A COMPUTER GRAPHICS APPROACH TO THE USE OF THE INTEGRAL METHOD IN KINETICS

J. M. SKAATES
Michigan Technological University
Houghton, MI 49931

THE EMPIRICAL determination of rate equations from batch reactor data by the integral method occupies a prominent place in chemical engineering kinetics courses. However, the application of the method is tedious and time-consuming. Students rarely complete homework problems involving the integral method. In an attempt to make these problems more palatable, and also to demonstrate the potential of computer graphics for data analysis, a microcomputer program was written to analyze rate data by the integral method. The program is written in Applesoft BASIC for an APPLE® computer having 32k of memory.

DATA REQUIRED

The problem can handle only constant-volume, single-phase reactions of the stoichiometry

$$aA + bB \underset{k'_{C_A}}{\overset{k_{C_A}}{\rightleftarrows}} rR + sS$$

where the stoichiometric coefficients a, b, r and s are either positive real numbers or zero. Data can be in the form C_A versus t, x_A versus t, P_A versus t, or P_{total} versus t. Initial conditions (concentrations or partial pressures at time $t = 0$) must be given for all species, including inerts. If the reaction is reversible, the value of the equilibrium constant in concentration units, K_C, must be supplied. If the reaction is irreversible, K_C must be set equal to zero. The first data point must be at time $t = 0$.

Students rarely complete problems involving the integral method . . . to make these problems more palatable, and to demonstrate the potential of computer graphics for data analysis, a microcomputer program was written to analyze rate data by the integral method.

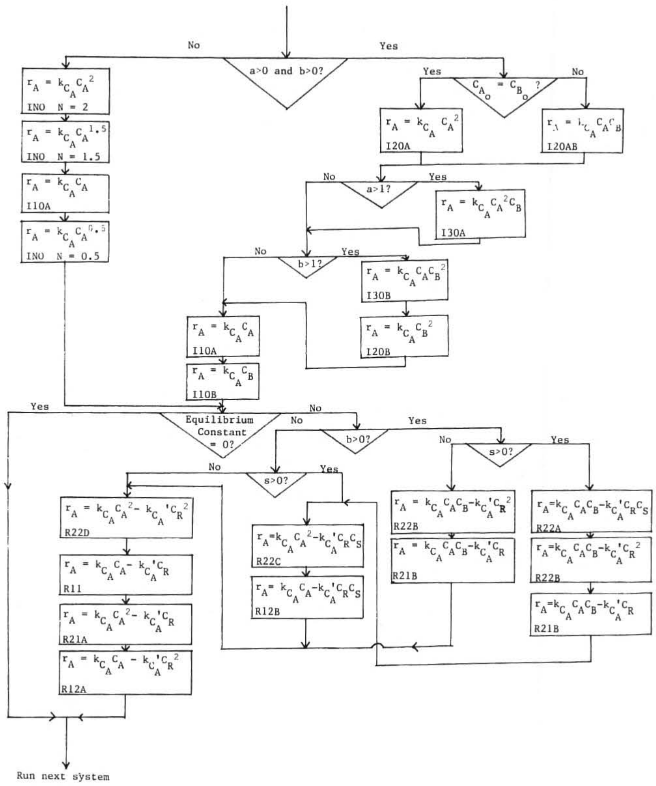

FIGURE 1.

PROGRAM STRUCTURE

From the data given the program calculates x_A, fractional conversion of reactant A, for each data point. Based on the stoichiometry of the reaction the program selects for testing a number of possible rate equations according to the flowchart in Figure 1. The integrated forms for each rate equation are in the format $\beta(x_A) = k_C t$. For ease of reference each rate equation is coded, with the first letter (I or R) signify-

J. M. Skaates received his B.Sc. (1957) at Case Institute of Technology and M.S. (1958) and Ph.D. (1961) at Ohio State University in chemical engineering. He worked at California Research Corporation for three years before joining the faculty of Michigan Tech. His teaching duties have included undergraduate and graduate courses in thermodynamics and kinetics, an undergraduate course in process control, and graduate courses in catalysis and in process optimization. He has been involved in research in catalysis, biomass pyrolysis, and wet oxidation.

---

ing an irreversible or reversible reaction, the next two integers giving the reaction order in the forward and reverse directions, and the last letter as a supplementary identifier. In the BASIC program each integrated form is computed in a separate subroutine having the appropriate code name.

STUDENT USAGE OF THE PROGRAM

Students, working in groups of two, check out a diskette containing the program. They also receive an instruction booklet containing a description of the program and directions for use. Since, surprisingly, many students have not used a personal computer, there are instructions on everything from how to handle a diskette to how to turn on the machine. After the program is loaded, detailed instructions appear on the video monitor, and the student enters the required data according to a series of prompts.

For each rate equation the monitor first displays the individual data points of the $\beta(x_A)$ versus t plot. After a slight pause, the linear-least-squares line is also displayed, making it easier to judge if the data points swerve from a straight line. The rate equation being tested is shown on the monitor, as well as the value of k_{C_A} determined by linear least squares. Although the use of linear least squares is not strictly correct due to the nonlinearity of the functions, more sophisticated non-linear parameter estimation techniques are ruled out by the limited machine memory.

Four homework problems are assigned to each student group. Students are instructed to write down their observations for each rate equation tested. It is emphasized that they are to make their judgments not on the degree of scatter of the data points, but on their overall deviation from linearity.

EXAMPLE PROBLEM

Smith [1] studied the gas-phase dissociation of sulfuryl chloride into chlorine and sulfur dioxide at 279.2°C. Under constant volume conditions the following results were obtained, starting with pure sulfuryl chloride.

$$\underset{A}{SO_2Cl_2} \rightarrow \underset{R}{SO_2} + \underset{S}{Cl_2}$$

t min	P_{total} mm Hg
0	322
15.7	335
41.1	355
68.3	375
96.3	395

The conversion is 100% as $t \rightarrow \infty$.

Solution: From the video monitor the following were noted:

Rate equation tested	Observations
$r_A = k_{C_A}C_A^2$	slightly concave upwards
$r_A = k_{C_A}C_A^{1.5}$	straight $k_{C_A} = 1.58 \times 10^{-4}$
$r_A = k_{C_A}C_A$	straight $k_{C_A} = 2.66 \times 10^{-3}$
$r_A = k_{C_A}C_A^{0.5}$	slightly concave downwards

SUMMARY

Class discussion of the homework problems highlights the imprecision of the integral method, a point not adequately covered in textbooks. For an n^{th} order irreversible reaction, n can be estimated only to ± 0.2 with perfect (computer-generated) data having no scatter, ± 0.5 for data with small scatter, and ± 1 for appreciable scatter. It is emphasized that this imprecision is an inherent result of the integration of data-suppression of noise accompanied by loss of fine detail.

Student reception of the computer graphics program has been enthusiastic. It serves to revive interest in the course at a point where the math becomes tedious and student interest starts to flag. Further information on this program may be obtained from the author.

ACKNOWLEDGMENTS

It is a pleasure to acknowledge the help of students Thomas S. Sanicola and Michael G. Krueger in the development of this program.

REFERENCES

1. Smith, D. F., *JACS 47*, 1862 (1925). □