

One Run Kinetics—A Computer Program

Richard T. O'Neill, Robert A. Lodder,¹ and Steven M. Scheffers²

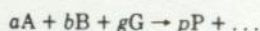
Xavier University
Cincinnati, OH 45207

In recent years there has been a great increase in the use of computers to determine the rate constant and the partial orders from concentration-time data for chemical reactions (1). The programs written for this data processing usually are severely limited in the number of sets of partial orders tested and often require the user to supply functions, first derivatives, weighting factors, estimated values of the rate constant, and the like. To use these programs for all but the simplest reactions, the investigator must run the experiment so that the rate depends on the concentration of only one reactant, with other reactants being absent, in excess, or initially at the same equivalent concentration as the reference reactant. This requires the reaction to be run several times, obtaining a partial order and a pseudo rate constant from each run, in order to obtain the entire set of partial orders and a true rate constant. This repetition can be expensive and time consuming and sometimes, because of solubility constraints, impossible.

This paper describes a user-friendly computer program that will analyze the data from one kinetics experiment for 84 different rate laws, i.e., sets of partial orders. Unless the user wishes to determine the partial order of a substance not used up by the reaction, this one set of concentration-time points is usually all that is needed to determine the best set of partial orders and the corresponding rate constant with its uncertainty. In practice, of course, several experiments with different initial concentrations should always be run to check reproducibility, systemic errors, and the assumptions under which the data analysis was made, i.e., that no parallel reactions are occurring and that there is no appreciable buildup of intermediates. The analyses of all runs should be in agreement. If two or more rate laws are found to fit the experimental data for one run equally well, these runs with different initial concentrations may resolve the ambiguity.

Background

For an isothermal closed-system reaction with no parallel reactions, no autocatalysis, no appreciable buildup of intermediates, and three or fewer reactants



the rate law has the form

$$\begin{aligned} \text{Rate} &= -\frac{1}{a} \frac{dC_A}{dt} \\ &= kC_A^\alpha C_B^\beta C_G^\gamma \end{aligned}$$

where α , β , and γ are the partial orders with respect to A, B, and G, respectively. Taking C_i and C_{i0} to be the instantaneous and initial concentrations of the i th component, and using the stoichiometric relationships

$$C_B = C_{B0} - (b/a)(C_{A0} - C_A)$$

and

$$C_G = C_{G0} - (g/a)(C_{A0} - C_A)$$

the differential equation can be rearranged to the form

$$\frac{dC_A}{C_A^\alpha (C_A - P)^\beta (C_A - Q)^\gamma} = -ka^{1-\beta-\gamma} b^\beta g^\gamma dt = -k'dt \quad (1)$$

where $P = C_{A0} - aC_{B0}/b$ and $Q = C_{A0} - aC_{G0}/g$. This differential rate expression can usually be integrated for a selected set of partial orders to yield an expression of the form

$$F(C_A) = -k't + F(C_{A0}) \quad (2)$$

A linear least-squares analysis can determine the correlation coefficient, which helps confirm the validity of the set of partial orders chosen, and the slope of the line, from which the rate constant can be calculated.

It is because of the difficulty of integrating eqn. (1) that the experimenter is forced to use special initial concentrations for all but the simplest of reactions. If the reactants are initially at equivalent concentrations ($P = Q = 0$), the expression is easy to integrate, but only the total order can be determined. If all but one reactant are in great excess, only one partial order and one pseudo rate constant can be determined. With the advent of the computer it is much more convenient to analyze one set of time-concentration points for a large number of sets of partial orders, if the corresponding integrated rate expressions eqn. (2) are readily available.

The computer program KINOR tests the integrated rate expression for all cases where the partial orders are positive integers or half integers and where the total order is three or less. These 84 cases actually correspond to more than 84 different functions because a given differential rate expression (eqn. (1)) may lead to up to six different integrated expressions (eqn. (2)) depending on the values of P and Q . Most of the integrals can be evaluated (2) but some are elliptical and cannot be obtained in closed form. For these cases Romberg numerical integration (3) is used. This technique is also used for one case for which a closed form solution exists but produces excessive roundoff error.

Weighted Linear Least Squares

The linear expression (eqn. (2)) contains only one independent variable, time, the uncertainty in which is generally much less than the uncertainty in the concentration. Therefore the weighted least-squares equations of Irvin and Quickenden (4) can be used with the simplification of setting the variance of the independent variable equal to zero. The resultant equations for the slope, intercept, and correlation coefficient are then the same as for the nonweighted, least-squares situation (5), except that sums are replaced by weighted sums and N , the number of data pairs, is replaced by the sum of the weights. The weighting factor, when only the dependent variable is subject to error, is

$$W = (\text{constant})/\sigma_F^2 = (\text{constant})/((dF/dC_A)\sigma_{C_A})^2$$

¹ Part of a thesis submitted in partial fulfillment of the requirements for the degree of Master of Science, Xavier University, 1983. Present address is Department of Chemistry, Indiana University, Bloomington IN 47405.

² Part of a thesis submitted in partial fulfillment of the requirements for the degree of Master of Science, Xavier University, 1981. Present address is Department of Chemistry, Purdue University, West Lafayette IN 47907.

If the variance of the concentration is a constant, then

$$W = (\text{constant}') / (dF/dC_A)^2$$

In the computer program the derivative is approximated by

$$\frac{dF}{dC_A} \approx \frac{F(C_A) - F(C_A - \Delta)}{C_A - (C_A - \Delta)} = \frac{F(C_A) - F(C_A - \Delta)}{\Delta}$$

where Δ is taken to be $10^{-6} C_A$. The program has a provision for increasing this value of Δ if it results in a value of the derivative so small that over/underflow errors are produced, but this was never needed for the 1092 sets of data tested.

Results

The program was tested with synthetic data appropriate to each of the 84 cases, each with 13 relative concentration conditions ($C_{A0}/a = C_{B0}/b = C_{G0}/g$; $C_{A0}/a > C_{B0}/b = C_{G0}/g$; etc.) With the conditions under which the program is expected to be used—no stoichiometric equivalences for initial conditions—a correlation coefficient of unity and the correct rate constant (five significant digits using six-significant-digit concentrations) were obtained for each appropriate case. No overflow, division by zero, or root or log of negative number errors occurred for any case under these conditions. (Such errors could probably be forced by using very large or very small concentrations, initial conditions very close to stoichiometric equivalence, or situations where the C_A values changed only slightly. These conditions, however, were not tested.)

When the initial concentrations were in equivalent amounts, such errors were sometimes generated internally but these were trapped and the rate constant calculated from the results of a simpler case that was mathematically equivalent,³ if such a case existed. The program has a provision to use the Romberg routine if no simpler case existed, but this was never necessary for the data sets tested. For the 588 sets of data tested which had some stoichiometric equivalence, all sets gave good correlation (>0.999942) and the correct rate constant. The price was additional running time and the inability to choose between equivalent cases. The problem is avoided if equivalent initial concentrations are not used.

Operation

The user supplies the program with the stoichiometric coefficients and initial concentrations of reactants (all may be zero except for the first reactant), the number of pairs of data points, and the set of C_A , t values measured. The program then prints, for each of the 84 cases, the case number, the partial orders, the correlation coefficient, the rate constant, and the uncertainty in the rate constant. For each individual case the user can then obtain details, i.e., a table whose columns are time, C_A , F calculated from C_A , F calculated from the best linear fit, and the percentage difference between these two F 's. This last column is particularly useful for deciding between cases with similar correlation coefficients. If the percent difference constantly decreases/increases, changes sign, passes through a minimum/maximum, and then increases/decreases, changing sign again, this is a good indication that the function being tested is not correct for the data, even if the correlation is good. Similarly, a

random distribution of signs and values in this column indicates that the function could be correct, and any poor correlation could be due to imprecise concentration data. (If the function changes sign, the difference, not the percentage difference, should be used to check the trend.) The user should always check the individual case details to confirm a fit.

The program also gives the user the option of specifying a set of partial orders, not necessarily positive or integral or half-integral, for calculation by the Romberg method of the correlation coefficient, the rate constant, the uncertainty in the rate constant, and details as described above. It is not recommended that the user vary the partial orders by tiny amounts, and attempt to find the "best" set of partial orders by maximizing the correlation coefficient. This might only be a local maximum and would not necessarily yield a uniquely "best" set of partial orders.

The program is constructed to use the concentration of a reactant as the variable that changes with time. It could easily be modified to use the concentration of a product, $C_A = C_{P0} + (a/p)(C_P - C_{P0})$, or any physical property, λ , that is a linear function of concentrations (6), $C_A = C_{A0}(\lambda_\infty - \lambda)/(\lambda_\infty - \lambda_0)$. In the last case, however, the substance A would have to be associated with the limiting reagent, not the substance whose concentration is measured with time. Furthermore, the weighting would not be correct if the variance for the physical parameter measurements was not a constant, as for example, if λ were absorbance.

Availability

KINOR is written in VAX-Basic and is implemented on a VAX-780 computer. Uncompiled it uses 98 blocks of storage and requires double precision. The program, its instructions, and other kinetics programs developed at Xavier University can be obtained on magnetic tape for \$20, which includes an 800-ft tape and domestic postage. Orders may be placed with Rev. Ronald J. Ferguson, S. J., Director of Academic Computing, Xavier University, Cincinnati OH 45207.

Acknowledgment

The authors wish to thank Richard J. Pulskamp, James A. Delaney, and David C. Flaspohler for many helpful discussions.

Literature Cited

- (1) Hogg, J. L., *J. CHEM. EDUC.*, **53**, 109 (1974).
- (2) The integrals were obtained from Spiegel, M. R., "Mathematic Handbook of Formulas and Tables," McGraw-Hill Book Company, New York, 1968 and Weast, R. G., and Astle, M. J., "CRC Handbook of Chemistry and Physics," CRC Press, Boca Raton, Florida, 1981.
- (3) Gerald, C. F., and Wheatley, P. O., "Applied Numerical Analysis," 3rd ed., Addison-Wesley, Reading, MA, 1984, p.250 ff.
- (4) Irvin, J. A., and Quickenden, T. L., *J. CHEM. EDUC.*, **60**, 711 (1983).
- (5) Natrella, M. G., "Experimental Statistics," National Bureau of Standards Handbook 91, Washington, DC, 1963, p. 5-10.
- (6) Moore, J. W., and Pearson, R. G., "Kinetics and Mechanism," 3rd ed., John Wiley and Sons, New York, 1981, p. 38 ff.

An Undergraduate Program on Computer Interfacing

Robert J. Anderson¹ and Paul H. Woodworth

Ithaca College
Ithaca, NY 14850

The most recent guidelines for "Undergraduate Professional Education in Chemistry" published by the American Chemical Society's Committee on Professional Training call for instruction in the use of laboratory computers (1). Sever-

³ For example, consider eqn. (1) with $\nu = \nu' = 0$. The case $\alpha, \beta, \gamma = 0, 2.5, 0.5$ is equivalent to the case $\alpha, \beta, \gamma = 3, 0, 0$ and both will have the same value for K' . The k for the former case can be calculated from the k for the latter, since the stoichiometric coefficients are the same.