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A METHOD FOR COMPUTER ANALYSIS OF
THE FORMATION CURVE OF A TRANSIENT,
WHERE CONCURRENT REACTIONS
CAUSE CONSUMPTION OF THE TRANSIENT

by

Myran C. Sauer, Jr.

RELEASED FOR ANNOUNCEMENT
IN NUCLEAR SCIENCE ABSTRACTS

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ABSTRACT

A method is presented for the computer analysis of data on the concentration of B vs time where the reactions occurring are

The analysis yields a value for $k_1 + k_5$.

INTRODUCTION

In a previous report,¹ a method for the automatic reading and analysis of oscilloscope pictures representing concentrations of chemical species as a function of time for fast chemical reactions has been described. The process described here makes use of the same curve-reading method, but the analysis of a kinetically more complex transient curve is described. The process involves the use of a method of successive approximations to construct a hypothetical curve for which complicating side reactions have been eliminated.

¹M. C. Sauer, Jr., ANL-7113.

The method described is illustrative of the usefulness of computers and automatic data-handling techniques in the analysis of a typical type of data on chemical kinetics of fast reactions. The data are obtained from a chemical system where the analysis is complex, due to a variety of competing reactions, and can therefore be handled best by computer techniques.

DEFINITIONS OF SYMBOLS

$[X]$ $\equiv$ concentration of X (moles liter⁻¹)

$X \equiv [X] \epsilon_B \ell$ (dimensionless)

$B \equiv$ optical density of the species B, defined by $B = \log I_0/I_{tr} = \epsilon_B[B] \ell$

$\epsilon_B \equiv$ decadic molar extinction coefficient of the species B (moles⁻¹ liter cm⁻¹)

$\ell \equiv$ optical path length (cm)

$I_0 \equiv$ initial light intensity (arbitrary units)

$I_{tr} \equiv$ transmitted light intensity (same units as I_0).

$t \equiv$ time (sec)

$k_X \equiv$ rate constant for reaction (X) (in units of moles⁻¹ liter sec⁻¹ where the reaction is written as a bimolecular reaction, or in units of sec⁻¹ where the reaction is written as a unimolecular reaction). k_2 , for example, is defined in the usual manner of chemical kinetics, by either of the differential equations describing reaction 2,

$$\frac{d[BB]}{dt} = k_2[B]^2 \text{ or } \frac{d[B]}{dt} = -2k_2[B]^2$$

$F_3 \equiv k_3/2k_2$ (dimensionless)

$F_4 \equiv k_4/k_2$ (dimensionless)

$F_5 \equiv 1 + (k_5/k_1)$ (dimensionless)

$S \equiv$ slope of $1/B$ vs t plot of the last part of the transient curve (sec⁻¹)

$M \equiv$ moles liter⁻¹.

DESCRIPTION OF THE REACTIONS INVOLVED

Although the method to be presented was developed to analyze data from pulse radiolysis experiments with a particular chemical system, it is applicable to any system which has the characteristics set forth below.

The observed transient B, represented by curve c in Fig. 1, is produced in a first-order (or pseudo-first-order) reaction from transient A:

An important requirement is that after the beginning of curve c (or, alternatively, after the point on curve c where we begin the analysis), the species A is not produced by any reaction.

Fig. 1. Oscilloscope Trace Representing Data on $[B]$ vs t

If (1) were the only reaction involving A and B, the analysis of the curve for k_1 could be carried out exactly the same as has been previously described.¹ However, consider the situation in which reactions (2), (3), and (4) are important:

The possibility that A reacts to form another species, C, which does not contribute (directly) to the transient curve representing B is also included in the additional reactions

The actual species in reactions (1)-(8) corresponding to the particular chemical system represented by Fig. 1 are:

A $\equiv$ atomic hydrogen;

B $\equiv$ the radical observed by its optical absorption (see Fig. 1), produced in a pseudo-first-order reaction of hydrogen atoms with toluene;*

C $\equiv$ other radicals, produced in pseudo-first-order reactions of hydrogen atoms with toluene.

BB, BA, AA, CA, CB, and CC represent the products of the reactions between these species.

The analytical method to be described yields a value of $k_1 + k_5$.

MATHEMATICAL DESCRIPTION OF THE METHOD USED TO OBTAIN THE VALUE OF $k_1 + k_5$

I. Requirement Concerning the Curve to be Analyzed

The method described in the following requires that for the part of the transient curve c designated by Z in Fig. 1, reactions (1), (3), (4), (5), and (6) are negligible in comparison to (2), (7), and (8); in other words, the concentration of A is effectively zero. If this requirement is satisfied, curve c can be corrected to yield a hypothetical curve which reaches a "plateau," and the analysis of this hypothetical curve is the same as has been described in a previous report.¹

This requirement places limitations on the size of $k_2[B]$, $k_3[A]$, $k_3[B]$, and $k_4[A]$, compared to $k_1 + k_5$. No investigation has been made of how large the ratios of the former quantities to $k_1 + k_5$ can be, since the experimental curves were all such that $k_2[B]$, $k_3[A]$, $k_3[B]$, and $k_4[A]$ were less than about 30% of $k_1 + k_5$. In general, the method is expected to be more dependable the smaller the former quantities are compared to $k_1 + k_5$, especially in view of the fact that for most systems, the rate constants of reactions (3), (4), and (6)-(8) are not known relative to (2), and assumptions have to be made, as described in the next two sections.

*The toluene concentration was $1.1 \times 10^{-3}M$.

II. Assumptions Concerning the Values of Rate Constant

It is assumed that reactions between the products of reactions (1) and (5) are such that

$$2k_2 = k_7 = 2k_8,$$

i.e., the three reactions have equal rate constants except for the statistical factor of 2. The analogous assumption is made that $k_3 = k_6$.

III. Quantities Which Are Treated as Variable Input Parameters in the Method of Computation

Values for k_3 and k_4 must be known or assumed. The program allows for the use of as many sets of these constants as desired, in order to test the dependence of the final results on these values.

IV. Use of the Data from Fig. 1

The curves of Fig. 1 represent light intensities; a is 100% and b is 0% on a scale with an amplification factor of unity. Hence, the difference between a and b is I_0 , the initial light intensity. d corresponds to 100% light at an amplification of AMP (AMP is 10.0 in the case of Fig. 1). Curve c represents the change in light intensity produced when the transient is formed following the electron pulse. We define the following:

$$I_0 \equiv y_a - y_b,$$

where y_a and y_b are the average y-coordinates of curves a and b, and

$$I_{abs} = (y_d - y_c)/AMP,$$

where y_d is the average y-coordinate of curve d, and y_c is the y-coordinate of any point on curve c. The quantities I_0 and I_{abs} , which are directly measurable from the curves, are related to the concentration of the transient, $[B]$, by the following:

$$\log \left(\frac{I_0}{I_0 - I_{abs}} \right) = \epsilon_B [B] \ell,$$

where ϵ_B is the decadic molar extinction coefficient (in $M^{-1} \text{ cm}^{-1}$) of the transient B, and ℓ is the optical path length (in cm). (The light intensity corresponding to curve d is assumed to correspond to $[B] = 0$.) The left-hand side of this equation is defined as B, the optical density:

$$B = \epsilon_B [B] \ell. \quad (I)$$

Fig. 2. Simplified Representation of B vs t Values Obtained from Fig. 1, and a Pictorial Representation of Some Defined Quantities

think of the data existing in the form of Fig. 2, where B vs t has been plotted. For clarity, the number of points shown is much smaller than that actually taken from a typical curve.

V. Use of the B vs t Data Corresponding to the Time Range Z of Fig. 2

On the part of the B vs t curve in Fig. 2 designated by Z, it is required that the only reactions taking place are, as has already been explained, (2), (7), and (8). The rate of disappearance of B is therefore given by

$$\frac{d[B]}{dt} = -2k_2[B]^2 - k_7[B][C].$$

However, by use of the assumptions listed in Section II,

$$[C] = (k_5/k_1)[B]. \quad (\text{II})$$

This can be shown as follows: At any time on a curve of [B] vs t, we have the following description of processes consuming B and C:

$$\frac{d[B]}{dt} = -2k_2[B]^2 - k_7[B][C] - k_3[B][A] \quad (\text{III})$$

and

$$\frac{d[C]}{dt} = -2k_8[C]^2 - k_7[B][C] - k_6[C][A].$$

Since ϵ_B is often not known, the following treatment will be written, showing how the desired rate constants may be obtained without knowing ϵ_B .

The raw experimental data from Fig. 1 are converted, by means of the automatic curve-reading method previously described,¹ to a set of values of B vs time t. For convenience, the first point on the transient curve is taken to be zero time. For the purposes of the following mathematical analysis of the data, it is convenient to

Using the assumptions mentioned, we find that

$$\frac{d[B]}{[B]} = \frac{d[C]}{[C]},$$

which means that the fractional decreases in $[B]$ and $[C]$ during a given time interval dt are equal. Therefore, since B and C are formed in first-order reactions from the same precursor, the formation rate constants k_1 and k_5 govern the ratio of $[B]$ to $[C]$, as stated in equation (II). Therefore we have

$$\frac{d[B]}{dt} = -2k_2[D]^2 - k_7[B]^2 \frac{k_5}{k_1}. \quad (IV)$$

As has been stated, the actual concentration of B is not known unless ϵ_B is known; therefore, we rewrite (IV) as

$$\frac{dB}{dt} = -\frac{2k_2}{\epsilon_B \ell} B^2 - \frac{k_7 k_5 B^2}{k_1 \epsilon_B \ell}.$$

Furthermore, since $2k_2 = k_7$ (see Section II), we have

$$\frac{dB}{dt} = \frac{-2k_2 B^2}{\epsilon_B \ell} \left[1 + \frac{k_5}{k_1} \right]. \quad (V)$$

By integrating (V), we find that a plot of $1/B$ vs t should yield a straight line with a slope, S , of

$$S = \frac{2k_2}{\epsilon_B \ell} \left[1 + \frac{k_5}{k_1} \right]. \quad (VI)$$

The value of S , thus obtained from the experimental curve, can be used directly to correct the last part of the experimental curve to a plateau, i.e., a constant value of optical density corrected for decay of B by reactions (2) and (7). However, as will be shown in the next section, corrections for the other reactions are also necessary to obtain a meaningful hypothetical curve.

VI. Method of Obtaining the Hypothetical Curve of B vs t , and the Value of $k_1 + k_5$

For convenience, the quantity $[1 + (k_5/k_1)]$ is called F_5 , and as will be described later, the following calculations are independent for the value of F_5 , i.e., the value obtained for $k_1 + k_5$ does not depend on F_5 .

As has been described in Section III, k_3 and k_4 are considered as variable parameters, and are varied by using different values of F_3 and F_4 in the following equations:

$$\frac{k_3}{\epsilon_B \ell} = F_3 \frac{2k_2}{\epsilon_B \ell} = \frac{F_3 S}{F_5};$$

$$\frac{k_4}{\epsilon_B \ell} = F_4 \frac{k_2}{\epsilon_B \ell} = \frac{F_4 S}{2F_5},$$

and also, since $k_6 = k_3$ (see Section II),

$$\frac{k_6}{\epsilon_B \ell} = F_3 \frac{2k_2}{\epsilon_B \ell} = \frac{F_3 S}{F_5};$$

The experimental data of Fig. 1 yield an array of points, of which Fig. 2 is a representation with the number of points greatly reduced, representing optical density vs time. This array is B_n, t_n , where n assumes integer values from unity to n_{tot} , and n_{tot} is the total number of points in the array.

The first step carried out is the calculation of a corrected array of B_n , where the amount of B which has disappeared by reactions (2), (3), and (7) from t_1 (time zero) to time t_n is added to B_n . The basic equation for this correction is (III), which, using the assumptions in Section II and the definitions already stated, may be written as

$$\frac{dB}{dt} = -SB^2 - F_3 \frac{S}{F_5} B[A] \epsilon_B \ell.$$

$[A] \epsilon_B \ell$ is the concentration of A in a dimensionless form, and we will define $A \equiv [A] \epsilon_B \ell$. Likewise,

$$C \equiv [C] \epsilon_B \ell.$$

Therefore,

$$\frac{dB}{dt} = -SB^2 - F_3 \frac{S}{F_5} BA. \quad (\text{VII})$$

Since the data array B_n, t_n consists of many closely spaced points, the integration of (VII) is carried out numerically as follows:

$$\Delta B_1 = 0$$

and

$$\Delta B_{n+1} = S \sum_{i=1}^{i=n} B_{av,i}^2 \Delta t_i + F_3 \frac{S}{F_5} \sum_{i=1}^{i=n} B_{av,i} A_{av,i} \Delta t_i, \quad (\text{VIII})$$

where $n \geq 1$, and where $\Delta B_n \equiv$ the amount to be added to B_n to correct for B which reacts by (2), (3), and (7), and

$$B_{av,i} = (B_{i+1} + B_i)/2; \quad A_{av,i} = (A_{i+1} + A_i)/2; \quad \Delta t_i = t_{i+1} - t_i.$$

These definitions are used throughout the following calculations. The definitions of $B_{av,i}$ and Δt_i are shown also in Fig. 2.

In order to calculate ΔB_n , a set of values A_n , t_n corresponding to B_n , t_n must be used. A_n is not known, so a method of successive approximations is used to arrive at the best set of A_n and ΔB_n . As the first approximation,

$$A_n = (B_{\max} - B_n) F_5, \text{ for } n < \text{the value of } n \text{ for } B_{\max}$$

and

$$A_n = 0, \text{ for } n \geq \text{the value of } n \text{ for } B_{\max}.$$

Values of ΔB_n are then calculated from (VIII), and a corrected set of B_n , i.e., $B_{\text{cor},n}$ is calculated from

$$B_{\text{cor},n} = B_n + \Delta B_n. \quad (\text{IX})$$

The values of $B_{\text{cor},n}$ will reach a good plateau (i.e., a constant value) even on this first approximation because the first term in (VII) or (VIII) is responsible for the correction of the last part of the curve (where we have assumed that the concentration of A will be negligible), and this first term involves no approximations. Therefore, the average value of $B_{\text{cor},n}$ is determined for points on this plateau, and is called $B_{\text{cor,plateau}}$.

Now, using the value of $B_{\text{cor,plateau}}$, the array of $B_{\text{cor},n}$ (the original array of B_n) and the values of A_n (a new set of values of A_n) is determined as follows:

$$A_n = F_5(B_{\text{cor,plateau}} - B_{\text{cor},n}) + X_n + Y_n + Z_n. \quad (\text{X})$$

The first term, $F_5(B_{\text{cor,plateau}} - B_{\text{cor},n})$, represents the concentration A_n which must necessarily be present at t_n to produce enough B in order that the plateau value of B_{cor} is reached. [The factor F_5 is necessary to account for the A which reacts by reaction (5).] The terms X_n , Y_n , and Z_n are

corrections which are necessary for reaction of A by (3), (4), and (6), respectively, and are given by the following equations:

$$X_n = F_3 \frac{S}{F_5} \sum_{i=n}^{i=ntot-1} B_{av,i} A_{av,i} \Delta t_i;$$

$$Y_n = F_4 \frac{S}{F_5} \sum_{i=n}^{i=ntot-1} G A_{av,i}^2 \Delta t_i,$$

where $G = 1$ if $A_{av,i} > 0$ and $G = -1$ if $A_{av,i} < 0$; and

$$Z_n = F_3 \frac{S}{F_5} (F_5 - 1) \sum_{i=n}^{i=ntot-1} B_{av,i} A_{av,i} \Delta t_i.$$

X_n , for example, represents the amount of A which reacts with B between time t_n and the final point on the plateau, t_{ntot} . Note that because of the nature of equation (IX), A_n could have negative values for points near the plateau which, because of "noise" in the data, have $B_{cor,n} > B_{cor,plateau}$. For this reason, Y_n has a factor G which is +1 except when $A_{av,i}$ is negative; then it is -1. This is necessary, for otherwise all terms in Y_n would be positive, regardless of the sign of $A_{av,i}$.

The new set of A_n obtained from (X) are used in (VIII) and (IX) to obtain a new set of $B_{cor,n}$. This cycle is continued until the values of $B_{cor,n}$ for two successive approximations agree within some preset limit. In this process, the values of A_n are also determined, and correspond to the actual concentrations of A at times t_n . The values of $B_{cor,n}$, on the other hand, represent the observed values of optical density, B_n , corrected by adding B which has disappeared by reactions with B, A, or C. These values of $B_{cor,n}$ are not, however, the desired final values which would result from the absence of reactions (2)-(4) and (6)-(8), because, although the B which disappears by these reactions has been corrected for, the correction due to the A which disappears by reactions (3), (4), and (6) [which would otherwise react by (1) or (5)] has not been made. This second (and final) step in the correction method is described next.

A value of $k_1 + k_5$ is obtained by plotting

$$\log_e \left(\frac{B_{cor,plateau} - B_{cor,n}}{B_{cor,plateau}} \right) \quad (XI)$$

vs t_n , using the last set of $B_{cor,n}$ values determined above. This plot should yield a straight line whose slope is approximately equal to $k_1 + k_5$, the degree

of approximation depending on the size of the correction still to be made in $B_{\text{cor},n}$. This value of $k_1 + k_5$ is used to calculate new values of $B_{\text{cor},n}$ by adding to the previous values of $B_{\text{cor},n}$ the amount of B which would be formed if the A which reacts by (3), (4), and (6) reacted instead by reactions (1) and (5). Thus, each $B_{\text{cor},n}$ is corrected by addition of $\Delta B_{\text{cor},n}$, i.e.,

$$(\text{new}) B_{\text{cor},n} = (\text{old}) B_{\text{cor},n} + \Delta B_{\text{cor},n} \quad (\text{XII})$$

These corrections, $\Delta B_{\text{cor},n}$, are calculated as follows: Let A'_n be the total amount of A which has reacted by (3), (4), and (6) from t_1 through t_n , minus the additional amount of A which would have reacted from t_1 through t_n by reactions (1) and (5) if reactions (3), (4), and (6) did not occur. Also, let A''_n be the amount of A which reacts by (3), (4), and (6) between t_{n-1} and t_n :

$$\begin{aligned} A''_{i+1} &= (F_3 S / F_5) B_{\text{av},i} A_{\text{av},i} \Delta t_i \\ &+ (F_4 S / F_5) G A_{\text{av},i}^2 \Delta t_i (F_3 S / F_5) (F_5 - 1) B_{\text{av},i} A_{\text{av},i} \Delta t_i. \end{aligned} \quad (\text{XIII})$$

Now, $A'_1 = 0$, and, for $n \geq 1$,

$$A'_{n+1} = \sum_{i=1}^{i=n} A''_{i+1} - (k_1 + k_5) \left\{ \sum_{i=1}^{i=n} A'_i \Delta t_i + \frac{1}{2} \sum_{i=1}^{i=n} A''_{i+1} \Delta t_i \right\}. \quad (\text{XIV})$$

The negative term in the latter expression accounts for the A which reacts by (1) and (5). However, $\Delta B_{\text{cor},n}$ is related to only the A which reacts by (1). Since $k_1 = (k_1 + k_5) / F_5$, we have

$$\Delta B_{\text{cor},n+1} = \frac{k_1 + k_5}{F_5} \left\{ \sum_{i=1}^{i=n} A'_i \Delta t_i + \frac{1}{2} \sum_{i=1}^{i=n} A''_{i+1} \Delta t_i \right\}. \quad (\text{XV})$$

By this method, a set of $\Delta B_{\text{cor},n}$ is determined, and by means of (XII) a new set of $B_{\text{cor},n}$ is calculated, from which a better value of $k_1 + k_5$ is determined by plotting the data according to (XI). The cycle is repeated, using the newest value of $k_1 + k_5$ in (XIV) and (XV), until two successive values of $k_1 + k_5$ agree within some preset limit.

We have obtained, then, the set of hypothetical optical densities, $B_{\text{cor},n}$, where the experimental data has been completely corrected for all reactions of A other than (1) and (5). In this case, it can be easily shown that a plot of the data according to (XI) should yield a linear plot with a slope of exactly $k_1 + k_5$.

The following section includes a discussion of the effect of variation of the input parameters F_3 and F_4 on the value of $k_1 + k_5$ obtained in the analysis of a typical experimental curve. Although the reason is not immediately

obvious, the value of F_5 has no effect on the value obtained for $k_1 + k_5$. This may be seen by a detailed examination of the equations, beginning with (VII), in which F_5 occurs, and is essentially due to the fact that as F_5 is increased, $2k_2/\epsilon_B l$ decreases since $2k_2/\epsilon_B l = S/F_5$ [see equation (VI)]. A larger value of F_5 therefore causes us to use smaller values of k_3 , k_4 , etc., since the rate constants are taken to be some factor times $2k_2/\epsilon_B l$. Therefore, although a larger value of F_5 will lead to higher calculated values of A_n , the fact that the rate constants used are smaller exactly counterbalances the higher concentration of A.

Therefore, the analysis described here yields no information on the actual value of F_5 , and it is impossible to obtain an estimate of F_5 from a kinetic analysis of such curves. However, the value obtained for $k_1 + k_5$ is not affected by this fact.

VII. Discussion of the Dependence of the Result for $k_1 + k_5$ on the Values of F_3 and F_4

In this section the results of the analysis of the data represented by Fig. 1 are presented. Figure 3 is a plot of $1/B$ vs t for the part of curve c of Fig. 1 designated by Z. From the slope of the least-squares straight line, the value of S is obtained.*

The curve made up of X's in Fig. 4 shows the data of B vs t as determined from Fig. 1, and the curve made of O's shows the hypothetical B vs t curve calculated using $F_3 = F_4 = 0$. Figure 5 is a plot of the latter according to (XI). Figures 6 and 7 are the same as Figs. 4 and 5 except that $F_3 = 3$ and $F_4 = 3$. The slopes of the least-squares lines drawn through the points of Figs. 5 and 7 are $1.34 \times 10^5 \text{ sec}^{-1}$ and $1.28 \times 10^5 \text{ sec}^{-1}$, respectively. One can see that the slope changes only slightly in this case, but often the change was larger. The problem which arises in determining the best value of $k_1 + k_5$ is how to decide upon the best values of F_3 and F_4 . If data on this are not available from the literature, one can examine the plots, such as Figs. 5 and 7, and try to determine whether better linearity results from certain values of F_3 and F_4 . For the particular system investigated here, sometimes there was not much change in the linearity of the resulting plots as F_3 and F_4 were changed from 0 to 3, but often a slightly better linearity resulted from F_3 and F_4 values of unity or less (compare Figs. 5 and 7). Such values of F_3 and F_4 are also more reasonable on the basis of the nature of the reactions involved. Therefore, the value of $k_1 + k_5$ from Fig. 5 is preferred in this example.**

In order to determine how sensitive plots such as those in Figs. 5 and 7 are to the value of F_3 and F_4 used, and at the same time, to test the

*Figures 3-11 are reproductions of graphs made completely automatically, as explained in Ref. 1.

**Since the toluene concentration was $1.1 \times 10^{-3} \text{ M}$, the bimolecular rate constant corresponding to $k_1 + k_5$ is $1.2 \times 10^8 \text{ M}^{-1} \text{ sec}^{-1}$.

Fig. 3. $1/B$ vs t Plot for Time Range Z of Fig. 1

Fig. 4. X - B vs t, Determined from Fig. 1 and O - Corrected Curve of B vs t Using $F_3 = F_4 = 0$

Fig. 5. First-order Formation Plot, According to Equation (XI), of the $\odot$ Curve of Fig. 4

Fig. 6. X - B vs t, Determined from Fig. 1 and O - Corrected Curve of B vs t Using $F_3 = F_4 = 3$

Fig. 7. First-order Formation Plot, According to Equation (XI), of the $\odot$ Curve of Fig. 6

accuracy of the method as a whole, a set of data was generated from the differential equations describing the reactions. Values of F_3 and F_4 of unity were used, as well as $k_1 = k_5 = 0.6 \times 10^5 \text{ sec}^{-1}$ and $k_2/\epsilon_B l = 0.75 \times 10^5 \text{ sec}^{-1}$. (The other rate constants involved were given values according to Section II.)

Figure 8 shows the second-order plot of the resulting data (using the last 50% of the generated points after maximum optical density). The value of the slope is $2.99 \times 10^5 \text{ sec}^{-1}$, compared to the value of $3.00 \times 10^5 \text{ sec}^{-1}$ which should have resulted [see equation (VI)]. Figure 9 shows the "generated" curve (X's) and the corrected curve (O's) using $F_3 = F_4 = 1$, and Fig. 10 shows the resulting first-order growth plot, of which the slope is $1.23 \times 10^5 \text{ sec}^{-1}$ (the value of $k_1 + k_5$), compared to the value of $1.20 \times 10^5 \text{ sec}^{-1}$ which was used to generate the data. (The difference is probably due to the fact that both the analysis and the generation of the data were done by using a finite set of points rather than a continuous function.) Figure 11 shows the generated curve again, and the corrected curve using values for F_3 and F_4 of 3 (remembering that $F_3 = F_4 = 1$ was used to generate the curve), and Fig. 12 is the resulting first-order growth plot. One can see that the linearity is not nearly as good as in Fig. 10, and the slope obtained is $1.09 \times 10^5 \text{ sec}^{-1}$ (compared to the "true" value of $k_1 + k_5$ of 1.20×10^5).

Of course, the actual experimental curves have more noise, and deviation from linearity such as that in Fig. 12 is therefore more difficult to notice. However, the above serves the purpose of testing the computer program and gives a good indication of the effects to be expected if the wrong values of F_3 and F_4 are used.

Fig. 8. $1/B$ vs t Plot for "Generated" Data

Fig. 9. X - Generated Curve and O - Corrected Curve Using $F_3 = F_4 = 1$

Fig. 10. First-order Formation Plot, According to Equation (XI), of the $\odot$ Curve of Fig. 9

Fig. 11. X - Generated Curve and O - Corrected Curve Using $F_3 = F_4 = 3$

Fig. 12. First-order Formation Plot, According to Equation (XI), of the $\odot$ Curve of Fig. 11