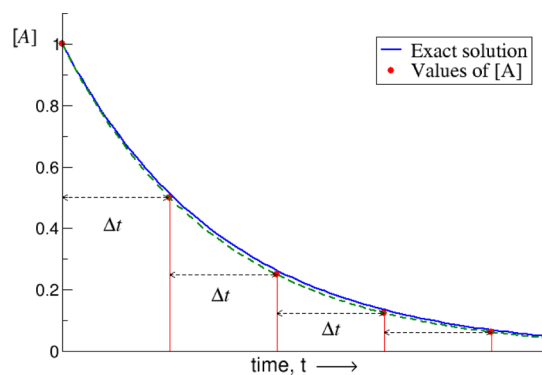


Figure 1. Values of $[A]$ at steps $n = 1, 2, 3,$ and 4 as indicated in Table 1 as a function of time. The exact solution, given by eq 15, is also included for comparison. Note that all computed values of $[A]$ belong to the approximate solution in eq 20, and this is represented here by a dashed line.

Consider the time interval Δt in which $[A]$ changes from $[A]_0$ to $[A]_0(1 - 1/M)$. Note that if M equals 2, the concentration changes to one-half of the initial value and that calculation has already been done. So we imagine here that M is a large number with which we can control how close are the successive points of the function. In particular, it is clear that the larger the value of M , the closer the values of the concentration will be.

The change in concentration in this instance is

$$\Delta[A] = [A]_0 \left(1 - \frac{1}{M}\right) - [A]_0 = -\frac{[A]_0}{M} \quad (10)$$

The value of the concentration can be estimated as before through its midpoint, and this is

$$[A] = \frac{1}{2} \left[[A]_0 + [A]_0 \left(1 - \frac{1}{M}\right) \right] = \left(1 - \frac{1}{2M}\right) [A]_0 \quad (11)$$

Then, the corresponding time interval is given by

$$\Delta t = \frac{1}{k} \left(1 - \frac{1}{2M}\right)^{-1} \frac{1}{M} = \frac{1}{k} \left(\frac{1}{M - \frac{1}{2}} \right) \quad (12)$$

If we now analyze the change of the concentration for the second step, from $[A]_0(1 - 1/M)$ to $[A]_0(1 - 1/M)^2$, we will find exactly the same result as in eq 12. In fact, it is straightforward to verify that for any step n we will obtain this same value of Δt . Thus, after n steps the concentration will be

$$[A] = [A]_0 \left(1 - \frac{1}{M}\right)^n \quad (13)$$

and since the time involved in the concentration change from $[A]_0$ to $[A]$ is the sum of the n time intervals,

$$t = n\Delta t = \frac{n}{k \left(M - \frac{1}{2}\right)} \approx \frac{n}{kM} \quad (14)$$

where in the last step we used the fact that M is a very large number.

Solving for n in this last expression and placing the result in eq 13 we find

$$\begin{aligned} [A] &= [A]_0 \left(1 - \frac{1}{M}\right)^{kMt} \\ &= [A]_0 \left[\left(1 - \frac{1}{M}\right)^M \right]^{kt} \\ &= [A]_0 e^{-kt} \end{aligned} \quad (15)$$

where the large M limit of eq 9 has been used. The result in eq 15 is in fact the exact analytic solution of the first order kinetics. A comparison between the exact solution and the values estimated earlier appears in Figure 1.

Analysis of the Convergence

Knowing the exact solution for the process, it is a simple matter to compute the exact time required for the concentration to reach one-half of its initial value, or half-life. The result is simply

$$t_{1/2} = \frac{\ln(2)}{k} \quad (16)$$

The estimate found earlier for this quantity, $\Delta t = 2/3k$ (see Table 1), can be compared with $t_{1/2}$ as

$$\frac{t_{1/2}}{\Delta t} = \frac{3}{2} \ln(2) = 1.0397... \quad (17)$$

which shows that $\Delta t < t_{1/2}$. This is due to the fact that the exponential is a concave function and our midpoint evaluation of the concentration always overestimates the actual value of the function. As a result, the value of Δt computed according to eq 4 will always be smaller than the actual time associated with any given concentration change.

A crucial feature shared by the exact and approximate solutions is that the half-life is independent of the concentration. This means that the parametric solution can be cast in the form of an exponential decay in time with an effective rate constant which we can denote as κ_M . Indeed, using eqs 13 and 14, we can write

$$[A] = [A]_0 \left(1 - \frac{1}{M}\right)^{kt \left(M - \frac{1}{2}\right)} = [A]_0 e^{-\kappa_M t} \quad (18)$$

which implies that the parametric constant κ_M and the constant k are related by the exact expression

$$\kappa_M = k \left(M - \frac{1}{2}\right) \ln \left(1 + \frac{1}{M - 1}\right) \quad (19)$$

Note that the discrepancy between κ_M and k is a consequence of taking the rate equation in eq 3 to be valid for arbitrary values of Δt . However, since we know that eq 3 is only meaningful at very small Δt , and according to eq 12 this occurs at large values of M , it is precisely at this limit that the effective constant becomes the actual rate constant.

This last expression in eq 19 generalizes the relation between the actual half-life of the process $t_{1/2}$ and the half-life associated with the approximate solution corresponding to a given value of M . Specifically, for the case $M = 2$, this expression reduces to

$$\frac{\kappa_2}{k} = \frac{3}{2} \ln(2) \quad (20)$$

in complete agreement with eq 17. So, for example, all the concentration values in Table 1 belong to the approximate solution

$$[A] = [A]_0 e^{-kt(\ln(2\sqrt{2}))} \quad (21)$$

and fall slightly below the exact values as illustrated graphically in Figure 1. The practical advantage of writing the approximate solution in this manner is that t is not restricted to multiples of Δt ; it is instead a continuous variable that can be evaluated to yield any concentration value.

The limiting process $M \rightarrow \infty$ has, in summary, two effects. First, it brings the concentration points closer together, as Δt approaches zero in the manner prescribed by eq 12. Second, it decreases the effective constant κ_M to match the actual value k according to the form indicated by eq 19. It is useful to point out that the seemingly inconspicuous term *uniform convergence* mentioned in the Introduction entails some subtle aspects. It means that it is possible to find a value of M for which all the corresponding approximate concentrations differ from their limiting value by a (positive) quantity that can be made arbitrarily small. As a result, the parameter M characterizes through a single value the simultaneous convergence of all approximate concentration values at once. This fact is analyzed in more detail in the Supporting Information (section B).

ZERO ORDER KINETICS

The solution of the zero order kinetics is obviously very simple, however we review it here using the approach outlined in the preceding section. The resulting analysis will turn out to be rather informative as we compare it with the solution of the first order and second order kinetic equations.

The kinetic equation for zero order must be first written in the form

$$\Delta t = -\frac{\Delta[A]}{k} \quad (22)$$

It is straightforward to find the time interval needed for the concentration to successively decrease to half of its initial value, and the results obtained appear in Table 2. The time intervals

Table 2. Zero Order Kinetics

Step No.	Δt_n	$[A]_{\text{initial}}$	$[A]_{\text{final}}$
1	$\frac{[A]_0}{2k}$	$[A]_0$	$\frac{[A]_0}{2}$
2	$\frac{[A]_0}{4k}$	$\frac{[A]_0}{2}$	$\frac{[A]_0}{4}$
3	$\frac{[A]_0}{8k}$	$\frac{[A]_0}{4}$	$\frac{[A]_0}{8}$
\vdots	\vdots	\vdots	\vdots
n	$\frac{[A]_0}{2^n k}$	$\frac{[A]_0}{2^{n-1}}$	$\frac{[A]_0}{2^n}$

not only depend on the initial concentration but in fact become smaller as the number of steps increases. Indeed, the time interval associated with the n th step is

$$\Delta t_n = 2^{-(n-1)} \Delta t_1 \quad (23)$$

where $\Delta t_1 = [A]_0/2k$ is the time interval associated with the first step. (Note that since the time interval is different for each step, a subindex n has been added rendering the notation Δt_n , with $n = 1, 2, 3, \dots$)

The values of the concentration after each time interval are represented graphically in Figure 2 and compared with the exact solution (derived below). An important distinction in relation to the analysis in the previous section is that all the estimates are here exact. This is obviously a consequence of the

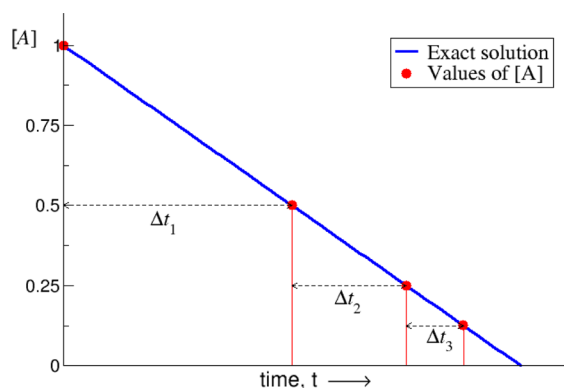


Figure 2. Values of $[A]$ at steps $n = 1, 2,$ and 3 as indicated in Table 2. The exact solution corresponding to zero order kinetics is also included. Note that in this case the estimated time interval equals the half-life, i.e., $\Delta t_n = t_{1/2}$.

fact that Δt_n only depends on $\Delta[A]$ so there is not inherent estimation performed; see eq 22. As a result, each time interval Δt_n is exactly equal to the half-life $t_{1/2}$ associated with each step n as indicated in Figure 2.

We now analyze the process, used in the previous section, of taking the limit $M \rightarrow \infty$. For convenience, we introduce the M -dependent factor

$$P = 1 - \frac{1}{M} \quad (24)$$

which represents the fraction of the original concentration remaining after a given time interval Δt_n . Since we are interested in large values of M , it is quite general to consider $1 < M \leq \infty$, which implies $0 < P \leq 1$. It is clear in particular that, as M approaches infinity, the factor P approaches one.

For the case in which the concentration changes between $[A]_0$ and $[A]_0(1 - 1/M)$, it is straightforward to verify that the time interval is

$$\Delta t_1 = -\frac{[A]_0}{k}(P - 1) \quad (25)$$

For the next step, involving a concentration change from $[A]_0(1 - 1/M)$ to $[A]_0(1 - 1/M)^2$, we find

$$\Delta t_2 = -\frac{[A]_0}{k}(P^2 - P) \quad (26)$$

By continuing this exercise, one finds that the time interval associated with the n th step is

$$\Delta t_n = -\frac{[A]_0}{k}(P^n - P^{n-1}) \quad (27)$$

Thus, after n steps the overall concentration change is

$$[A] = [A]_0 \left(1 - \frac{1}{M}\right)^n = [A]_0 P^n \quad (28)$$

And this occurs during the time

$$t = \sum_{l=1}^n \Delta t_l = -\frac{[A]_0}{k} \sum_{l=1}^n (P^l - P^{l-1}) = -\frac{[A]_0}{k}(P^n - 1) \quad (29)$$

Combining these last two equations, we find the expected result:

$$[A] = [A]_0 - kt \quad (30)$$

The result is expected because the only function that changes in constant proportion to changes of its argument is the straight line. And since the proportionality constant is $-k$, one anticipates this to be its slope.

It is interesting to point out that in obtaining eq 30 there seems to be no need for a limit to be evaluated. This is because all concentration points generated for any given choice of the parameter M are exact. However, for t to become a continuous variable, the limit $M \rightarrow \infty$ must be formally taken; see eq 29. This can be rigorously established by verifying that Δt_n goes to zero for all n when M goes to infinity.

Solving for P^n in eq 29 and placing the result in eq 27 we find

$$\Delta t_n = \frac{1}{M-1} \left(\frac{[A]_0}{k} - t \right) \quad (31)$$

where eq 24 has been used. It is therefore clear that when M goes to infinity, Δt_n goes to zero and t becomes a continuous variable. In other words, as the value of M becomes larger, the concentration points in Figure 2 approach each other forming a straight and continuous line defined by eq 30.

■ SECOND ORDER KINETICS

Approximate Solution and Limit

We now turn to solve the second order kinetics using the strategy described in the preceding sections. The time interval in this case is given by

$$\Delta t = -\frac{1}{k[A]^2} \Delta[A] \quad (32)$$

The estimation of $[A]$ in the denominator is performed through the midpoint value associated with a given concentration change (as done previously in first order kinetics). Then, in particular, when the concentration changes to half of its initial value, the n th step of the process requires the time

$$\Delta t_n = 2^{n-1} \Delta t_1 \quad (33)$$

where

$$\Delta t_1 = \frac{8}{9k[A]_0} \quad (34)$$

Here, Δt_1 is the time required for the first step, when the concentration changes from $[A]_0$ to $[A]_0/2$.

Table 3 summarizes the corresponding time intervals associated with each step. These results indicate that the size of the time intervals increases quite rapidly (as 2^n) with the number of steps, and later steps produce points that are ever

Table 3. Second Order Kinetics

Step No.	Δt_n	$[A]_{\text{initial}}$	$[A]_{\text{final}}$
1	$\frac{8}{9k[A]_0}$	$[A]_0$	$\frac{[A]_0}{2}$
2	$\frac{16}{9k[A]_0}$	$\frac{[A]_0}{2}$	$\frac{[A]_0}{4}$
3	$\frac{32}{9k[A]_0}$	$\frac{[A]_0}{4}$	$\frac{[A]_0}{8}$
⋮	⋮	⋮	⋮
n	$\frac{8 \times 2^{n-1}}{9k[A]_0}$	$\frac{[A]_0}{2^{n-1}}$	$\frac{[A]_0}{2^n}$

farther away between them. This is depicted graphically in Figure 3.

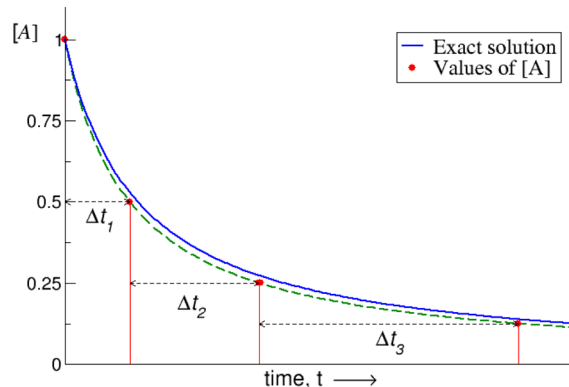


Figure 3. Values of $[A]$ at steps $n = 1, 2$, and 3 as indicated in Table 3 as a function of time. The exact solution, given by eq 41, is also included for comparison. Note that all computed values of $[A]$ belong to the approximate solution in eq 46, and this is represented here by a dashed line.

We now analyze the time intervals associated with changes of concentration parametrized by M , as described in previous sections. Naturally, the exact solution is found in the limit when M goes to infinity. However, the limit here is most easily evaluated in terms of the parameter P defined by eq 24.

For the n th step we find

$$\Delta t_n = -\frac{4(P^n - P^{n-1})}{k[A]_0(P^n + P^{n-1})^2} \quad (35)$$

Thus, the concentration changes to the value

$$[A] = [A]_0 P^n \quad (36)$$

when the time becomes

$$t = -\frac{4}{k[A]_0} \sum_{l=1}^n \frac{P^l - P^{l-1}}{(P^l + P^{l-1})^2} \quad (37)$$

It is straightforward to show that the sum can be evaluated as

$$\begin{aligned} \sum_{l=1}^n \frac{P^l - P^{l-1}}{(P^l + P^{l-1})^2} &= \frac{(P-1)P}{(P+1)^2} \sum_{l=1}^n \left(\frac{1}{P} \right)^l \\ &= \frac{P}{(P+1)^2} \left(1 - \frac{1}{P^n} \right) \end{aligned} \quad (38)$$

where in the last line we used the standard result¹¹

$$\sum_{l=1}^n a^l = \frac{a(a^n - 1)}{a - 1}, \quad a \neq 1 \quad (39)$$

with $a = 1/P$. A brief but important account regarding this sum is given in the Supporting Information (section C).

Placing the result from eq 38 into eq 37 we find

$$t = -\frac{4}{k[A]_0} \frac{P}{(P+1)^2} \left(1 - \frac{[A]_0}{[A]} \right) \quad (40)$$

where eq 36 has been inserted. Finally, since in the limit $M \rightarrow \infty$ the parameter P becomes 1, we find

$$[A] = \frac{[A]_0}{1 + [A]_0 kt} \quad (41)$$

which is the exact analytic solution for the second order kinetics.

Analysis of the Convergence

Using the exact solution, one can find the half-life of the process to be

$$t_{1/2} = \frac{1}{k[A]_0} \quad (42)$$

As in the first order case, we find that our estimate Δt_1 here is smaller than the actual value of the half-life, that is,

$$\frac{t_{1/2}}{\Delta t_1} = \frac{9}{8} = 1.125 \quad (43)$$

This is, once again, a consequence of the concavity of the exact solution and the fact that we use a linear interpolation to estimate the concentration at each step.

The exact expression for the half-life above indicates that successive concentration changes to one-half of its preceding value imply the doubling of the half-life. This behavior is clearly reproduced by the time interval estimates in Table 3. Because of that, the approximate values of the concentration in this table can be expressed as a function with the same structure as the exact solution but involving an effective constant κ_M . Indeed, by comparing eqs 40 and 41, the relation between this parametric constant κ_M and k is found to be $\kappa_M = k(P + 1)^2/4P$ and, in terms of the parameter M , takes the form

$$\kappa_M = k \left[1 + \frac{1}{4M(M-1)} \right] \quad (44)$$

In particular, for $M = 2$,

$$\frac{\kappa_M}{k} = \frac{9}{8} \quad (45)$$

in agreement with the half-life analysis above. Thus, all concentration values in Table 3 belong to the function

$$[A] = \frac{8[A]_0}{8 + 9[A]_0 kt} \quad (46)$$

where now t is a continuous variable; see Figure 3.

Thus, as in the case of first order kinetics, the limit operation $M \rightarrow \infty$ has here two effects. It brings the values of the concentration closer together according to

$$\Delta t_n = \frac{1}{M-1} \left(t + \frac{1}{\kappa_M [A]_0} \right) \quad (47)$$

where we have solved for P^n in eqs 36 and 40 and placed the result in eq 35. At the same time, the effective constant κ_M decreases to become identical to k . The uniform character of the convergence to the exact solution is shown explicitly in Supporting Information (section B).

A comparison of the convergence with M of the effective constant in the first and second order kinetics is shown in Figure 4. Although the effective constant corresponding to a first order kinetics converges faster, both constants converge rather quickly. In particular, the value of κ_{10} overestimates the value of k by 3.3% and 0.09% for second and first order, respectively.

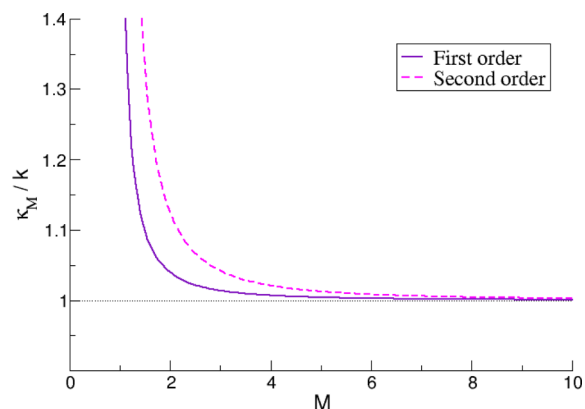


Figure 4. Graphical representation of the convergence of the ratio κ_M/k as a function of M for first and second orders. These plots are based on eqs 18 and 44 for first and second order, respectively.

CONCLUSIONS

In this work, we have described an elementary strategy for the solution of simple kinetic equations based on straightforward algebraic manipulations. No reference is made to any topic from differential equations or integral calculus throughout the solution process. Instead, guided by the physical meaning of the rate equation represented by eq 1, we outline a general protocol that allows the derivation of well-known results associated with simple kinetic processes, and that are otherwise typically obtained through integration methods.

The scheme discussed in this work relies on estimating the time intervals associated with given concentration changes, which are in turn chosen to keep a specified ratio between successive values. This constant ratio of successive concentrations is conveniently parametrized by M , with M being a number arbitrarily larger than one. For any given value of M , the estimated time intervals are found to become ever smaller for zero order, remain constant for first order, or successively increase for second order.

For the simplest case, the zero order kinetics, all estimates are obviously exact and the direct evaluation of the limit is merely a formality. For the first and second order, the estimated time intervals, although approximate, reproduce in an identical fashion the trends afforded by the exact solution. Due to this fact, the approximate concentration values can be cast in the form of a continuous function with the same form as the exact solution of the corresponding problem but involving an effective rate constant. Analytic expressions for the convergence of the effective rate constant κ_M are derived, demonstrating that even for small values of the discretization parameter the estimated values of the concentration are relatively accurate.

In the limit when the parameter M goes to infinity, the effective constant becomes identical to the rate constant of the process. Hence, the exact solution arises naturally by means of a limiting process that involves the uniform convergence of the approximate solution. This strategy, in addition, generalizes without additional complications to the case of kinetics with an arbitrary fractional order. It is worth noting that the limits considered in this discussion can be found straightforwardly by direct evaluation, except perhaps for the limit in eq 9. This limit, however, can be obtained by elementary algebraic methods as discussed in the Supporting Information.

Overall, the approach outlined here is therefore elementary, systematic, exact, and general, and its educational value can be

realized on several levels depending on the instructor goals and objectives. At an elementary level, the instructor's focus could be limited to obtaining and analyzing the results in Tables 1, 2, and 3, which represent the correct solution of the problem except for the fact that the rate constant is slightly off. A deeper understanding can be gained by considering the convergence to the exact solution in first and second order, in comparison with zero order. A more complete discussion could be based on analyzing the case of an arbitrary fractional order with the goal of finding, for example, the corresponding half-life of a certain process. Other standard exercises on chemical kinetics can also be addressed within this framework. From the perspective of the student learning value, on the other hand, it is important to note that the strategy discussed in this work relies the physical meaning of "the half-life of a process", which is an essential concept throughout chemical kinetics.

As a representative test, a total of 32 students in the first-year General Chemistry II class at Kettering University were exposed to the material shown in the lecture file and were required to do the accompanying assignment. The results were as follows: 30 students (94%) completed the first exercise correctly, while 23 students (72%) completed both exercises correctly. Of the 9 students that failed to do the second exercise correctly, 4 of them followed the procedure correctly but made simple mistakes while adding the corresponding fractions. One student (3%) had previously taken a differential equations class. Finally, the students were asked to evaluate the following statement: "Overall, I believe that this is an effective approach to introduce chemical kinetics to a first-year class." The results were as follows: 28% strongly agree, 44% agree, 16% neither agree/disagree, 9% disagree, 3% strongly disagree.

Finally, the analysis presented here underscores the effectiveness of symbolic analytical methods as well, simply because the use of integrals simplifies the derivations given in this manuscript to only a few lines. Yet, the underlying rationale argued throughout this work is quite powerful on its own. It represents, at its core, the conceptual basis for the use of numerical schemes in the solution of differential equations. Such schemes, as it turns out, can properly handle almost any differential equation including those that might not be tractable analytically.

■ ASSOCIATED CONTENT

📄 Supporting Information

The Supporting Information is available on the ACS Publications website at DOI: 10.1021/acs.jchemed.5b00634.

Evaluation example (PDF)

First order kinetics lecture (PDF)

Limiting procedure details (PDF)

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Notes

The authors declare no competing financial interest.

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