strengthen the belief in qualitative reasoning and normally the time schedule of an introductory course in CRE and applied kinetics does not enable a rigorous work with many kinds of reaction sequences.

Conclusions

We have run this type of exercise several years in our basic undergraduate course in CRE and the students have cooperated with an admirable interest. They consolidate their knowledge of basic principles of CRE and kinetics, and they learn about the application of numerical methods to problems of this kind. This approach is very useful when they treat more complicated systems in the future: analysis of nonisothermal reactors (e.g., fixed beds), investigation of reactor stability and parametric sensitivity, studies on reactor dynamics, analysis of multicomponent systems (e.g., thermal cracking and combustion processes). Numerical simulation of the reactor model is the essence of the matter, also in reactor optimization and in parameter estimation. The recent advances in numerical mathematics should be utilized in education; an obstinate use of poor numerical methods that demand a lot of computer time should never be called a "practical" or an "engineering" approach.

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Computer-Assisted Analysis of Reaction Rate Data

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The ability to determine rate laws and obtain accurate reaction rate constants is central to the proper understanding of the mechanisms of many chemical reactions (*3*). In an ideal case, rate laws and constants can be obtained if it is possible to determine the concentration of all reactants periodically as the reaction progresses (*4*). The data can then be fitted to an integrated rate expression and the rate constants calculated (*5*). Since it is sometimes difficult to determine the concentration of more than one reactant at a time, the experiments are often carried out under pseudo-order conditions where all but one of the reactants are held in a constant large excess throughout the course of the reaction (*4*). Under less than ideal conditions (the usual case) it is frequently not possible to determine the concentrations of the reactants directly, and the rate of reaction is monitored instead by following changes in some physical property (*6*). Most often the disappearance of an absorption band in the UV–Vis spectrum is used for this purpose, although a number of other physical properties also have been effectively employed (*7*). In this article only absorbance measurements will be considered, but the discussion could, with equal validity, apply to any physical property (*6*).

Reactant concentrations can be accurately determined when an absorbance band attributable to one of the reactants disappears without interference from product bands as the reaction progresses. The concentration of the reactant, R, at any time, t, is then given by eq 5 where ϵ_R is the molar absorptivity and A the absorbance.

$$[R]_t = A_t/\epsilon_R \tag{5}$$

Unfortunately examples of such reactions are not numerous because the products are often found to absorb at the wavelength that is most conveniently used to monitor the decrease in reactant concentration. If, however, it is possible to obtain a reliable value for the final absorbance, A_f, it can be shown that the concentration of the reactant may be obtained from eq 6 where ϵ_p is the apparent molar absorptivity of the products at that wavelength (*6*).

$$[R]_t = (A_t - A_f)/(\epsilon_R - \epsilon_p) \tag{6}$$

In many cases, however, it is impossible to obtain a stable value for A_f. For example, if the product coagulates, precipitates, or undergoes a subsequent slow reaction it is not possible to determine A_f accurately, and the validity of this approach diminishes. Occasionally the method recommended by Guggenheim (*8*) can be used, but it is often more expedient to abandon the use of integrated rate expressions altogether and turn to the differential forms of these equations.

When a differential method is used, the change in absorbance with time is monitored over the first 10–20% of the reaction and a plot of A_t vs. t is prepared. A tangent to this curve $-dA_t/dt$, is then related to the differential rate law through eq 5 or eq 6. In principle, tangents could be taken anywhere along the curve, but there is an advantage to choosing the point of zero time, that is, the initial rate (*3*). Although obtaining a tangent at this point may require a short extrapolation it avoids all of the possible complications discussed above, for at time zero the concentrations of the reactants are known precisely, and the absorbance measurements are free from interference by the products.

Furthermore, as Laidler has pointed out, there are at least two ways in which the use of differential rates are preferable to the more familiar integrated forms (*9*). First, he notes that the use of an integral method to determine the order of the reaction is satisfactory only if the order is an integer. Fractional orders may be missed because the data give an adequate fit to one of the integrated rate equations. He also demonstrates that use of rate equations in their differential forms leads to orders for the reactions with respect to concentration—the so-called *true orders* (*10*). Use of integrated rate equations, on the other hand, leads to orders of the reactions with respect to time (*11*).

Determination of Initial Rates

Obtaining an accurate value of $-[dA/dt]_0$ has been done classically by placing a mirror normal to the curve such that the curve and its image appear to be continuous. The tangent is then drawn perpendicular to the face of the mirror and its slope obtained graphically (*9*). Since this method is time consuming and subject to personal biases, we have simplified and depersonalized the procedure by computing a theoretical fit to the absorbance vs. time curve using eq 7.

$$A = a_0 + a_1t + a_2t^2 + a_3t^3 + a_4t^4 + a_5t^5 + \ldots + a_nt^n \tag{7}$$

Differentiation of this expression with respect to time then gives an equation from which the slope of the tangent can be calculated at any point.

As an example of the use of this procedure we have used data for a reaction that is of current interest to our research group—the oxidation of alkynes of quaternary ammonium permanganates ($QMnO_4$) in methylene chloride solutions (*12, 13*). This reaction (eq 8) is subject to most of the difficulties described above.

$$-C{\equiv}C- + MnO_4^- \rightarrow \underset{-C-C-}{\overset{O\ \ O}{\|\ \ \|}} + MnO_2 \tag{8}$$

One of the products, MnO_2, forms a colloid that interferes with spectral measurements at 526 nm, the wavelength best suited for monitoring the disappearance of permanganate, and as a consequence A_f increases continuously until precipitation eventually begins. Because flocculation of manganese dioxide occurs at a rate that is only slightly slower than the rate at which permanganate is being reduced (*14*), a sharp isobestic point is not observed when successive spectra are superimposed as the reaction progresses.

Table 1. Calculated Coefficients To Fit Time/Absorbance Data to Eq 7[a]

Order	$a_0 \times 10$	$a_1 \times 10$	$a_2 \times 10^2$	$a_3 \times 10^2$	$a_4 \times 10^3$	$a_5 \times 10^3$	$a_6 \times 10^3$	$a_7 \times 10^3$
1	8.39	−1.18						
2	8.53	−1.58	1.84					
3	8.53	−1.61	2.24	−0.122				
4	8.55	−1.83	6.82	−3.45	7.68			
5	8.55	−1.83	6.96	−3.63	8.62	−0.174		
6	8.55	−1.82	6.38	−2.53	−0.99	3.74	−0.599	
7	8.55	−1.81	6.18	−2.05	−6.53	7.05	−1.60	0.120

[a] $[QMnO_4]_i = 3.57 \times 10^{-4}$ M, [ethyl 2-butyrate] = 1.52×10^{-2} M, temp. = 22.0 °C. The coefficients were calculated by the Gauss–Jordan method written in BASIC using double-precision variables and run on an IBM-PC.

Table 2. Calculated Coefficients To Fit Time/Absorbance Data to Eq 7[a]

Order	$a_0 \times 10$	$a_1 \times 10^2$	$a_2 \times 10^2$	$a_3 \times 10^2$	$a_4 \times 10^3$	$a_5 \times 10^3$	$a_6 \times 10^3$	$a_7 \times 10^3$
1	4.45	−5.68						
2	4.53	−7.50	0.683					
3	4.53	−7.62	0.801	−0.029				
4	4.55	−8.73	2.77	−1.18	2.17			
5	4.55	−9.27	4.21	−2.66	8.42	−0.936		
6	4.54	−6.91	−5.23	1.18	−0.936	0.326	−4.16	
7	4.55	−8.02	−0.524	3.94	−0.30	6.30	1.15	0.407

[a] $[QMnO_4] = 1.90 \times 10^{-4}$ M, [ethyl 2-butyrate] = 1.52×10^{-2} M, temp. = 22.0 °C. The coefficients were calculated by the Gauss–Jordan method written in BASIC using double-precision variables and run on an IBM-PC.

Attempts to fit absorbance vs. time data at 526 nm to eq 7 using up to seventh-order polynomial give the coefficients listed in Tables 1 and 2.

The first coefficient, a_0, is the calculated initial absorbance; that is, when $t = 0$, $a_0 = A_0$. The second coefficient is the initial slope; that is, at $t = 0$, $-[dA/dt]_0 = a_1$. The third coefficient gives the initial curvature; that is, at $t = 0$, $[d^2A/dt^2]_0 = 2a_2$. Consequently, it can be seen that a_0 should be positive and close to the experimental value for the initial absorbance. The value of a_1, the initial slope, should be negative and the value of a_2, the initial curvature, should be positive.

It is the values for a_1 that are most important for kinetic studies. The negative values of these constants are the initial reaction rates expressed in absorbance units. Division by the difference between the molar absorptivities of permanganate and MnO_2 at 526 nm ($\Delta\epsilon = 1500$) easily converts them into concentration units (*15*), although as we will see this is usually unnecessary.

Inspection of the data in Table 1 indicates that, for orders 4 to 7, a_1 has an average value of -0.182 ± 0.001 min^{-1}. The uncertainty in this value is less than the experimental errors associated with studying the reaction rates and can therefore be accepted as a reliable initial reaction rate.

A careful examination of the data in Table 2 reveals that the initial curvatures, a_2, for the sixth- and seventh-order polynomials are negative. In other words, it has been possible for the program to fit the experimental curve by assuming that the time/absorbance plot is initially concave down. Such a situation is physically unrealistic and the corresponding values of a_1 should therefore be ignored. When this is done, the initial slope obtained by averaging the results for the fourth and fifth-order equations is -0.0900 ± 0.0027 min^{-1}.

It is apparent from the above calculations, which have been represented graphically in Figure 4, that a decrease in the concentration of permanganate has produced a nearly proportional reduction in the initial rate of reaction. In other words, the rate of reaction appears to be first order in permanganate concentration. This can, in fact, be proven to be so by measuring initial rates at several permanganate concentrations, as we have shown elsewhere (*13*). A plot of ln a_1 vs. ln (initial concentration) gives a straight line whose slope, the reaction order, is one. Similarly, it can be shown that the rate of reaction is directly proportional to the concentration of alkyne present in the solution (*13*). Hence, this is an example of a typical second-order reaction.

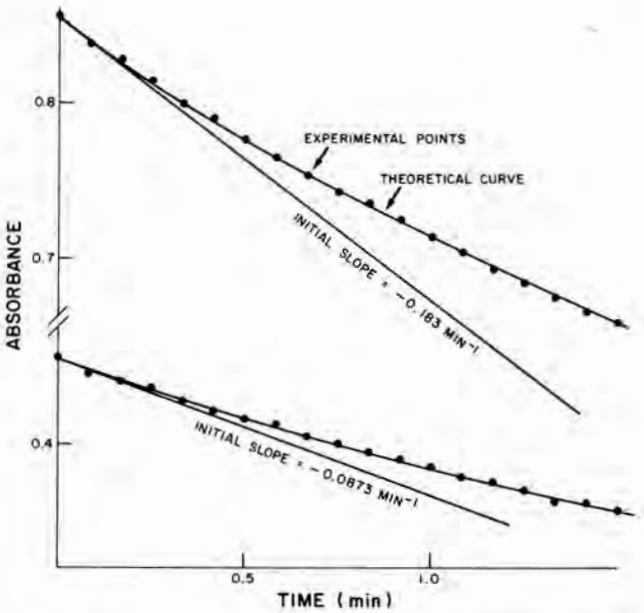

Figure 4. Graphical depiction of data. The theoretical curves and initial slopes were calculated using the coefficients for fourth-order polynomials found in Tables 1 and 2.

To obtain the pseudo-first-order rate constant for the reaction, we must rearrange the rate expression, eq 9:

$$-d[QMnO_4]_i/dt = k_1[QMnO_4]_i \quad (9)$$

$$k_1 = (-d[QMnO_4]_i/dt)/[QMnO_4]_i \quad (10)$$

$$= -a_1/\Delta\epsilon[QMnO_4]_i \quad (11)$$

where $\Delta\epsilon$ is the difference between the molar absorptivities of permanganate and the product species at 526 nm. Using eq 6 to replace the initial permanganate concentration gives eq 12.

$$k_1 = -a_1/(A_o - A_f) \quad (12)$$

A_o, the initial absorbance is known or can be replaced by a_o. The final absorbance, A_f, on the other hand, cannot be measured directly because MnO_2 begins to coagulate before the reaction is complete. $A_o - A_f$ can, however, be obtained by a second least-squares fit of the time/absorbance data to the expression given by eq 13.

$$A = (A_o - A_f)e^{-kt} + A_f \quad (13)$$

Table 3 presents values for the rate constant found using eq 12 with average values of the initial rate, a_1, and calculated estimates of $(A_o - A_f)$. The two examples give rate constants that, within the uncertainties, are identical, particularly if only the first 18 data points are used; points chosen from earlier in the reaction should be freer of the complication caused by MnO_2. As it turns out, the difference between using all the data and only part of it is significant only for the oxidation carried out with an initial permanganate concentration of 1.90×10^{-4} M. The absorbances in this case are less reliable and the calculated uncertainty in the rate constant is larger as well. Since the rate constant calculated from eq 12 uses the initial rate (a_1) it is not surprising to find it larger than obtained from the exponential regression, which implicitly involves rates taken over the entire time range; rates closer to the reaction's completion would be less reliable.

Hence, by use of this approach, accurate and reliable values of the rate constants can be obtained directly without resorting to time-consuming graphical methods (*11*). The use of this approach also relieves the experimenter of the necessity of following the reaction through several half-lives in order to obtain a value for A_f. The time required to determine the rate law and rate constants for a particular reaction is thereby significantly reduced. This may be an important consideration when attempts are made, for example, to illustrate the principles of chemical kinetics in an undergraduate laboratory class, or when it is necessary to monitor the rate of a reaction routinely for some other purpose.

Curve Fitting

Methods for fitting an expression, such as eq 7, involving an nth-order polynomial, to a large number of data points (t_i, A_i) are well known and can be found in many books on applied mathematics or numerical analysis. The coefficients $a_0, a_1, a_2 \ldots a_n$ are treated as variables to be adjusted until the "best fit" is obtained. If the sum of the residuals squared is minimized with respect to each coefficient the result is a series of $n + 1$, linear simultaneous equations, eq 14, where m is the number of data points used.

$$\begin{aligned}
a_0 m &+ a_1 t_i &+ a_2 t_i^2 &+ \ldots + a_n t_i^n &= A_i \\
a_0 t_i &+ a_1 t_i^2 &+ a_2 t_i^3 &+ \ldots + a_n t_i^{n+1} &= t_i A_i \\
a_0 t_i^2 &+ a_1 t_i^3 &+ a_2 t_i^4 &+ \ldots + a_n t_i^{n+2} &= t_i^n A_i \\
\cdot & & & \cdot & \cdot \\
\cdot & & & \cdot & \cdot \\
\cdot & & & \cdot & \cdot \\
a_0 t_i^n &+ a_1 t_i^{n+1} &+ a_2 t_i^{n+2} &+ \ldots + a_n t_i^{2n} &= t_i^n A_i
\end{aligned} \quad (14)$$

The solution of these equations can be achieved using an iterative technique such as the Gauss–Seidel method or by using a matrix method (Gauss–Jordan, Gauss elimination, Crout LU decomposition etc.). Following the approach of Miller (*16*), we have chosen the Gauss–Jordan method since it is readily adaptable to a short computer program, finds the solutions rapidly, and can be used to estimate the error in each calculated coefficient.

Table 3. Calculated Pseudo-First-Order Rate Constants[a]

	All Data		First 18 points	
$[QMnO_4]_i$ M	k	$-a_1/A_0 - A_f$	k	$-a_1/A_0 - A_f$
3.57×10^{-4}	0.312 ± 0.013	0.348 ± 0.029	0.323 ± 0.035	0.346 ± 0.062
1.90×10^{-4}	0.241 ± 0.017	0.280 ± 0.040	0.298 ± 0.075	0.322 ± 0.145

[a] k and $(A_0 - A_f)$ are obtained from a regression using the function of eq 13. a_1 is obtained from averaging values from nth-order regressions. When $[QMnO_4]_i = 3.57 \times 10^{-4}$ M orders 4–7 were averaged. When $[QMnO_4]_i = 1.90 \times 10^{-4}$ M orders 4 and 5 were averaged.

The actual time required for a calculation depends on the computer, the language used, the number of data points and the desired order of regression. For example, using a program written in BASIC on an IBM-PC and 25 data points, a fifth-order regression took 34 seconds to complete. The same calculation on an Apple II+ or a Commodore Computer was 90 seconds, and on an IBM-AT it was 10 seconds.

Since matrix methods of regression analysis, such as a Gauss–Jordan, are susceptible to an accumulation of errors and are sensitive to the matrices used, a test of the approach was made using the function,

$$A = 0.400e^{-0.70t} + 0.400 \quad (15)$$

This function approximates the sort of data typically seen in kinetic runs and can be expanded as a polynomial in t (eq 7) with known coefficients. Thirty-one data points, in the interval $0 \leq t \leq 3$, were used as input in curve-fitting programs written in a variety of languages, using three different algorithms, and running on several computers. The results were virtually identical for orders of regression up to 4. Thereafter, the higher-order coefficients varied quite dramatically. The Gauss–Jordan Method used in this paper gave results as reliable as those obtained from other methods such as the Crout LU decomposition. Interestingly, while the compiler languages we used made use of accurate floating-point arithmetic routines, interpreted BASIC on IBM computers did not. Our programs written in C and Pascal came near to reproducing the exact coefficients, even at an eighth-order of regression. The results from BASIC programs were less accurate at the high orders, even when double-precision variables were used; in fact Commodore and Apple II series computers seemed to be better. Nonetheless, even BASIC gave reliable values for the coefficients a_0 and a_1 for all orders, and, as previously noted, it is these two coefficients that are of interest in analyzing kinetic data. The correct values for a_0 and a_1 were reached in a fourth-order regression, and neither they nor the correlation coefficient change significantly for higher orders.

Fitting the data to eq 13 must be done in a slightly different way (*17*). A_o, A_f, and k may be varied to obtain the "best fit", but since the three simultaneous equations are not linear in these variables an iterative approach is necessitated. An initial guess is made for A_o, A_f, and k; the sum of the residuals squared is then minimized with respect to each variable and the three resulting simultaneous equations solved for new values of A_o, A_f, and k. The process can be repeated until changes in the variables become smaller than some predetermined value. Although the time necessary to complete a regression depends on the number of iterations it is usually comparable to that required for a fifth-order linear regression.

As a check on the use of this entire approach to kinetic

analysis we have compared the results obtained using some typical kinetic data with those found by other methods such as graphical analysis (*3*) and integrated rate equations. In reactions for which a stable final A_f has been determined the calculated A_f and k agree within experimental error with previously estimated values. That is true even if the data are limited to the early part of the reaction. Typically, for good time/absorbance data, an acceptable fit can be made and reliable rate constants obtained using fourth- and fifth-order regression. Since the purpose of the analysis is to obtain rate constants, $-a_1/(A_o - A_f)$, from initial rates, it is important that there be as much reliable data as possible obtained early in the reaction before interference from precipitation or competing reactions becomes important.

The kinetic analysis source programs are available in standard BASIC or Pascal so that they can be used on almost any microcomputer with only minor alterations. Double-precision, real variables are recommended for those computers that support them. Compiled programs are also available for IBM-compatible computers, with or without a math-coprocessor chip. In the BASIC version the time/absorbance data are typed into DATA statements, whereas in all others the data are entered and edited as part of the program. The exponential regression is carried out first, then the user is prompted for the desired order of regression. The program ends by giving as either screen or printer output each coefficient in the polynomial $-a_o$, a_1, a_2 . . . a_n, A_f, k, $-a_1/(A_o - A_f)$, the standard error (sigma) in each; the correlation coefficient, and the residual in absorbance for every time chosen.

Summary

It has been found that reliable, initial reaction rates can be obtained by fitting absorbance–time data to a polynomial expression (eq 7) and calculating the slope of the tangent at time zero (a_1). First-order rate constants can be produced from these initial rates as well as A_o and A_f. The calculations can be completed quickly and accurately using a microcomputer. This approach removes personal biases from the task of selecting the proper tangent at zero and simplifies what had previously been a very time-consuming graphical process.

When working with real data, erroneous results can occasionally be obtained for a particular order of eq 7 because the program may fit the data in a way that has no physical reality. Hence, it is best to average results for several orders of regression having deleted any series that exhibits an irregular or impossible curvature. It is also best to avoid seventh- and eighth-order regressions, if possible, since these are less reliable and require longer to perform.

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