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Analog Computers and Kinetics of Hydrogenation[1]

R. O. BUTTERFIELD, E. D. BITNER, C. R. SCHOLFIELD, and H. J. DUTTON,
Northern Regional Research Laboratory,[2] Peoria, Illinois

Abstract

Investigations of the kinetics of consecutive reactions frequently require complicated calculations to determine specific reaction rate constants from experimental data. Analog computers permit a convenient empirical adjustment of rate constants in kinetic equations to match experimental results. Once an electronic network analogous to the chemical reaction system is set up, specific reaction rates can be determined by adjusting potentiometers, which are the analogs of the rate constants, until an acceptable fit of calculated and experimental data is reached. Applicability of a small analog computer to the kinetics of hydrogenation is presented.

Introduction

A SERIES OF calculations involving successive approximations is frequently required to arrive at an acceptable fit of experimental kinetic data and to determine the specific reaction rate constants (2). The application of digital computers to a study of the kinetics of hydrogenation has recently been described (4), but this procedure becomes awkward in experiments in which "isolinoleate" and the "oleate shunt" are considered and are studied with radioactively labeled intermediates (7).

Analog computers are ideally adapted for the solution of differential equations in chemical kinetics (6). Once an electronic network has been set up analogous to the kinetic equations, the problem of determining specific reaction rate constants consists merely in empirical adjustment of potentiometers, which are the analogs of the rate constants, until the desired fit of the experimental kinetic data is reached.

A small analog computer (9 amplifier, Heathkit *Educational Electronic* Analog Computer, Model EC-1) was applied to a variety of kinetic problems recently encountered in this laboratory in our research on kinetics of hydrogenation. Its successful use demonstrates that the gap between the fields of organic chemical research and electronic methods of computation can readily be bridged with a distinct advantage to research.

Experimental Procedures

Basic Computing Elements and Mathematical Operations

The following discussion is a simplification of analog computer operations based on Osburne's description (6). The fundamental component of an analog computer is its high-gain dc amplifier. The gain of this amplifier, which is represented by a triangular symbol (Fig. 1), ranges between ten thousand and several million, depending upon design and precision required; thus, an output of 100 v will frequently require an input of less than 10 mv. For mathematical purposes, this small input voltage may be considered as zero to simplify the algebraic equations.

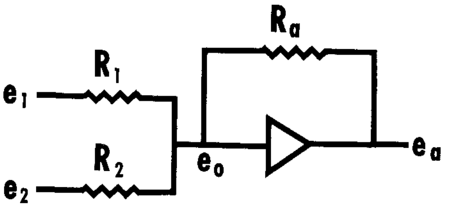

FIG. 1. Computer circuit for addition and multiplication.

Circuits for addition and multiplication, illustrated in Figure 1, operate as follows: The current through resistor R_1 is equal to the voltage drop divided by the resistance (Ohm's law); hence the current through R_1 is $\frac{e_1-e_o}{R_1}$, the current through R_2 is $\frac{e_2-e_o}{R_2}$, and the current through R_a is $\frac{e_o-e_a}{R_a}$. The current through the feedback resistor, R_a, is equal to the sum of currents through R_1 and R_2 since no current passes through the amplifier or

$$\frac{e_o-e_a}{R_a}=\frac{e_1-e_o}{R_1}+\frac{e_2-e_o}{R_2}$$

Since e_o as explained is essentially zero, then

$$-\frac{e_a}{R_a}=\frac{e_1}{R_1}+\frac{e_2}{R_2} \text{ or}$$

$$-e_a=\frac{R_a e_1}{R_1}+\frac{R_a e_2}{R_2}$$

If the ratios of resistors R_a/R_1 and R_a/R_2 are equal to 1, e_1 and e_2 have been added to give the voltage e_a of negative sign. Also, if the ratios R_a/R_1 and R_a/R_2 are other than unity, the input voltages e_1 and e_2 have been multiplied by these ratios. Then e_a becomes the sum of the product of e_1 multiplied by a constant and of e_2 multiplied by a constant; or, two incoming signals each multiplied by the ratio of the resistances have been algebraically added to give the negative output signal.

For multiplying by a positive constant less than 1 without an amplifier, a potentiometer is used as shown

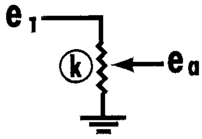

FIG. 2. Computer circuit for multiplication by less than 1.

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[2] A laboratory of the No. Utiliz. Res. & Dev. Div., ARS, U.S.D.A.

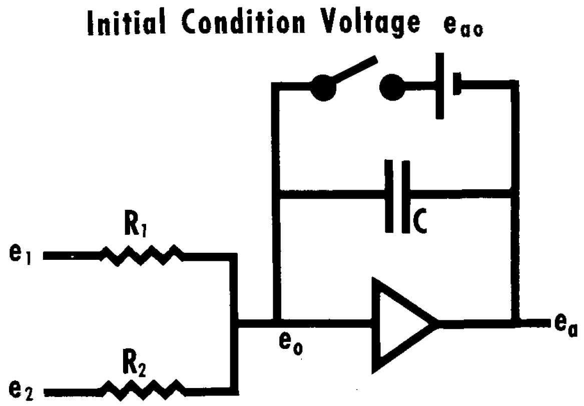


FIG. 3. Computer circuit for addition and integration.

in Figure 2, where k is the fraction of the resistance from the center tap to ground divided by the total resistance of the potentiometer. This is a simple voltage divider circuit and the output voltage e_a is equal to the input voltage e_1 multiplied by the fraction k or $e_a = ke_1$.

A circuit for addition and integration is given in Figure 3. The expression for the current through a capacitor is C(dE/dt), where C is the capacitance and E is the voltage. In equating the currents, one obtains

$$C\frac{d(e_o-e_a)}{dt} = \frac{e_1-e_o}{R_1} + \frac{e_2-e_o}{R_2}$$

Assuming $e_o = 0$

$$-\frac{de_a}{dt} = \frac{e_1}{CR_1} + \frac{e_2}{CR_2} \text{ or}$$

$$e_a = -\left[\frac{1}{CR_1}\int e_1dt + \frac{1}{CR_2}\int e_2dt\right] + e_{a_o}$$

where e_{a_o} is the constant of integration (initial condition) and is the initial voltage across the capacitor C at time = 0.

With this discussion of the mathematical operation, although brief, the combination of these basic computing elements for solving differential equations can be understood. A more complete discussion may be found in several references cited by Osburne (6).

Application to Kinetics of Consecutive Simultaneous Reactions

Programing the computer to solve differential equations can be illustrated by the classical problem of consecutive reaction that is described in Daniels and Alberty (3) and in other standard texts of physical chemistry:

$$A \xrightarrow{k_a} B \xrightarrow{k_b} C$$

The differential equations for this reaction are:

1) $d[A] = -k_a[A]\,dt$
2) $-d[B] = (-k_a[A] + k_b[B])\,dt$
3) $d[C] = k_b[B]\,dt$

The circuit analog for the first equation (Fig. 4) is a simple integration circuit. To satisfy the first equation, it is necessary to connect the center tap of the potentiometer (this signal is $-k_a[A]dt$) to the input (this signal is $d[A]$); the electrical analogs for the other two equations are set up in a similar fashion and require subtraction and integration circuits. The completed circuit is given in Figure 5.

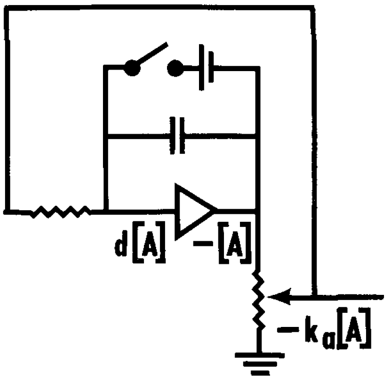


FIG. 4. Computer circuit for $d[A] = -k_a[A]dt$.

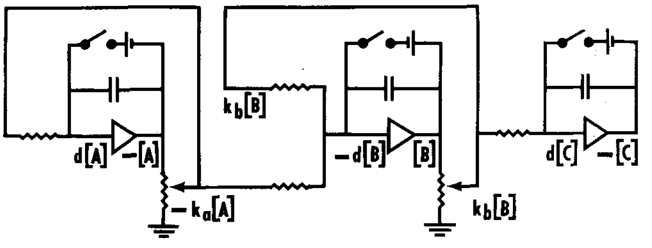


FIG. 5. Computer circuit for $A \xrightarrow{k_a} B \xrightarrow{k_b} C$.

To obtain the solution of a problem, potentiometers are set at positions analogous to the rate constants. Voltages are impressed on the capacitors in proportion to the percentages of A, B, and C present at the start of the reaction (initial conditions). To simulate the problem of chemical kinetics, the switches are simultaneously opened, and the capacitors are allowed to either bleed off their charge or build up their charge according to the requirements of the differential equations. Voltages representing the concentrations of the different constituents at points A, B, and C in Figure 5 are followed by means of a voltmeter, an oscilloscope, or a recorder. The problem described by Daniels and Alberty consists of the initial condition for A, 100%, and for B and C, zero, and a ratio for k_a to k_b of 2. The solution to this problem as seen on an oscilloscope (Fig. 6) duplicates the values calculated by Daniels and Alberty within the experimental error of reading the oscilloscope or its photographic reproduction.

A frequently encountered problem is the need for plotting concentration of starting material, intermediates, and products against a variable other than time like the percentage total reaction. For the lipid chemist the index may be iodine value or the average number of double bonds remaining per molecule. Figure 7 shows the circuit needed to display the composition of the reaction against the per cent of reaction; thus, for the hydrogenation of methyl linolenate the average number of double bonds remaining is three times the proportion of methyl linolenate plus two times the proportion of methyl linoleate plus one times the amount of methyl oleate. The sum of these products is calculated by the circuit of Figure 7. When the concentration function is impressed on the vertical input of the oscilloscope and when the average number of double bond function is impressed on the horizontal input, the curve in Figure 8 is obtained.

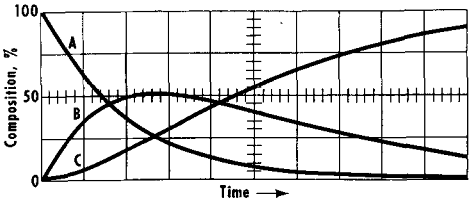


FIG. 6. Composition curve for the reaction $A \xrightarrow{k_a} B \xrightarrow{k_b} C$, where $k_a/k_b = 2$.

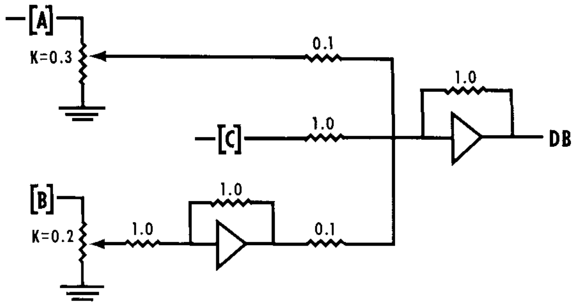


FIG. 7. Computer circuit for double-bond signal.

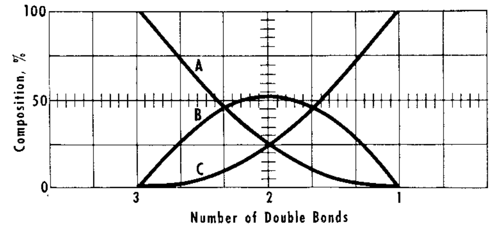


FIG. 8. Composition curve for the reaction $A \xrightarrow{k_a} B \xrightarrow{k_b} C$, where $k_a/k_b = 2$. A = linolenate, B = linoleate, C = oleate.

The oscilloscope is used for readout because of its speed and flexibility. Alternative and more accurate procedures of recording on multichannel recorders are useful if one can use the data plotted solely against time. A high-speed xy recorder with which multiple traces may be made with the same abscissa would appear to have distinct advantages in terms of accuracy and would permit plotting against an abscissa other than time.

Application to Problems of Hydrogenation

A procedure recently described (4) for evaluating hydrogenation catalysts by determining the ratio of hydrogenation rates for linolenate to linoleate involves consecutive reactions. Briefly, the method consists in reducing an equal mixture of linoleate and linolenate (2.5 average double bonds per molecule) with 0.5 mole of hydrogen to yield a partially hydrogenated mixture with 2.0 average double bonds per molecule. At this point the monounsaturated components formed must equal the diunsaturated components remaining. The ratio of reaction rate constants k_a/k_b is related to the percentage of monoene or triene component at this crossover point and is read off from the theoretically established curve. In terms of the analog computer, the initial conditions consisted of A = 50%, B = 50%, and C = zero. If the arrangement in Figure 5 is used with the percentage reaction calculated as indicated in Figure 7, the data shown in Figure 9 are obtained for $k_a/k_b = 2$. This problem is identical with that previously calculated with a digital computer and published as Figure 1 of reference 4.

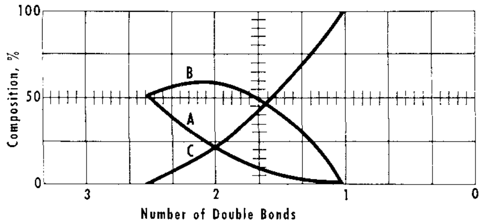


FIG. 9. Composition curve for the reaction $A \xrightarrow{k_a} B \xrightarrow{k_b} C$, where $k_a/k_b = 2$ with the initial conditions A = B= 50%. A = linolenate, B = linoleate, C = oleate.

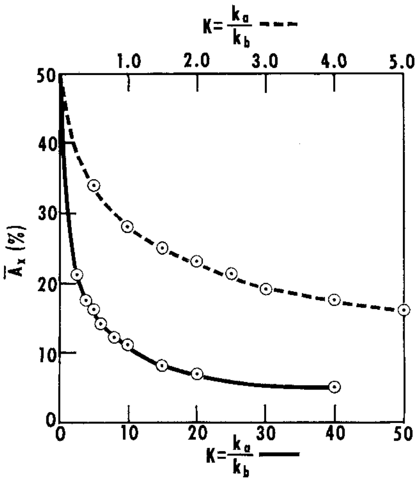


FIG. 10. The relationship of the ratio of reaction rates, K, to the amount of linolenate ($\bar{A}_x$) at the crossover point.

Establishment of the theoretical curve given in Figure 10 (Fig. 2 of reference 4) required the digital computer to make individual calculations corresponding to 33 different ratios of reaction rate constants for 11 time intervals of reaction, or 363 involved computations. After 33 plots corresponding to Figure 9 had been made and the crossover points determined graphically, they were plotted as the ordinate in Figure 10. While the digital computer calculation and plotting required several weeks of time to complete, it was repeated in 2 hr with an analog computer.

Reduction of linolenic acid with hydrazine has aroused much industrial interest. This reaction may be represented by an extension of the kinetic scheme:

$$\underset{\text{(Le)}}{A} \xrightarrow{k_a} \underset{\text{(Diene)}}{B} \xrightarrow{k_b} \underset{\text{(Monoene)}}{C} \xrightarrow{k_c} \underset{\text{(S)}}{D}$$

In this reduction, which follows first order kinetics, k_a was estimated by a least squares calculation, and k_b, from the crossover point for linolenate and monoene; k_c was taken as being half of k_b. The values found for $k_a{:}k_b{:}k_c$ were 3.46:2:1. The calculation of the

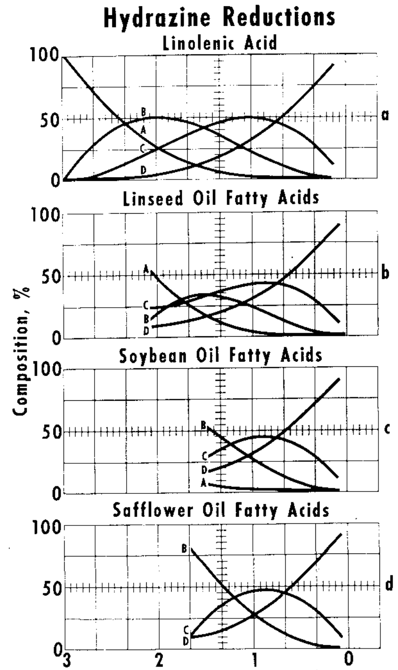


FIG. 11. Composite curve for the reaction $A \xrightarrow{k_a} B \xrightarrow{k_b} C \xrightarrow{k_c} D$, where $k_a{:}k_b{:}k_c = 3.41{:}2.0{:}1$. A = linolenic acid, B = linoleic acid, C = oleic acid, D = stearic acid.

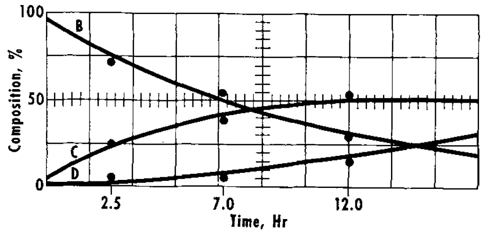


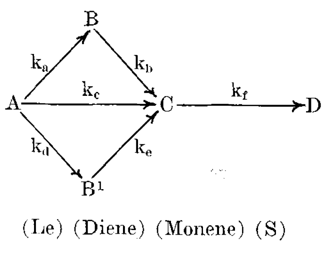
FIG. 12. Prediction of end point for hydrazine reduction of 95% linoleic acid (B) and 5% oleic acid (C). D = stearic acid.

theoretical curves for comparison with experimental data required 3–4 hr (7). In contrast, the same curves can be duplicated with an analog computer in 10 sec (Fig. 11a). The time course of the reactions shows immediately the maximum of any desired component that may be formed and indicates the optimal point for stopping the reaction so as to isolate the desired component.

In making industrial chemicals, composition of starting materials varies. For example, in the production of C_9, C_{12}, and C_{15} dibasic acids by hydrazine reduction and oxidative cleavage (5), instead of 100% linolenic acid (Fig. 11a), linseed oil fatty acids (Fig. 11b), soybean oil fatty acids (Fig. 11c), and safflower fatty acids (Fig. 11d) might be used. Starting with such varying fatty acid compositions one may see what the composition will be for various reaction periods. Once the coefficient potentiometers corresponding to k_a, k_b, and k_c have been set according to measured values for the rate constants, only the initial conditions (starting composition) need be inserted in order to reproduce the curves in Figure 11. This determination is accomplished with great ease and rapidity, but is an impressive task by arithmetical procedures.

Another problem frequently encountered is predicting the time of reaction to give one an optimal composition. An analog computation can be carried out with great rapidity; also, during the course of a reaction it can be used to predict when the reaction should be stopped; e.g.: a mixture of 95% linoleic acid and 5% oleic acid was reduced with hydrazine. The kinetics of the reaction corresponding to the initial conditions were run on the computer with an extended time-base. The composition of the reaction mixture for a sample removed at 2½ hr matched that predicted by the computer at 1.45 divisions. Thus 0.58 division on the computer scale equalled 1 hr and the desired optimal composition would be reached at 12 hr. Data points corresponding to the analysis at 2½ hr and at 12 hr together with a verifying sample removed at 7 hr, are compared with the calculated curve in Figure 12.

Complex reaction kinetic patterns involving secondary reactions and the like are frequently encountered. Bailey was first to point out that the kinetics of heterogeneous catalytic hydrogenation required not only the postulation of isolinoleate but also a direct linolenate to oleate conversion (2). In this scheme not only must the relative reaction rate constants be considered but the proportion of the linolenate going by the various pathways must be taken into account. The matching of experimental and theoretical data calculated arithmetically is an extremely laborious and time-consuming operation. When carried out by the method of successive approximation with an analog computer, the operation is easy and rapid. The potentiometers corresponding to the rate constants may be readily varied and adjusted. A new kinetic pattern is presented every 10 sec. The process of matching experimental and theoretical data by trial and error is greatly facilitated. Albright and Wisniak (1) have reported using an analog computer to solve a reaction scheme similar to Bailey's.



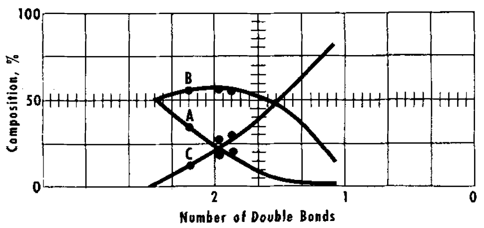


FIG. 13. Catalytic hydrogenation of 50% linolenate (A) and 50% linoleate (B). C = oleate.

When radioactively labeled intermediates are used to follow a complex reaction system, such as described and when they are analyzed by gas chromatography monitored for radioactivity, valuable data are obtained (7). However, all nine amplifiers of the present analog computer were employed in producing the curves in Figure 13. Thus the reaction rate does not involve radioactive intermediates. Simulations for both inactive and radioactive-labeled intermediates cannot be presented in a concerted calculation. Presently the specific reaction rate constants are calculated from the analyses for inactive fatty acids, and the constants are subsequently verified by testing them for the exactness of fit with the radioactive data. To perform the single concerted calculation six more amplifiers would be required.

Discussion

Analog computer techniques facilitate the empirical methods of trial and error, successive approximation, and curve matching. These techniques also allow one to predict the composition of the reaction mixture as a function of reaction time for a wide variety of starting materials.

From the applications presented, it is apparent that the ease, rapidity, and flexibility of analog procedures recommend this type of computation to basic and developmental research with lipids. Although a 9-amplifier unit gives much valuable information, the more complex kinetic problems recently encountered would require increased numbers of components with increased precision.

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