A Study of Consecutive Competitive Reaction Systems

M. H. FRIEDMAN and R. R. WHITE

The University of Michigan, Ann Arbor, Michigan

Experimental kinetic data are most conveniently correlated by the integrated form of the differential rate equations which the reactions are presumed to obey. A new method of obtaining an approximate integral solution of the differential equations is described and applied to a set of three consecutive competitive reactions.

The approximate integral solution is used to correlate experimental data on systems whose stoichiometry would indicate a consecutive competitive mechanism. The compositions of the reaction mixes are predicted with a standard error of estimate of less than 4% of the original concentration of the initiating reactant, in most cases less than 2%. The estimates of the rate constants, found by fitting the approximate solution to the data, are within experimental error of the values obtained by differentiation of the published results.

Consider a set of irreversible consecutive reactions carried out at constant temperature

$$A + B \xrightarrow{k_1} P_1 + \ldots \qquad (1)$$

$$P_1 + B \xrightarrow{k_2} P_2 + \ldots$$

etc.
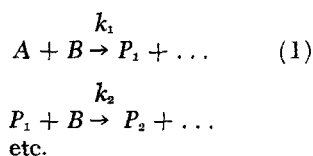
The differential equations governing the course of the reaction set are

$$\frac{d[A]}{dt} = -k_1[A][B] \qquad (2a)$$

$$\frac{d[P_i]}{dt} = k_i[P_{i-1}][B]$$
$$\qquad - k_{i+1}[P_i][B] \quad (k_l = 0, \; l > j) \qquad (2b)$$

$$\frac{d[B]}{dt} = -[B] \sum_{i=0}^{j-1} k_{i+1}[P_i] \qquad (2c)$$

Because many addition, substitution, and polymerization reactions are stoichiometrically characterized by Equation (1) an integrated solution of Equations (2) is desirable. In the discussion to follow it will be assumed that only A and B are originally present and that the density of the system does not change as the reaction proceeds.

To date the equations above have not been solved for the general case of any initial composition and any set of rate constants. In fact no solution has been reached for the simpler case in which only A and B are originally present. The equations have been solved for certain initial molar ratios and for particular sets of rate constants (7, 27), but these solutions can-

not be extended to more complex cases. Approximate solutions have been obtained (12, 13, 17, 28) for the special case in which the initial concentrations of A and B are the same. Experimental data have been used (5, 21, 24, 29, 30) to determine the individual rate constants for consecutive competitive reaction systems. By suitable treatment of the differential equations Fuoss (8), Natta and Mantica (18), and others (1, 4, 11, 15, 22, 23, 25, 26) have derived formulas which describe the distribution of converted A among the products as a function of the rate constants. Product distribution studies for similar but more complex reaction systems have also been reported (2, 3, 9). Thus, given the rate constants for the reaction set, if the quantity of A in the reaction mix could be computed, product distribution studies could then be used to predict the entire composition of the reaction mix at any time, for any set of initial conditions. Once this can be done, practical problems involving systems of consecutive competitive reactions can be solved. It will be possible to correlate the large body of experimental data on systems whose stoichiometry obeys Equation (1) to see whether the mechanism of the reactions is well represented by the differential rate equations and to find rate constants for the twin purposes of extrapolation and design. Hence the first purpose of this paper is the development of equations describing the time dependence of the concentration of A.

APPROXIMATE SOLUTION OF THE RATE EQUATIONS

Each consecutive competitive reaction system is a member of one of two classes. The first, exemplified by the

saponification of diesters, contains those reactions in which the reactant A has a few reacting groups which are changed to an unreactive form by addition of, or substitution with, B. The second class contains addition reactions, such as the reactions between ethylene oxide and the ethanolamines. Typical addition polymerizations are special cases of a consecutive competitive reaction set of this second class. A survey of the literature revealed no complete experimental data for systems of more than three reactions, so k_4 was taken to be zero in the study to follow.

Numerical Integration

Equations (2) were numerically integrated for a wide range of values of the rate constants. In order that the results might be applied to a wide variety of systems the equations were first put into dimensionless form. Define

$$y_0 = \frac{[A]}{[A]_o} \qquad (3)$$

$$t' = k_1[A]_o t \qquad (4)$$

$$\beta = \frac{[B]}{[A]_o} \qquad (5)$$

$$y_i = \frac{[P_i]}{[A]_o} \qquad (6)$$

and

$$K_i = \frac{k_i}{k_1} \qquad (7)$$

Equations (2) then become

$$-\frac{dy_0}{dt'} = y_0\beta \qquad (8a)$$

$$-\frac{dy_i}{dt'} = K_{i+1}y_i\beta - K_i y_{i-1}\beta \qquad (8b)$$

$$-\frac{d\beta}{dt'} = \beta \sum_{i=0}^{2} K_{i+1}y_i \qquad (8c)$$

An LM10 analogue computer was used for preliminary studies of the solution of the differential equations above. The results obtained on the analogue computer were confirmed,

M. H. Friedman is with the Minnesota Mining and Manufacturing Company, St. Paul, Minnesota. R. R. White is with the Atlantic Refining Company, Philadelphia, Pennsylvania.

and numerical solutions were obtained on an IBM-650 data processing machine. A Runge-Kutta subroutine was used for the numerical integration. It was assumed that equimolar amounts of A and B were initially present and that the original mix contained none of the reaction products. As will be shown below, the results of this integration can be used to predict the course of reaction for any initial molar ratio of A to B.

Form of the Approximate Solution

When no P_i is present at the start of reaction, y_0 is a function of only β_o, t', and the $\{K_i\}$. The equations giving the $\{y_i\}$ as functions of y_0 and the $\{K_i\}$ are

$$y_1 = \frac{y_0 - y_0^{K_2}}{K_2 - 1} \qquad (9a)$$

$$y_2 = \frac{K_2^2 y_0 - K_2 K_3 y_0 + K_3 K_2 y_0^{K_2} - K_2 y_0^{K_2}}{(1 - K_3)(1 - K_2)(K_2 - K_3)}$$
$$+ \frac{K_2 y_0^{K_3}}{(K_3 - 1)(K_3 - K_2)} \qquad (9b)$$

$$y_3 = 1 - y_0 - y_1 - y_2 \qquad (9c)$$

For the range of parameters studied here there are two useful correlation schemes, one applicable when K_2 is small and one for large values of this ratio.

When K_2 is small, the time dependence of y_0 may safely be approximated by neglecting the second reaction; the concentration of higher products are found from Equations (9). For small K_2 and $\beta_n \neq 1$

$$y_0 = \frac{(\beta_o - 1)\exp[t'(1 - \beta_o)]}{\beta_o - \exp[t'(1 - \beta_o)]} \qquad (10a)$$

When $\beta_o = 1$

$$y_0 = \frac{1}{t' + 1} \qquad (10b)$$

Deviations from material balance accuracy will be minor, as little P_2 and P_3 is formed. Equations (10) are simply the solutions of the rate equations for a single second-order reaction. The bulk of this paper will consider consecutive reaction sets in which the second reaction cannot be neglected.

To begin the search for an approximate solution of the rate equations when K_2 is large, define the rate of disappearance of P_i by

$$r_i = -\frac{dy_i}{dt'} = \beta f(K_i, y_j)$$
$$(i = 1,2,3; \; j = 0,1,2) \qquad (11)$$

where f is defined by Equations (8). A material balance on B gives

$$\beta = \beta_o - \sum_{i=1}^{3} iy_i = \beta_o - g(y_0, K_i)$$
$$(i = 1,2,3) \qquad (12)$$

where g is described by Equations (9). Clearly y_0 is a single-valued function of $\beta_o - \beta$, since both β and y_0 decrease continuously as the reaction proceeds. Equations (11) and (12) imply that for a given set of $\{K_i\}$, whenever a certain amount of B has been consumed, the quantities of the P_i produced and A reacted are determined and are independent of the amount of B initially present; that is the y_i are functions of $(\beta_o - \beta)$ alone. Equation (11) indicates that the effect of raising β_o is simply a reduction in the time required to reach a given B-free distribution of A. This being the case it should be possible to relate the solutions of Equation (8) for any runs in which the $\{K_i\}$ are the same, in terms of the value of β_o for each one.

Denote by the subscript r a reference run for which $\beta_o = 1$. Let t_r' be the time required to reach a given value of y_0 when $\beta_o = 1$. Let t' be the time required to reach this same value of y_0, for an arbitrary initial β, β_o. As y_0 is the same in each case, from Equation (12) the decrease in β must also be the same; call it B. Then

$$\frac{r_i}{r_{ir}} = \frac{\beta}{\beta_r} = \frac{\beta_o - \beta}{1 - B} = \frac{dt'_r}{dt'} \qquad (13)$$

Here the differential times are those required for the same differential change in y_i, after a diminution B of β has taken place. Rearranging and integrating one gets

$$\int_0^{t'} dt' = t' = \int_0^{t'_r} \frac{1 - B}{\beta_o - B} \, dt'_r \qquad (14)$$

For the reference case

$$B = 1 - \beta_r \qquad (15)$$

Equation (14) then becomes

$$t' = t'_r + (1 - \beta_o) \int_0^{t'_r} \frac{dt_r'}{\beta_o - 1 + \beta_r} \qquad (16)$$

In Figure 1 $\log \beta_r$ is plotted against t_r'. The graphs are nearly linear. For this reason Equation (17) was taken to represent the functional dependence of β_r on t_r'

$$\beta_r = e^{-bt'_r} \qquad (17)$$

where b is an empirical parameter of the approximation. Substituting Equation (17) into (16) and integrating one obtains

$$t_r' = -\frac{1}{b} \ln (\beta_o e^{-bt'} - \beta_o + 1) \qquad (18)$$

Substituting Equation (17) into (8a), separating variables and integrating one gets

$$y_{0r} = \exp\left[\frac{1}{b}(e^{-bt'_r} - 1)\right] \qquad (19)$$

But this value of y_0 obtains for any t' and β_o which satisfy Equation (18). Substitution of Equation (18) into (19) and (17) gives, respectively

$$y_0 = \exp\left[\frac{\beta_o}{b}(e^{-bt'} - 1)\right] \qquad (20)$$

and

$$\beta = \beta_o e^{-bt'} \qquad (21)$$

The dependences of the concentrations of the initiating reactants on time and initial composition, as given by Equations (20) and (21), are consistent with the known properties of the exact solution of the differential rate equations. It can further be shown that $y_1(t')$, given by Equations (9a) and (20), exhibits a maximum and point of inflection if β_o is large enough.

Construction of the Working Formula

In the derivation of the approximate solution given by Equations (20) and (21) only one empirical parameter b was proposed. This parameter is a function of only the $\{K_i\}$. The nature of this dependence was found by fit-

TABLE 1. CORRELATION OF PRODUCT DISTRIBUTION DATA

Reaction $A + B$	Conditions	K_2	K_3	s_e	References
Methanol + propylene oxide	NaOH catalyst, 45°C.	0.12	—	0.001	(14, 19)
1-methoxy-2-propanol + propylene oxide	NaOH catalyst, 60°C.	1.01	1.03	0.009	(14)
Monoethanolamine + ethylene oxide	10°C.	0.75	—	0.022	(20)
Ammonium hydroxide + ethylene oxide	10° to 30°C.	5.7	4.3	0.011	(20)
Propylene + chlorine	510° to 528°C.*, atmospheric pressure, flow reactor	1.02	1.01	0.011	(10)
Benzene + chlorine	440° to 450°C.*, atmospheric pressure, flow reactor	0.48	0.00†	0.015	(16)

* Chlorination found to be entirely substitutive.
† Found by fitting observed trichlorobenzene concentrations.

ting the data obtained from the digital-computer integration to Equation (20), through the method of least squares. The deviation was defined as

$$D = \sum_{\substack{\text{all} \\ \text{data}}} (\hat{y}_0 - y_{0P})^2 \qquad (22)$$

The zero of $(\partial D)/(\partial b)$ was found by means of Newton's method. Figure 2 shows the variation of b with K_2 for K_3 values of zero, three, and five. The values of b for $K_2 \geqslant 0.1$ were correlated by a second-degree multinomial in K_3 and $\log_{10}K_2$:

$$b = 0.897 + 0.429 \log K_2$$
$$+ 0.053 \log^2 K_2 + 0.1 K_3 (0.736$$
$$+ 0.632 \log K_2 + 0.273 \log^2 K_2)$$
$$- 0.01 K_3^2 (0.720 + 0.545 \log K_2$$
$$+ 0.262 \log^2 K_2) \qquad (23)$$

The standard error of prediction of y_0 is given by

$$\sigma_{\text{pred}} = \sqrt{\frac{D}{N+1}} \qquad (24)$$

The values of y_{0P} were taken from Equation (10b) or (20), and σ_{pred} was computed in either case to determine the ranges of applicability of the two approximations to y_0. Figure 3 is a plot of σ_{pred} vs. K_2 for two values of K_3 and for the two correlation schemes. The low-K_2 correlation is preferred when K_2 is less than 0.12, for $K_3 = 0$; or less than 0.04, when $K_3 = 5$.

The standard error in y_0 never exceeds 0.025. A material balance will show that this also limits the errors in the dimensionless product concentrations.

DATA CORRELATION

It is possible with the product distribution equations described above and the approximate time-dependent solution given by Equations (20) and (21) to directly correlate data on systems of consecutive competitive reactions without the tedium of guessing at the $\{k_i\}$, numerically solving the rate equations, and repeating the procedure until the best fit to the data is obtained. If one uses the equations derived above, not only can literature data be analyzed to find rate constants, but in addition if the fit is good, added confirmation of the presumed and theoretical model is obtained. Glaring difficulties in fit, beyond those shown in Figure 3, may be evidence of poor experimental method or a deviation between the true reaction mechanism and that required by Equations (2).

Two methods will be used to find the rate constants from experimental data, a differential approach and an integral method. First experimental data will be differenced and fit to a difference form of Equations (2). Second the $\{K_i\}$ will be found by fitting product distribution data to Equations (9). Lastly the approximate model derived above will be used to correlate time-composition data on reaction sets

whose stoichiometry follows Equation (1).

Differential Treatment of the Rate Equations to Find Rate Constants

Two differential methods of correlating kinetic data will be discussed below. Before proceeding to the actual problem of data analysis the basic steps in the differential treatment will be outlined:

1. The data consist of a set of times $\{t_j\}$ and associated compositions $\{[A]_j\}$, $\{[P_i]_j\}$, and $\{[B]_j\}$. Define the semidimensionless average rate of disappearance of P_i ($i = 0,1,2$) over the time interval t_j to t_{j+1} by

$$\bar{r}_{mij} = -\frac{\Delta y_i}{\Delta t} = \frac{y_{ij} - y_{i,j+1}}{t_{j+1} - t_j} \qquad (25)$$

2. Plot $\bar{r}_{mij}$ against t. If $\bar{r}_{mi}$ is the ordinate, this plot consists of a set of horizontal lines of height $\bar{r}_{mij}$, each extending from t_j to t_{j+1}.

3. Draw a smooth curve through this difference plot. This curve is a graph of the true reaction rate r_{mi} vs. time. Construct such derivative plots for each reacting component.

4. At each experimental point use Equations (2) to obtain the rate constants.

Exact Treatment when All Data are Based on the Same Initial Conditions. In this case the procedure described above is applied directly. The data are all obtained from runs having identical initial conditions; this is the case when aliquots are withdrawn from a reaction mix during the course of a single run. In order to study the production of ethanolamine from ethylene oxide and ammonium hydroxide Potter (20) mixed the two reactants and withdrew samples at intervals. The chemical reactions are
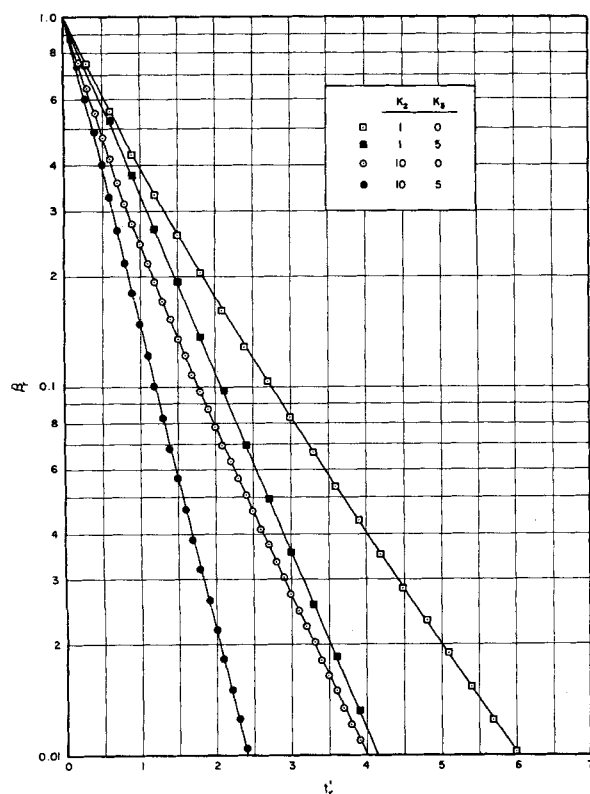

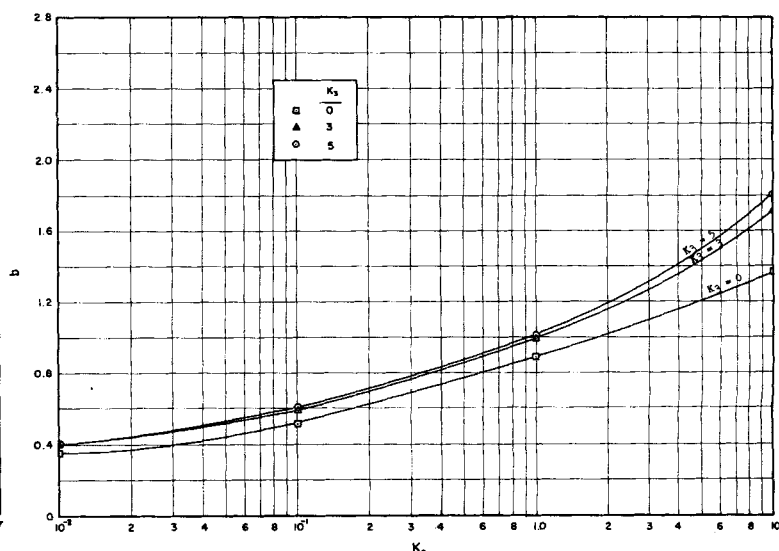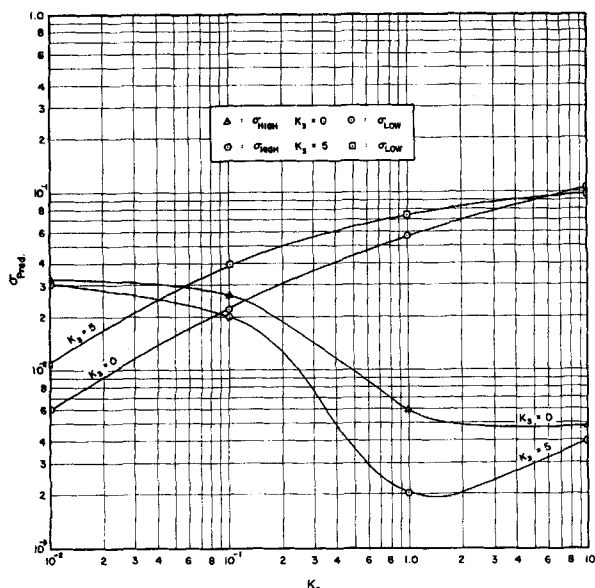Fig. 1. β_r vs. t'_r. High K_2 reference runs.

Fig. 2. b vs. K_2.

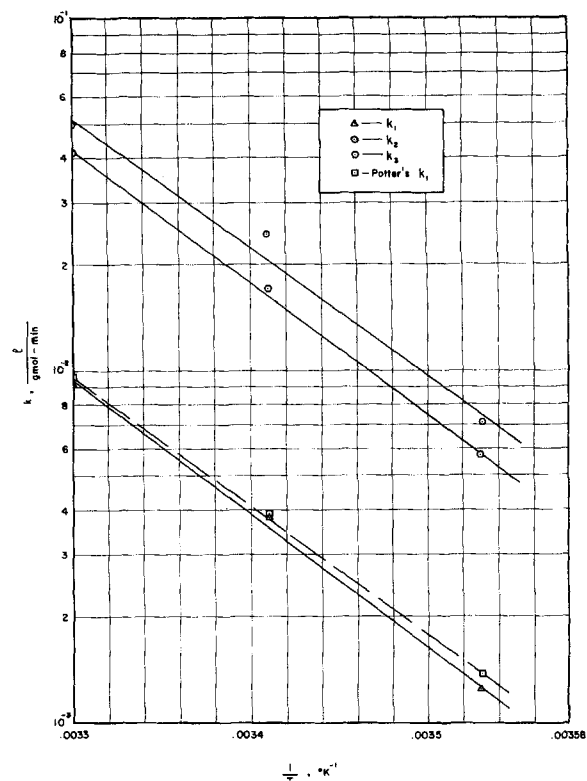Fig. 3. σ_{pred} vs. K_2 for high and low K_2 correlations.

$$NH_3 + H_2\overset{O}{\overset{/\backslash}{C}}{-\!-}CH_2 \text{ (ETO)} \rightarrow$$

$H_2NCH_2CH_2OH$ (monoethanolamine;

$$\text{MEA)} \quad (26a)$$

$$MEA + ETO \rightarrow HN(CH_2CH_2OH)_2$$

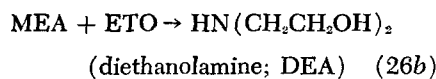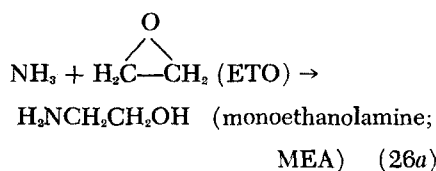$$\text{(diethanolamine; DEA)} \quad (26b)$$

$$DEA + ETO \rightarrow N(CH_2CH_2OH)_3$$

(triethanolamine; TEA) $\quad (26c)$
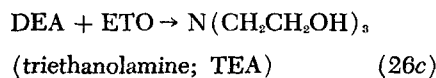
Potter's data were differenced to give smooth plots of r_{mk} vs. time, and the $\{k_k\}$ were computed from Equation (27):

$$\bar{k}_k = \frac{\overset{k}{\underset{l=0}{\Sigma}} \underset{j}{\Sigma} r_{mlj}}{[A]_o \underset{j}{\Sigma} y_{k-1,j} \beta_j} \quad (27)$$

The indicated summations were taken to minimize the effects of errors in the $\{y_i\}$ late in the reaction. The rate constants determined in this fashion are given in Table 2.

Approximate Treatment when Data are Based on Various Initial Conditions. Equation (25) can be applied directly only when the data to be differenced are based on the same value of β_o. If one wishes to correlate a set of data obtained from reaction mixes not hav-

ing common initial conditions, a correction must be applied to take the β_o associated with each run into account.

When the $\{\beta_o\}$ are not identical throughout, the times at which each sample is taken are replaced by the times at which the same product distribution would obtain if β_o were equal to some reference value. The reference value of $\beta_o = 1$ is chosen so that Equation (18) can be used. The procedure employed is:

1. Start with a set of guesses at the $\{k_i\}$, given by $k_1^{(1)}$, $K_2^{(1)}$, and $K_3^{(1)}$.
2. Compute $b^{(1)}$ from Equation (23).
3. Compute $t^{(1)}$ for each run from Equation (4), using $k_1^{(1)}$ and the initial conditions for each run.
4. Compute $t_r'^{(1)}$ for each run, using Equation (18).
5. Compute $\beta_r^{(1)}$ for each run

$$\beta_r^{(1)} = 1 - (\beta_o - \beta) \quad (28)$$

6. Proceed as in the exact differential treatment described above, using

t_r' as the independent variable. The rates to be determined by difference will be the dimensionless ones defined by Equation (11).

The best estimates of the rate constants are obtained when continued iteration yields values of the rate constants identical to those guessed before the last cycle. It should be remarked that these rate constants are not necessarily the best ones to represent the reaction system, but they are the best values consistent with the approximation used to reduce the times to the reference case.

This method of solution was applied to the data of Groll and Hearne (10) on the substitutive chlorination of propylene at 525°C. The calculated rate constants are listed in Table 2.

If enough data based on a single value of β_o are available, Equation (16) may be integrated numerically to reduce data based on other initial molar ratios to the modal case. Al-

Fig. 4. Arrhenius plot for ethanolamine synthesis.

TABLE 2. ESTIMATION OF ALL RATE CONSTANTS FOR SELECTED CONSECUTIVE COMPETITIVE REACTIONS

Reaction A + B	Temp.*	k_1	K_2	K_3	s_e	References
Benzene + chlorine	450°C.	11,600 cc./mole-min.	0.68	—	0.032	(16)
Propylene + chlorine	525 to 528	890† cc./mole-sec.	1.10†	1.45†	0.019	(10)
Methanol + propylene oxide	45	0.0174 cc./mole-hr.	0.88	—	0.011	(19)
Ammonium hydroxide + ethylene oxide	10	0.00125 cc./mole-min.††	5.7	4.6	0.014	(20)
	20	0.0039††**	6.0††	4.5††	0.013	(20)
	30	0.0091††	5.4	4.5	0.022	(20)

* Other conditions the same as in Table 1.
† Values obtained by differentiation: $k_1 = 830$, $K_2 = 1.19$, $K_3 = 1.40$.
** Values obtained by differentiation: $k_1 = 0.0038$, $K_2 = 6.2$, $K_3 = 4.7$.
†† k_1 reported by investigator (Potter): 10°C., 0.00135; 20°C., 0.0039; 30°C., 0.0095.
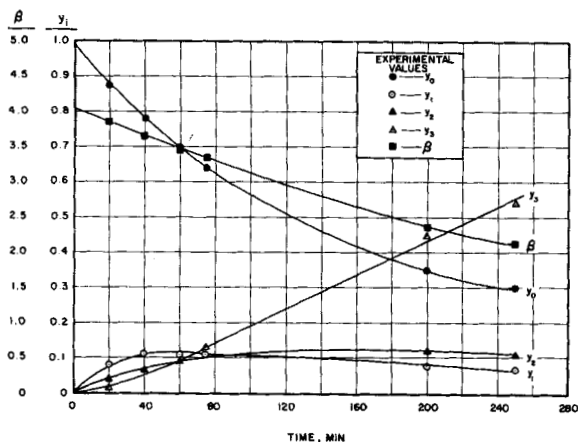
Fig. 5. Concentration-time profiles for ethanolamine synthesis at 10°C. Curves are computed from calculated rate constants and approximate model.
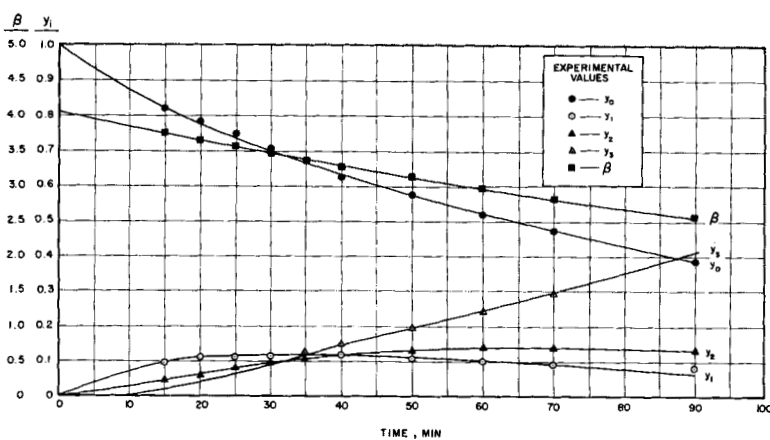

Fig. 6. Concentration-time profiles for ethanolamine synthesis at 20°C. Curves are computed from calculated rate constants and approximate model.

though that portion of the data used to evaluate the integral may be sufficient to give useful values of the rate constants, the use of the additional data checks the assumption that the rate constants are independent of composition.

Correlation of Product Distribution Data

The product distribution equations (9) may be used to estimate best values of K_2 and K_3 from experimental data when the reaction time is either unknown or infinite. The latter is the case when steady state product distributions are reported. A program was written for an IBM-704 to determine rate constant ratios from product distribution data; y_0 is the independent variable and the $\{K_i\}$ are the parameters of the approximation. Newton's method was used to find those values of the rate constant ratios which minimized the deviation between the predicted and experimental dimensionless product concentrations. The required second derivatives of the deviation were approximated by difference quotients. The best $\{K_i\}$ and the associated standard errors of prediction are given in Table 1 for several experimental systems.

The experimental data fit the product distribution equations quite well. The standard errors are a measure of experimental inaccuracy and deviations of the true rate equations for the reaction set from those assumed in Equation (2). Below, where time is reintroduced as an independent variable, the standard error of prediction will again be computed. The differences between the two corresponding variances may be used to measure the ability of the approximate model to describe the rate equations.

Determination of Rate Constants from Complete Reaction Mix Data

Equations (9), (20), and (21), which comprise the approximate solution of the rate equations, may be fit-

ted to experimental data when sampling times, as well as the compositions of the reaction mixes, are given. The value of β can be found from either Equation (21) or a material balance. These two methods predict different values for the dimensionless concentration of B. Although the use of Equation (21) would render any results internally inconsistent from a material balance point of view, the authors are more concerned with a representation of the true solution of the differential equations than with the internal consistency of the approximation. Eight points were chosen at random from the computer-generated solutions of the rate equations. The values of β predicted by the two methods were compared with the true solutions of the differential equations, and the corresponding variances were calculated. The results of an F-test showed that, at 90% confidence, the material balance does not predict β as well as the shorter Equation (21), when Equation (20) is used to determine the fractional conversion of A.

When K_2 is low enough to allow the reaction set to be represented by a single second-order reaction, β is found from a material balance:

$$\beta = \frac{\beta_o^2 - \beta_o}{\beta_o - \exp\left[t'(1 - \beta_o)\right]} \quad (29)$$

An IBM-704 program was written to correlate experimental kinetic data on consecutive competitive reactions, with the equations developed above to find the best values of the rate constants for each reaction step. Table 2 contains a summary of the results. When rate constants have also been computed by differential methods or reported by the experimenter, these values are included for comparison. The accuracy of the rate constants in Table 2 varies from system to system and depends on the number of pieces of data employed, the levels of the dimensionless concentrations and times, and the experimental error. Furthermore it should be noted that, in contrast to the product distribution correlation, the $\{k_i\}$ are adjusted not only to describe the product concentrations but also to give a value of b, through Equation (23), which describes as well as possible the time dependence of the concentrations of the initiating reactants. This explains the larger standard error in the present case.

As there was a large body of data available on ethanolamine synthesis, this system was treated in greater de-
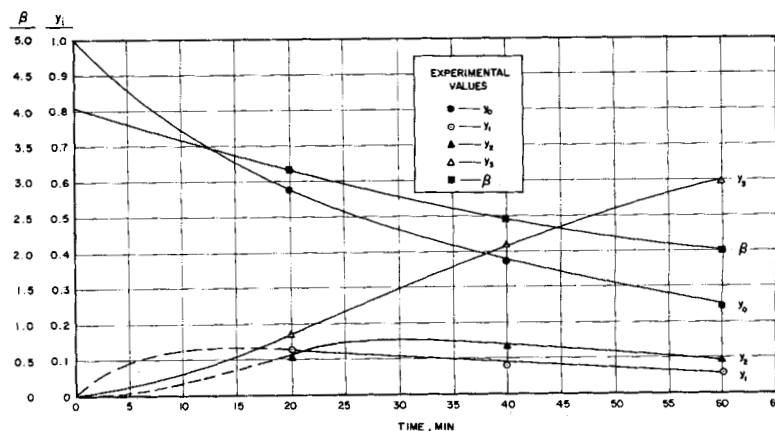

Fig. 7. Concentration-time profiles for ethanolamine synthesis at 30°C. Curves are computed from calculated rate constants and approximate model.

tail than were the others. Rate constants were estimated at 10°, 20°, and 30°C., so the activation energy could be calculated for each ethylene oxide addition. Figure 4 shows Arrhenius plots for the three reactions. The plots indicate an activation energy of about 17 kcal./mole for each addition. The predicted and observed compositions of the reaction mixes, for this system, are shown in Figures 5 through 7.

APPROXIMATE INTEGRATION OF DIFFERENTIAL RATE EQUATIONS

The approximate integral solution used above to treat consecutive competitive reaction systems is an application of a more general algorithm to a particular reaction set. This procedure will now be described briefly and generally to indicate its applicability in the analysis of other systems whose rate equations defy exact solution.*

1. An analogue or digital computer is used to integrate the proposed rate equations for a wide range of values of the rate constants and initial conditions. The effort required here can be reduced if the equations are first put in dimensionless form. Frequently some properties of the true solution can be found from the differential equations themselves. Among these are product distribution equations and equations, such as (16), which relate concentration-time profiles for two runs to their initial conditions.

2. The least possible number of dependent variables are represented empirically. The approximations should be simple, should be applicable over a wide range of conditions, should reduce to the known initial conditions at zero time, and should possess reasonable asymptotes at infinite time. The choice of the concentrations to be so represented will also depend upon the ease and accuracy with which the other variables can be predicted from the approximation.

3. With the approximations chosen in step 2 the rate equations are solved analytically, with any parameters of the approximations as yet unspecified.

4. The values of the parameters are found by fitting the results of step 3 to the computer-generated results given by step 1.

The integral solution of the rate equations is considerably more convenient than the equations themselves for the correlation of literature data and for the derivation of design equations (6). Although it is an inexact method, the greatest portion of the variance between experimental results and those predicted by the model presented here are almost certainly due

to experimental error and to the inability of the proposed rate equations to describe the true kinetics of the several reactions.

CONCLUSIONS

Equations explicit in concentration have been derived which describe to within 2% the theoretical course of a set of three consecutive competitive reactions, when only the initiating reactants are originally present. The equations are easy to apply and are applicable to diverse chemical systems.

These formulas have been used to correlate experimental data on consecutive competitive reaction systems. The standard deviation between the experimental and calculated compositions of the reaction mixes was always less than 4% and usually less than 2% of the initial concentration of A. The values of the rate constants which were used to obtain the best fit to the published data agree closely with the values found by more direct means, such as data differentiation and graphical integration.

ACKNOWLEDGMENT

NOTATION

B = decrease in dimensionless concentration of B

b = parameter of the approximation to the rate equations, dimensionless

D = deviation, defined by Equation (22)

j = number of reactions

K_i = dimensionless rate constant for the i-th reaction, defined by Equation (7)

k_i = rate constant for the i-th reaction, cu. ft./mole hr.

N = number of pieces of data

r_{mi} = semidimensionless rate of disappearance of P_i, defined by Equation (25), hr.$^{-1}$

r_i = dimensionless rate of disappearance of P_i, defined by Equation (11)

s_e = estimate of standard error

t = time

t' = dimensionless time, defined by Equation (4)

y_0 = dimensionless concentration of A, defined by Equation (3)

y_i = dimensionless concentration of P_i, defined by Equation (6)

β = dimensionless concentration of B, defined by Equation (5)

σ_{pred} = standard error of prediction, defined by Equation (24), dimensionless

$[\ ]$ = concentration, moles/cu.ft.

Subscripts

o = initial value

P = value obtained from Equation (20)

r = reference case

Superscripts

$\wedge$ = value obtained by numerical integration

$-$ = average value

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