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A STUDY OF CONSECUTIVE COMPETITIVE
REACTION SYSTEMS

Morton H. Friedman

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Doctoral Committee:

Professor Robert R. White, Chairman
Professor Richard B. Bernstein
Doctor Noel J. Hicks
Assistant Professor Dale Rudd
Associate Professor M. Rasin Tek

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NOMENCLATURE

- a function defined by Equation (4.59a)
- A initiating reactant in set of consecutive competitive reactions; cross-sectional area of flow reactor, L^2 ; cost of A, $\$/N$
- a initial concentration of A and B, when equal, N/L^3 ; parameter of the approximation in Equations (3.31), (3.34) and (3.35)
- a_{ij} element of matrix defined in Equation (F.21)
- B function defined by Equations (4.61) and (4.86)
- B common reactant in set of consecutive competitive reactions; decrease in the dimensionless concentration of B; cost of B, $\$/N$
- b parameter of the approximation in Equations (3.30), (3.31), (3.33), (3.34) and (3.35)
- b_i estimate of the i -th parameter of the approximate response function
- b^i byproduct rate, N/T
- C function defined by Equation (3.83)
- C one of two intermediates in the production of P_2
- C_1, C_2, C_3 functions defined by Equation (4.56)
- D function defined by Equation (4.75)
- D overall deviation; tube diameter, L
- d deviation; parameter of the approximation in Equations (3.31) and (3.35)
- E function defined by Equation (4.20a)
- E function defined by Equation (F.23)
- ΔE activation energy, LF/N
- E_n function defined by Equation (F.24)
- \mathcal{F} function defined by Equations (4.59b) and (4.85)

NOMENCLATURE (CONT'D)

f	function defined by Equation (3.23)
f_i	approximation to response function ϕ_i
g	function defined by Equation (3.24)
g_r	r'th function defined by Equation (F.15) or (F.20)
H	function defined by Equation (4.24a)
H	function defined by Equation (4.64)
h	precision constant; function defined by Equation (4.93)
i	reaction counter
J	k_3/k_2
j	number of reactions; number of time intervals in differential data-fitting
K	k_2/k_1
K_i	k_i/k_1
K_{bi}	ionization constant of P_i
K_{bi}°	function defined by Equation (3.100)
k	number of independent variables; iteration number; effective rate constant, L^3/NT
k_i	rate constant for i-th reaction, L^3/NT
k_i^N	rate constant defined by Equation (2.5), $/NT$
L	reactor length, L
L°	distance of injection point from inlet, L
l	number of dependent variables
M	flow reactor operating cost, $\$/LT$
M°	batch reactor operating cost, $\$/TL^3$
m	number of runs

NOMENCLATURE (CONT'D)

N	mols, N; number of pieces of data
n_i	number of non-reacting products of i-th reaction
P	probability; value of P_1 , $\$/N$
P_i	reacting product of i-th reaction
p	number of parameters of the approximate response function; number of functions g_r ; number of independent variables
pK_a	apparent ionization constant
R	gas constant, $LF/M\theta$; separation cost of product, $\$/N$
r_i	dimensionless rate of disappearance of P_i
r_{ci}	rate of disappearance of P_i , N/L^3T
r_{mi}	partially dimensionless rate of disappearance of P_i , $/T$
r_i	(sum of rate constants consuming P_1)/ k_1
s_e	estimate of standard error
γ	production cost, $\$/T$
τ_{op}	operating cost, $\$/T$
τ_{opBB}	operating cost per batch in batch reactor, $\$$
T	absolute temperature, θ
t	time, T; residence time, T
t^*	function defined by Equation (2.21); dimensionless time
t_f	effective residence time in flow reactor, T
u	function defined by Equation (2.6), N/L^3 ; function defined by Equation (3.11)
V	reaction volume, L^3 ; volumetric flow rate, L^3/T ; volume fraction
V_{Bi}	injection volume in batch operation, L^3
v_i	partial weight of P_i , ML^3/N

NOMENCLATURE (CONT'D)

v	molar volume, L^3/N ; variance
W	byproduct value, $\$/N$
w	weighting factor
x	function defined by Equation (2.6); mol fraction
x_i	cumulative number of mols of P_i formed, N ; i -th independent variable
y	function defined by Equation (2.6)
y_0	function defined by Equation (2.17); dimensionless concentration of A
y_i	i -th dependent variable; dimensionless concentration of P_i
Z	production rate of P_1 , N/T
α	step size in Method of Steepest Descent
α_{ij}	j -th non-reacting product of i -th reaction
$\alpha_1, \alpha_2, \alpha_3$	functions defined by Equations (3.4)
$(\alpha_n)_i$	function defined by Equation (2.24)
β	function defined by Equation (2.20); dimensionless concentration of B
β_i	i -th parameter of the approximate response function
$\beta_0, \beta_1, \beta_2, \beta_3$	functions defined by Equations (3.5)
Δ	error term defined by Equation (F.2); increment in the independent variable; error
δ_n	function defined by Equation (F.22)
$\delta_0, \delta_2, \delta_3$	functions defined by Equation (3.10)
ϵ_i	error in y_i
γ	function defined by Equation (F.16)
η	function defined by Equation (4.8)

NOMENCLATURE (CONT'D)

Φ	function defined by Equation (2.10)
ϕ_i	i-th response function
λ	undetermined multiplier
μ	ionic strength
ν	function defined by Equation (4.3)
σ_{pred}	standard error of prediction
θ	function defined by Equation (2.8), NT/L^3 ; angle
ζ	function defined by Equation (2.16), \sqrt{N}

Subscripts

A	of reactant A
B	of reactant B; for batch operation
c	for the common run
e	equivalent value
F	for flow operation
f	final value; of the feed
i	of the injection stream
ij	of the j-th i-substituted product; of P_i , at time t_j
max	maximum value
min	minimum value
o	initial value
P	predicted value
P_i	of product P_i
r	reference case
T	total quantity
1, 2	measurements at two data
∞	at infinite time

NOMENCLATURE (CONT'D)

Superscripts

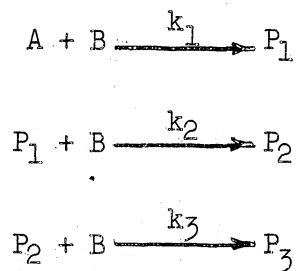
(k)	k-th iteration
-1	inverse function
→	vector
^	experimental value
—	average value
'	value immediately preceding injection
"	value immediately following injection

Miscellaneous

	matrix
	norm
$\Delta []$	change in concentration defined by Equation (4.19), N/L^3
[]	concentration, N/L^3

ABSTRACT

Experimental kinetic data are most conveniently correlated by the integrated form of the differential rate equations which the reactions are presumed to obey. The rate equations will generally not be integrable if the reaction set which they are to describe is at all complex. A method of obtaining an approximate integral solution, at least partially consistent with the differential equations, is applied to a set of three consecutive competitive reactions; this set may be represented generically by the equations



where k_1, k_2, k_3 = rate constants for the reactions.

Four differential equations can be written, describing the rates of disappearance of A, B, P_1 , and P_2 . To date, the integrated solution of these equations has been found only for particular values of the rate constants and initial concentrations. By dividing one rate equation into another, equations useful for correlation can be derived; these describe the distribution of converted A among the three products. The approximate integral expression for the

concentration of A, when no products are initially present, is

$$[A] = [A]_0 \exp \left[\frac{[B]_0}{[A]_0 b} (e^{-bk_1[A]_0 t} - 1) \right]$$

where [] = concentration
A = initial value
t = time

and b is a function of the rate constants of the three reactions.

The approximate integral solution is used to correlate experimental and published data on systems whose stoichiometry obeys the chemical equations above. The experimental systems studied include the chlorination of benzene, the hydrofluorination of carbon tetrachloride, ethylene oxide and propylene oxide addition reactions, and the chlorination of propylene. Except for the Freon synthesis, which probably is a free-radical reaction, the compositions of the reaction mixes are predicted with a standard error of estimate of less than four per cent of the initial concentration of A: in three cases, less than two percent. 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.

Two methods of reactor design, applicable to both batch and continuous systems, are considered: numerical and analytical. In each case, the integral approximation is used to describe the total production cost as a function of the design and operating variables.

In the numerical treatments, the values of the independent variables are adjusted until the cost is minimized; when analytical methods are used, equations in the independent variables are derived, the roots of which are the best values of the design parameters. The numerical approach is used to design reactors to produce monoethanolamine from ethylene oxide and ammonia, and acetanilid from aniline and acetic acid. The results of the former design are checked against the optimum found from the direct solution of the rate equations; the results of the latter design are compared to those obtained from an analytical treatment of the integrated rate equations for a single reaction. Excellent agreement is obtained in both comparisons. The possibility of injecting additional B downstream from the reactor inlet to reduce the production cost is investigated and discarded.

A generalized description of the method used to obtain the approximate integral solution is included, and the use of digital computation to correlate and apply kinetic data is discussed.

I. INTRODUCTION

A. Background

The set of reactions initiated by propylene oxide and methanol in alkaline media^(26,34) is typical of a particular class of chemical syntheses --consecutive competitive reactions. The differential equations governing these reactions have not yet been completely solved; the purpose of the present study is to gain as complete an understanding as possible of the generalized system of consecutive competitive reactions by extending the mathematical analysis and by correlating the experimental results of this and other investigations with such mathematical results as have been achieved.

B. Statement of the Problem

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



etc.

When the activities of the reacting species are replaced by concentrations, the course of the reaction may be described by a set of differential equations involving time, concentrations and rate constants. For instance, the rate of formation of the i -th product is given by

$$\frac{d[AB_i]}{dt} = k_i [AB_{i-1}] [B] - k_{i+1} [AB_i] [B] \tag{1.2}$$

where $[X]$ = concentration of X

t = time

k_i = rate constant of the i -th reaction.

To date, these equations 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 initially present. The equations have been solved for certain initial molar ratios of A to B and for particular sets of rate constants^(13,45), but these solutions cannot be extended to more complex cases. By suitable treatment of the differential equations, formulae have been derived which describe the distribution of converted A among the products as a function of the rate constants, first by Fuoss⁽¹⁴⁾ for four reactions, and then by Natta and Mantica⁽³²⁾ for any number. Thus, given the rate constants for the reaction set, if the quantity of A in the reaction mix could be computed, then product distribution studies and material balances could 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. Of greatest importance, it will be possible to correlate the large body of experimental data on systems whose stoichiometry obeys Equation (1.1), 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, a primary purpose of this dissertation is to develop equations describing the time-dependence of the concentration of A.

The true value of any solution of this sort, for the engineer, lies in its applicability and usefulness in engineering development: for kinetic studies, in reactor design. Hence, design equations applicable to both batch and flow reactors are derived. The possibility of later or downstream injection of B is considered and equations derived and verified for

design of reactors on which a rather general cost function is defined.

This study is necessarily somewhat mathematical, as the integral equations are not readily apparent, but once these have been found, they are used to correlate data on real chemical systems and to solve real engineering problems.

C. Summary

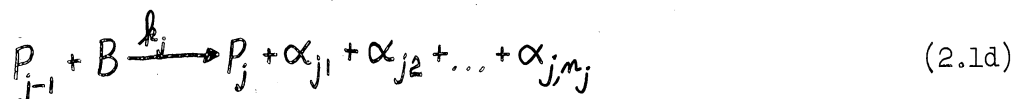
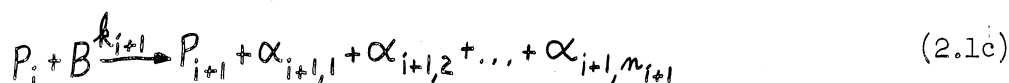
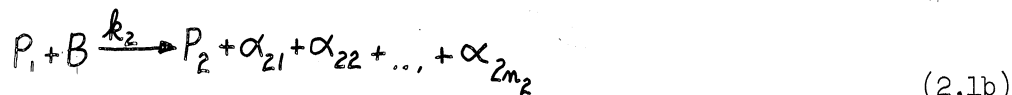
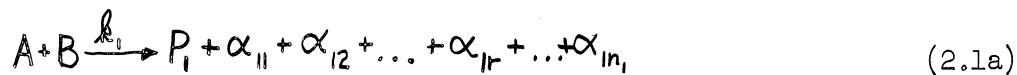
Chapter II is a review of previous work done towards solving the differential rate equations of which Equation (1.2) is typical. This chapter is divided into two parts; first, a survey of attempts to determine rate constants for the reactions by applying approximate solutions of the rate equations to experimental data; and second, a review of exact time-independent solutions of the rate equations to give product distribution formulae implicit in the ratios of pairs of rate constants.

Chapters III B and IV present the bulk of the practical results obtained from this study. Part A of Chapter III deals with the use of analog and digital computation in the development of the time-dependent model. Part B treats the fitting of this model to experimental data, using differential and integral methods. In Chapter IV, numerical and analytical design procedures are developed for batch and flow reactors; the degenerate case of a single second-order reaction is also considered.

Chapter V treats the possibility of the extension of the methods used here to more complex reaction systems. The use of digital computers is emphasized, not only for correlation work, but for mechanism and design studies as well.

II. STUDY OF PREVIOUS CORRELATIONS OF LITERATURE DATA

A system of irreversible consecutive competitive reactions can be represented by the series of equations below.



The value of j need not be finite. For polymerization processes or certain addition reactions, j is not bounded, while for processes such as ethanola- mine synthesis, j assumes a finite value: in this case, of three. Further- more, n_i may or may not be zero. For the addition of propylene oxide to methanol and the propylene glycol methyl ethers, $n_i = 0$ ($i = 1, \dots, \infty$); in the case of saponification of diesters, $n_i = 1$ ($i = 1, 2$).

Until the work of Natta and Mantica⁽³²⁾, the kinetics of consecu- tive, competitive reactions was investigated only for finite j . These stud- ies fall into two categories; first, that in which the experimental data are treated to find the rate constants; and second, that where known rate constants are used to predict product distribution during the course of reaction. The work done in each of these areas will be followed histori- cally in this chapter. Many of the conclusions arrived at by the earlier experimenters cited here are seen to be special cases of a later, more

general solution. But this does not detract from the value of the results obtained by each experimenter and theorist whose work is described below. A thorough survey of the literature has been useful in culling the promising approaches to the solution of the problem from those which could not be expected to be so fruitful. The "special cases" derived prior to the "general solutions" have frequently been more directly applicable than the latter: two examples are the equations for the maximum concentrations of the several products and the introduction of the concept of the dimensionless rate equation.

A. Calculation of Rate Constants from Experimental Data

Prior to 1931, rate constants for two consecutive competitive reactions; that is, for $k_1 = 0$ ($i > 2$), were found by assuming the disappearance of B to be the result of a single bimolecular reaction and by computing a single value of k , the effective rate constant, for the pair of reactions. No P_1 was included in the original reaction mix so the value of k , extrapolated to zero time, was taken as k_1 ; for large time, k was assumed to become equal to k_2 , as essentially all the A was consumed. Both values of k_i so determined were subject to considerable error. k_1 lacked accuracy because of initial unsteady-state temperature fluctuations and because of uncertainties in starting time. Towards the end of reaction, the rate of disappearance of B was so small that k_2 could not be found with much accuracy. An obvious solution to this problem was to carry out a reaction starting with P_1 and B alone, but, for some systems, P_1 was not available, and the problem of accurately determining k_1 still remained.

Ingold⁽²³⁾, while studying the hydrolysis of paraffin $\alpha\omega$ -dicarboxylic esters, partially solved this problem for the special case in which the initial concentrations of base and ester are the same.

Assuming the Law of Mass Action to hold, the rate equations which govern the progress of the reactions, in concentration units, are

$$-\frac{d[A]}{dt} = k_1[A][B] \quad (2.2a)$$

$$-\frac{d[P_i]}{dt} = k_{i+1}[P_i][B] - k_i[P_{i-1}][B] \quad (P_0 = A) \quad (2.2b)$$

$$-\frac{d[B]}{dt} = [B] \sum_{i=0}^{i-1} k_{i+1}[P_i] \quad (2.2c)$$

where $[]$ = concentration, mols/volume
 t = time
 k_i = specific reaction rate constant.

The density of the system is taken to be constant, so the volume of the reaction mix does not change. This is tantamount to stipulating, for cases where $n_i \neq 1$, that the reaction takes place in the liquid phase.* Under such conditions,

$$N_A = V[A] \quad (2.3)$$

$$dN_A = Vd[A] \quad (2.4)$$

$$-\frac{dN_A}{dt} = k_1^N N_A N_B = k_1 V[A][B], \dots \quad (2.5)$$

where N = number of mols
 V = volume of the system
 $k_i^N = k_i/V$.

* All the literature treated here will be described as originally presented, and the restrictions under which conversions from concentration units to molar units are permitted should be understood.

Ingold re-expressed the rate equations (2.2) as

$$\frac{du}{dt} = (a-u)(k_1(a-u+y) + k_2(u-2y)) \quad (2.6)$$

where $u = x + y$
 $a = [A]_0 = [B]_0$
 $y = [P_2] - [P_2]_0$
 $x = [A]_0 - [A]$
 $\hat{\Delta} = \text{initial value}$.

He further assumed that $u \ll a$, and obtained a power series solution of (2.6) which, including third degree terms in u/a , is

$$t = \frac{u}{k_1 a^2} \left[1 + \left(\frac{u}{a}\right) \left(1 - \frac{K}{2}\right) + \left(\frac{u}{a}\right)^2 \left(1 - \frac{7K}{6} + \frac{2K^2}{3}\right) \right] \quad (2.7)$$

where $K = k_2/k_1$.

The value of u can be found as a function of time and k_2 and k_1 were to be determined by curve-fitting. The assumption that u is very much less than a makes Equation (2.7) generally valid for only a short time after initiation of the reactions. The power series solution was extended by Morrow⁽³¹⁾, Homan⁽²¹⁾, and Westheimer, Jones and Lad⁽⁴⁹⁾ also considered a set of two consecutive competitive reactions with equimolar initial amounts of the two reactants.

Widequist^(50, 51) approached the two-reaction problem by defining a variable, θ , by

$$([B]_0 - u) dt \equiv d\theta \equiv [B] dt \quad (2.8)$$

He arrived at Equation (2.9), which can be solved for k_1 and k_2 by approximation methods.

$$u = [A]_0 \left[2 - \frac{k_1 e^{-k_2 \theta}}{(k_1 - k_2)} - \frac{(k_1 - 2k_2) e^{-k_1 \theta}}{(k_1 - k_2)} \right] \quad (2.9)$$

These results were extended by French⁽¹²⁾.

Schwemer and Frost⁽⁴¹⁾ defined a second parameter of the reaction,

Φ ,

$$\Phi(t) = \frac{d \ln [B]}{dt} \quad (2.10)$$

Potter and McLaughlin⁽³⁷⁾, while studying the kinetics of ethan-
amine synthesis, found k_1 in a very straightforward fashion; they used ex-
perimental data to integrate graphically the differential rate equation,
(2.2a), for k_1 .

B. Product Distribution Studies

The rate equations, (2.2), can be solved if time is eliminated
and a concentration made the independent variable. Then, the concentration
of any component is determined solely by the initial conditions and the
concentration of A or B. As the concentrations of the P_i ($i < j$) pass
through maxima, a single value of $[P_i]$ does not uniquely determine the
composition of the reaction mix. Solution of the rate equations by elimi-
nation of time yields the several results reviewed below. In all cases,
 $[P_i]_0$ ($i > 0$) was assumed to be zero.

We have already noted that the concentrations of the intermediate
products, P_i ($0 < i < j$), go through maxima. Stuurman⁽⁴³⁾ found that for
 $j = 2$, when $[P_1]$ peaks, the concentrations of A and B are related by

$$[B]_0 - [B] = [A]_0 \left(2 - 2K^{\frac{1}{1-K}} - K^{\frac{K}{1-K}} \right) \quad (2.11)$$

Riggs⁽³⁹⁾ found that the maximum value of $[P_1]$ and the concentra-
tion of A at that time were given by

$$[P_i]_{max} = [A]_0 K \frac{K}{1-K} \quad (2.12)$$

$$[A] = [A]_0 K \frac{1}{1-K} \quad (2.13)$$

Equations (2.12) and (2.13) are consistent with Equation (2.11). Other studies related to the maximum concentrations of the several products were undertaken by Ritchie⁽⁴⁰⁾, Ames⁽¹⁾, and Dobrovolskii and Polotnyuk⁽¹⁰⁾.

Fuoss⁽¹⁴⁾ determined the product distribution for four consecutive competitive reactions. Time-independent concentration profiles do not depend on the magnitudes of the velocity constants, k_i , but only on their relative values. Let us define

$$K_i = \frac{k_i}{k_1} \quad (i=1, \dots, j) \quad (2.14)$$

Thus, what we have previously called K will now be referred to as K_2 , and

$$K_1 = 1 \quad (2.15)$$

Fuoss' results are formulated in molar units but, as k_1^N is directly proportional to k_1 , the K_i are unchanged and the results may readily be converted to concentration units by Equation (2.3). Fuoss' rate equations were

$$dN_A = -\int N_A dN_B \quad (2.16a)$$

$$dN_{P_1} = \int (N_A - K_2 N_{P_1}) dN_B \quad (2.16b)$$

$$dN_{P_2} = \int (K_2 N_{P_1} - K_3 N_{P_2}) dN_B \quad (2.16c)$$

$$dN_{P_3} = \int (K_3 N_{P_2} - K_4 N_{P_3}) dN_B \quad (2.16d)$$

$$dN_{P_4} = \int K_4 N_{P_3} dN_B \quad (2.16e)$$

where $\zeta^{-1} = (1/N_{A0})(N_A + K_2 N_{P_1} + K_3 N_{P_2} + K_4 N_{P_3})$

These equations were integrated to give N_{P_1} as a function of the remaining mols of A. Let

$$y_0 = \frac{N_A}{N_{A_0}} \quad (2.17)$$

Then

$$\frac{N_{P_1}}{N_{A_0}} = \frac{y_0 (y_0^{K_2-1} - 1)}{1 - K_2} \quad (2.18a)$$

$$\frac{N_{P_2}}{N_{A_0}} = K_2 y_0 \left[\frac{y_0^{K_3-1}}{(K_2 - K_3)(1 - K_3)} - \frac{y_0^{K_2-1}}{(K_2 - K_3)(1 - K_2)} + \frac{1}{(1 - K_2)(1 - K_3)} \right] \quad (2.18b)$$

$$\frac{N_{P_3}}{N_{A_0}} = K_2 K_3 y_0 \left[\frac{y_0^{K_4-1}}{(K_2 - K_4)(K_3 - K_4)(1 - K_4)} - \frac{y_0^{K_3-1}}{(K_2 - K_3)(K_3 - K_4)(1 - K_3)} + \frac{y_0^{K_2-1}}{(K_2 - K_3)(K_2 - K_4)(1 - K_2)} - \frac{1}{(1 - K_2)(1 - K_3)(1 - K_4)} \right] \quad (2.18c)$$

$$\frac{N_{P_4}}{N_{A_0}} = 1 - y_0 - \frac{1}{N_{A_0}} (N_{P_1} + N_{P_2} + N_{P_3}) \quad (2.18d)$$

Potter and MacDonald⁽³⁶⁾ applied Fuoss' results to the case of three consecutive reactions, with $n_1 = 0$, and expressed N_B in terms of y_0 , N_{P_1} , and N_{P_2} .

$$\frac{N_{B_0} - N_B}{N_{A_0}} = 3 - 3y_0 - \frac{2N_{P_1}}{N_{A_0}} - \frac{N_{P_2}}{N_{A_0}} \quad (2.19)$$

If $N_{B_0} < nN$. . . a steady-state mixture of products obtains when no B remains. HIGGINS AND WILLIAMS⁽¹⁹⁾ thoroughly studied the steady state for two consecutive competitive reactions, in particular the coupling of amino acids and diazonium salts.

Frost and Schwemer⁽¹³⁾ suggested the use of the dimensionless groups y_0 , K_2 , β , and t' in studying the problem of two consecutive competitive reactions. The last two groups were defined by

$$\beta = \frac{[B]}{[B]_0} \quad (2.20)$$

$$t' = [B]_0 k_1 t \quad (2.21)$$

Natta and Mantica⁽³²⁾ developed a time-independent solution similar to Fuoss', valid for any j . Their rate equations are expressed in terms of x_i , the cumulative number of mols of P_i formed, so that

$$N_{P_i} = x_i - x_{i+1} \quad (2.22a)$$

$$N_A = N_{A_0} - x_1 \quad (2.22b)$$

$$N_{P_j} = x_j \quad (2.22c)$$

The rate equations are

$$\frac{dx_i}{dt} = k_i N (\alpha_{i-1} - \alpha_i) N_B \quad (2.23)$$

x_i is given by Equation (2.24). Equations (2.22) are used to find N_{P_i} .

$$x_i = N_{A_0} \left[1 + (\alpha_1)_i y_0 + (\alpha_2)_i y_0^{K_2} + \dots + (\alpha_i)_i y_0^{K_i} \right] \quad (2.24)$$

where $(\alpha_n)_i = K_1 K_2 K_3 \dots K_i (-1)^i / (K_n \prod_{\substack{m=1 \\ m \neq n}}^i (K_n - K_m))$.

By using the appropriate boundary conditions in the solution of the rate equations (2.23), product distributions may be determined for any set of initial conditions.

The product distribution equations derived above have been used to estimate rate constant ratios from kinetic data^(28,44,48). Product distribution studies have also been made for more complex reaction systems. Gold⁽¹⁵⁾ treated the reaction of chlorine with benzene, considering the isomeric polychlorides as distinct species. Chen⁽⁸⁾ considered the reaction set in which the same second product is reached through two intermediates. Brown and Coller⁽⁶⁾ applied Widequist's treatment to a set of two consecutive competitive reactions, complicated by a parallel reaction, in which B was consumed. Under the proper simplifications, all these solutions degenerate to previously reported ones.

III. PRESENT CORRELATION OF LITERATURE AND EXPERIMENTAL DATA

Much data on consecutive competitive reactions have been presented in the literature; these fall into two classes. The first class contains those reactions in which the reactant A has a few reacting groups which are changed to some unreactive form by addition of or substitution with, B. In this case, the number of reactions, j , is limited to the number of such groups on A. For instance, $j = 2$ for the saponification of diesters. The second class contains addition reactions, such as the reactions between propylene oxide and the methyl ethers of mono-, di-, tri-, and higher propylene glycols. These reactions can be differentiated from polymerizations by noting that the rate constants for each addition in the former case are distinct, while polymerizations are normally characterized by only two constants: k_i , the initiation constant, for the first reaction, and k_p , the propagation constant, for all later ones⁽¹⁶⁾.

Table III.1 is a summary of measured rate constants for some consecutive competitive non-polymerization reactions. As many as three reactions are considered only for ethanolamine synthesis and the propylene oxide-methanol reaction set; these reactions are characteristic, respectively, of the two classes mentioned earlier. It was decided, as no data for k_4 had yet been reported, to restrict this study to a set of only three consecutive reactions.

A. Mathematical Treatment to Obtain Explicit Solution

1. Considerations on Direct Integration of the Rate Equations

For three reactions, the differential rate equations are:

TABLE III.1 EXPERIMENTAL VALUES OF THE RATE CONSTANTS FOR SELECTED CONSECUTIVE COMPETITIVE REACTION SYSTEMS

Author	Reaction	Medium	Temp. °C	1/mol-min		
				k ₁	k ₂	k ₃
Ingold ⁽²³⁾	Base saponification of					
	methyl succinate	water	20	14.74	1.526	
	methyl glutarate	water	20	7.24	1.123	
	ethyl glutarate	water	20	5.77	0.902	
	methyl adipate	water	20	4.18	0.844	
	ethyl adipate	water	20	3.52	0.704	
	methyl pimelate	water	20	2.09	0.481	
Ritchie ⁽⁴⁰⁾	methyl suberate	water	20	1.24	0.317	
	methyl azelate	water	20	0.82	0.227	
	ethyl malonate	water	25	127	1.08	
	ethyl malonate	water	15	76.7	0.56	
	ethyl malonate	water	0	29.2	0.190	
	ethyl methylmalonate	do	25	35.1	0.40	
	do	do	15	19.5	0.195	
	ethyl malonate	water-ethanol	25	16.9	0.217	
	ethyl malonate	do	15	6.11	0.088	
	ethyl methylmalonate	do	25	2.40	0.0838	
	do	do	15	1.11	0.041	
	ethyl dimethylmalonate	do	25	0.0570	0.0042	
	ethyl diethylmalonate	do	25	0.00110	0.00024	
	ethyl malonate	ethanol	25	0.220	0.006	
	ethyl succinate	water-ethanol	25	1.87	0.325	
	ethyl succinate	do	15	0.80	0.136	
ethyl succinate	do	0	0.211	0.038		
ethyl succinate	ethanol	25	0.024	0.0195		
Homan ⁽²¹⁾	di t-butyl malonate	water	25	0.717	0.00647	
	t-butyl oxalate	water	25	1300	0.286	
	t-butyl succinate	do	25	0.0810	0.0184	
	t-butyl glutarate	do	25	0.111	0.0252	
	t-butyl adipate	water	25	0.0690	0.0203	
	methyl malonate	water	25	170	1.85	
	Potter and McLaughlin ⁽³⁷⁾	ethanolamine synthesis	water	10 - 30	K ₂ = 6; K ₃ = 4	
Frost and Schwemer ⁽¹³⁾	base saponification of ethyl adipate	dioxane-KCL-water	25	5.20	1.83	
	ethyl succinate	do	25	11.40	2.12	
Lay ⁽²⁶⁾	propylene oxide-methanol	organic	45	l ² /mol ² -min		
	do	do	85	0.00147	0.00097	0.00066
				0.0268	0.0072	0.0100

$$-\frac{d[A]}{dt} = k_1[A][B] \quad (3.1a)$$

$$-\frac{d[P_i]}{dt} = k_{i+1}[P_i][B] - k_i[P_{i-1}][B] \quad (i=1,2,3; k_4=0; P_0=A) \quad (3.1b)$$

$$-\frac{d[B]}{dt} = [B] \sum_{i=0}^3 k_{i+1}[P_i]. \quad (3.1c)$$

These equations have been solved by Svirbely⁽⁴⁵⁾ for an initial value of [B]/[A] of three, when k_2 is twice k_3 . However, no complete solutions of the equations have been published. Before resorting to an empirical approach, a few attempts were made at the solution of Equations (3.1), to find out why previous attempts had met with so little success.

Substitution of Equations (2.18a) and (2.18b) into (2.19) gives

$$\frac{N_{B0} - N_B}{N_{A0}} = 3 - 3y_0 - 2 \left[\frac{y_0 (y_0^{k_2-1} - 1)}{1 - K_2} \right] - K_2 y_0 \left[\frac{y_0^{k_3-1}}{(K_2 - K_3)(1 - K_3)} - \frac{y_0^{k_2-1}}{(K_2 - K_3)(1 - K_2)} \right] \quad (3.2)$$

Rearranging,

$$N_B = (N_{B0} - 3N_{A0}) + N_A \left(3 - \frac{2}{1 - K_2} + \alpha_3 K_2 \right) + N_A^{k_2} \left[\frac{2}{N_{A0}^{k_2-1} (1 - K_2)} - \frac{K_2 \alpha_2}{N_{A0}^{k_2-1}} \right] \quad (3.3)$$

$$\text{where } \alpha_1^{-1} = (K_2 - K_3)(1 - K_3) + \frac{K_2 N_A^{k_3} \alpha_1}{N_{A0}^{k_3-1}} \quad (3.4a)$$

$$\alpha_2^{-1} = (K_2 - K_3)(1 - K_2) \quad (3.4b)$$

$$\alpha_3^{-1} = (1 - K_2)(1 - K_3). \quad (3.4c)$$

Define β_1 , β_2 , β_3 , and β_0 by

$$\beta_1 = (1 - 2K_2 - K_3 + 3K_2 K_3) \alpha_3 \quad (3.5a)$$

$$\beta_2 = N_{A0}^{1-K_2} (K_2 - 2K_3) \alpha_2 \quad (3.5b)$$

$$\beta_3 = N_{A0}^{1-K_3} K_2 \alpha_1 \quad (3.5c)$$

$$\beta_0 = N_{B0} - 3N_{A0} \quad (3.5d)$$

Substituting Equations (3.4) and (3.5) into (3.3),

$$N_B = \beta_0 + \beta_1 N_A + \beta_2 N_A^{K_2} + \beta_3 N_A^{K_3} \quad (3.6)$$

The $\{\beta\}$ are constant for any given run. Transforming Equation (3.1a) into molar units,

$$-\frac{dN_A}{dt} = \frac{k_1 N_A N_B}{V} \quad (2.5)$$

The integral equation to be solved for k_1 is

$$-\frac{k_1 t}{V} = \int_{N_{A0}}^{N_A} \frac{dN_A}{\beta_0 N_A + \beta_1 N_A^2 + \beta_2 N_A^{K_2+1} + \beta_3 N_A^{K_3+1}} \quad (3.7)$$

Define dimensionless time, t' , by

$$t' = [A]_0 k_1 t \quad (3.8)$$

Substituting Equations (2.17) and (3.8) into (3.7),

$$-t' = \int_1^{y_0} \frac{dy_0}{y_0 (\delta_0 + \beta_1 y_0 + \delta_2 y_0^{K_2} + \delta_3 y_0^{K_3})} \quad (3.9)$$

where

$$\delta_0 = \frac{\beta_0}{N_{A0}} \quad (3.10a)$$

$$\delta_2 = \beta_2 N_{A0}^{K_2-1} \quad (3.10b)$$

$$\delta_3 = \beta_3 N_{A0}^{K_3-1} \quad (3.10c)$$

The denominator cannot be factored and is not integrable by parts. If we let

$$y_0 = e^u \quad (3.11)$$

then the integral in Equation (3.9) can be evaluated with some accuracy if enough terms of the power series in u are employed.

$$y_0 = 1 + u + \frac{u^2}{2} + \dots \quad (3.12)$$

Only the first three terms of the expansion may be used if the approximation to the integrand of Equation (3.9) is to be integrable. Making the substitution

$$y_0 = 1 + u + \frac{u^2}{2}, \quad (3.13)$$

Equation (2.5) is approximated by

$$\begin{aligned} -\frac{du}{dt} \sim (\delta_0 + \beta_1 + \delta_2 + \delta_3) + \frac{u[K_2 - K_2^2 + K_2^2 K_3 - K_3 + K_3^2 - K_2 K_3^2]}{(1 - K_2)(1 - K_3)(K_2 - K_3)} \\ + \frac{u^2[K_2 - 2K_2^2 + K_2 K_3 + K_2^2 K_3 - K_3 + K_3^2 - 2K_2 K_3^2 + K_2^3 - K_2^2 K_3 + K_2 K_3^2]}{2(1 - K_2)(1 - K_3)(K_2 - K_3)} \end{aligned} \quad (3.14)$$

Equation (3.14) is soluble, but is only applicable when $|u|$ is small; that is, for low conversions.

As the analytic integration of Equation (2.5) appears impossible, it is very doubtful that the rate equations governing the concentrations of any of the other components are soluble, as the integrals arrived at would be even more complex than that in Equation (3.7). Even if a solution were obtained, the implicit equations which would have to be solved for y_0 would be formidable. For these reasons, a partly empirical approach appeared more promising.

2. Derivation of the Form of the Solution

a. Numerical Integration. The time-composition data given in the literature cover only a small range of K_2 and K_3 , and are subject to experimental errors. It was decided to integrate numerically Equations (3.1) for a wide range of initial conditions and values of the $\{K_i\}$. So that the results could be applied to a wide variety of systems, the equations were first

put into dimensionless form. Define

$$y_i = \frac{[P_i]}{[A]_0} \quad (i=0, \dots, 3) \quad (3.15)$$

$$K_i = \frac{k_i}{k_1} \quad (3.16)$$

$$\beta = \frac{[B]}{[A]_0} \quad (3.17)$$

Equations (3.1) then become

$$-\frac{dy_0}{dt'} = y_0 \beta \quad (3.18a)$$

$$-\frac{dy_i}{dt'} = K_{i+1} y_i \beta - K_i y_{i-1} \beta \quad (3.18b)$$

$$-\frac{d\beta}{dt'} = \beta \sum_{i=0}^2 K_{i+1} y_i \quad (3.18c)$$

(1). Analog Computer. For the non-analytical solution of a simple set of ordinary non-linear differential equations, such as Equations (3.18), the electronic differential analyzer is a useful tool. An LM10 computer with a servomultiplier was used for preliminary studies. Figure 3.1 shows the electronic circuit employed and Figure 3.2 is a Brush recording for a typical set of initial conditions and rate constant ratios.

(2). Digital Computer. The results obtained on the analog computer were confirmed and numerical solutions obtained on the IBM 650 Data Processing Machine. The program used is listed in Appendix A1, with a more thorough discussion than is permitted here. The computer reads the initial values of y_0 , y_1 , y_2 , y_3 , β , and t' ; the values of K_2 and K_3 ; and the time interval for punchout, $\Delta t'$. At integral multiples of $\Delta t'$, the Runge-Kutta-computed compositions are punched out. It was assumed here that only A and B were present at zero time. The initial value of y_0 , y_{00} , is identically unity; β_0 was

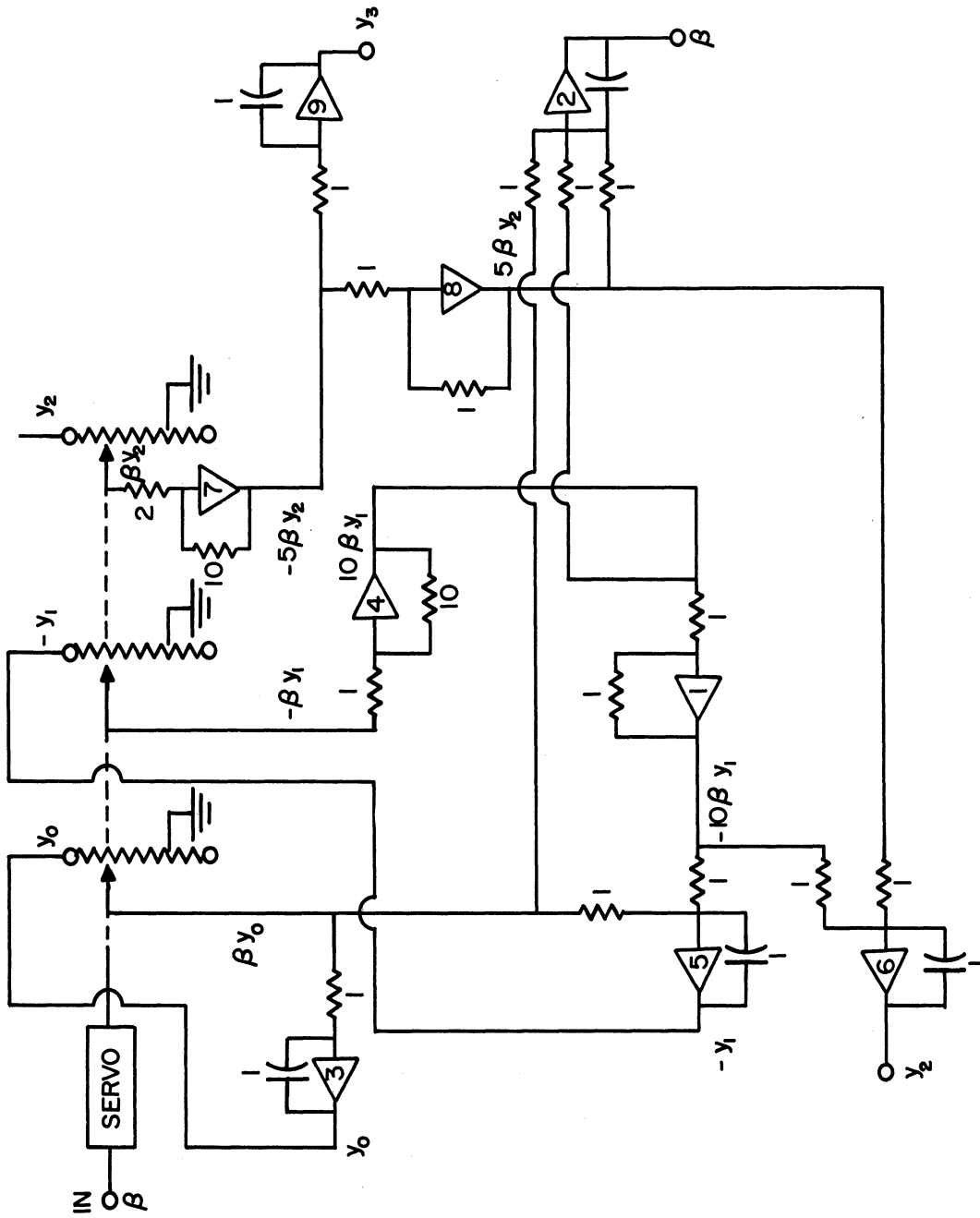


Figure 3.1. Analog Computer Circuit for Solution of Rate Equations.

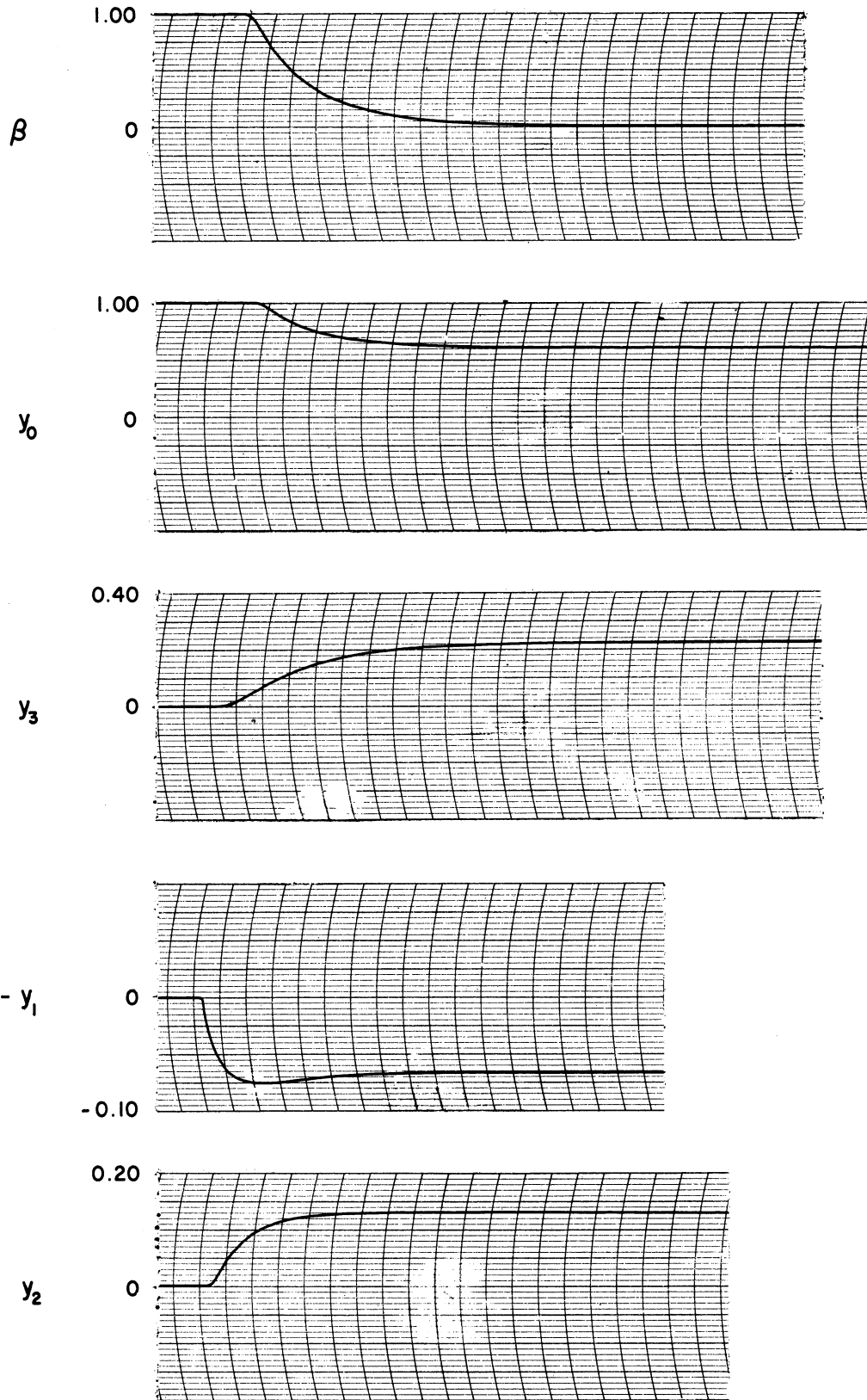


Figure 3.2. Typical Analog Computer Output.

$K_2 = 10$
 $K_3 = 5$
 $\beta_0 = 1$

taken as 1, 1/2, 1/3, 1/4, and 1/5; K_2 as 0.01, 0.1, 1, and 10; and K_3 as 0 and 5. Part of the output from these data production runs is given in Appendix B.

The program was checked by comparing its output with the solutions of the difference equations for a pair of consecutive competitive reactions.

TABLE III.2. DIFFERENCE CHECK ON PROGRAM 1

$$t_1 = 0.64583$$

$$t_2 = 0.65625$$

$$k_1 = 1.010$$

$$k_2 = 10.10$$

Component	Initial concentration	Final Concentration Computed	Equation (3.19)
A	0.1984	0.1973	0.1974
B	0.5135	0.5113	0.5113
P_1	0.02165	0.02155	0.02155
P_2	0.08992	0.09109	0.09108

$$[A]_2 - [A]_1 = \Delta[A] = -k_1[A]_1[B]_1(t_2 - t_1) \quad (3.19a)$$

$$[P_2]_2 - [P_2]_1 = \Delta[P_2] = k_2[P_1]_1[B]_1(t_2 - t_1) \quad (3.19b)$$

$$[P_1]_2 - [P_1]_1 = \Delta[P_1] = -\Delta[A] - \Delta[P_2] \quad (3.19c)$$

$$[B]_2 - [B]_1 = \Delta[B] = \Delta[A] - \Delta[P_2] \quad (3.19d)$$

where $\hat{2}$ = measurements made at time t_2
 $\hat{1}$ = measurements made at time t_1 , shortly before t_2 .

The results of this check are given in Table III.2; the computer solution clearly fits Equations (3.19) very well.

b. Derivation of Form. When no P_i is present at the start of the reaction, y_0 is a function of only β_0 , t' , and the $\{K_i\}$. Once y_0 is found, the time-independent product-distribution equations described earlier may be applied to find the concentrations of the several products. The equations giving the $\{y_i\}$ as functions of y_0 and the $\{K_i\}$ can be obtained readily from those reported by Fuoss, by setting $K_4 = 0$.

$$y_1 = \frac{y_0 - y_0^{K_2}}{K_2 - 1} \quad (3.20a)$$

$$y_2 = \frac{K_2^2 y_0 - K_2 K_3 y_0^{K_2} + K_3 K_2 y_0^{K_2} - K_2 y_0^{K_2}}{(1 - K_3)(1 - K_2)(K_2 - K_3)} + \frac{K_2 y_0^{K_3}}{(K_3 - 1)(K_3 - K_2)} \quad (3.20b)$$

$$y_3 = 1 - y_0 - y_1 - y_2 \quad (3.20c)$$

When $K_2 = 1$, application of l'Hopital's rule gives

$$y_1 = -y_0 \ln y_0 \quad (3.21a)$$

$$y_2 = \frac{y_0^{K_3} - y_0}{(K_3 - 1)^2} - \frac{y_0 \ln y_0}{K_3 - 1} \quad (3.21b)$$

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.

Low K_2 : When K_2 is less than 0.2, the time dependence of y_0 may safely be approximated by neglecting the second reaction; the concentrations of higher products are found from Equations (3.20). For small K_2 and $\beta_0 \neq 1$ (22),

$$y_0 = \frac{(\beta_0 - 1)e^{t'(1 - \beta_0)}}{\beta_0 - e^{t'(1 - \beta_0)}} \quad (3.22a)$$

When $\beta_0 = 1$,

$$y_0 = \frac{1}{t' + 1} \quad (3.22b)$$

Large K_2 . Define the rate of disappearance of P_i by the equation

$$r_i = -\frac{dy_i}{dt} = \beta f(K_i, y_j) \quad (i=1,2,3); (j=0,1,2) \quad (3.23)$$

where f = a function described by Equations (3.18). A material balance on B gives

$$\beta = \beta_0 - \sum_{i=1}^3 i y_i = \beta_0 - g(y_0, K_i) \quad (i=1,2,3) \quad (3.24)$$

where g = a function described by Equations (3.20). $g'(y_0)$ is everywhere positive and finite for all finite K_i , so y_0 is a single-valued function of $\beta_0 - \beta$.

$$y_0 = g^{-1}(\beta - \beta_0, K_i) \quad (i=1,2,3) \quad (3.25)$$

Equations (3.20) and (3.25) 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 $\beta_0 - \beta$ alone. Equation (3.23) indicates that the effect of raising β_0 is simply to shorten the time required to reach a given B-free product distribution. This being the case, it should be possible to relate the solutions of Equations (3.18) for any runs in which the $\{K_i\}$ are the same, in terms of the values of β_0 for each one.

Let us denote by the subscript, r , a reference run, for which $\beta_0 = 1$. Let t_r^y be the time required to reach a given y_0 when $\beta_0 = 1$. Let t' be the time required to reach this same value of y_0 , for an arbitrary

initial β , β_0 . As y_0 is the same in each case, from Equation (3.24) the decrease in β must also be the same; call it B. Then,

$$\frac{n_i}{n_{in}} = \frac{\beta}{\beta_n} = \frac{\beta_0 - B}{1 - B} = \frac{dt'_n}{dt'_i} \quad (3.26)$$

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

$$\int_0^{t'} dt' = t' = \int_0^{t'_n} \frac{(1-B)}{(\beta_0 - B)} dt'_n \quad (3.27)$$

If B is known as a function of time for the reference run, t' can be found as a function of t'_r and β_0 , thus relating all runs with the same rate constants. For the reference case,

$$B = 1 - \beta_n \quad (3.28)$$

Equation (3.27) then becomes

$$t' = t'_n + (1 - \beta_0) \int_0^{t'_n} \frac{dt'_n}{\beta_0 - 1 + \beta_n} \quad (3.29)$$

To evaluate the integral in Equation (3.29), it is required to assume some relationship between β_r and t'_r . The functions proposed to represent the data in Appendix B are listed below.

$$\beta_n = e^{-bt'_n} \quad (3.30)$$

$$\beta_n = ae^{-dt'_n} + (1-a)e^{-bt'_n} \quad (3.31)$$

$$\frac{1}{\beta_n} = t'_n + 1 \quad (3.32)$$

$$\frac{1}{\beta_n} = (t'_n)^b + 1 \quad (3.33)$$

$$\frac{1}{\beta_n} = ae^{bt'_n} + 1 - a \quad (3.34)$$

$$\frac{1}{\beta_n} = ae^{bt'_n} - (a-1)e^{-dt'_n} \quad (3.35)$$

where b, a, d, e = parameters of the approximations.

Of these, Equation (3.30) is the simplest and, for sufficiently large K_2 , satisfactorily represents the rate of disappearance of B. In Figure 3.3, $\log \beta_r$ is plotted against t'_r for four reference runs; the graphs are nearly linear. Substituting Equation (3.30) into (3.29), and integrating,

$$t'_n = -\frac{1}{b} \ln(\beta_0 e^{-bt'} - \beta_0 + 1). \quad (3.36)$$

This simplifies, for $\beta_0 = 1$, to

$$t'_n = t'. \quad (3.37)$$

Equation (3.18a) becomes, for the reference case,

$$-\frac{dy_{0n}}{dt'_n} = y_{0n} \beta_n. \quad (3.38)$$

Substituting Equation (3.36) into (3.38), separating variables, and integrating,

$$y_{0n} = \exp\left[\frac{1}{b}(e^{-bt'_n} - 1)\right] \quad (3.39)$$

But this value of y_0 obtains for any t' and β_0 which satisfy Equation (3.36).

Substitution of Equation (3.36) into (3.39) and (3.30) gives, respectively,

$$y_0 = \exp\left[\frac{\beta_0}{b}(e^{-bt'} - 1)\right] \quad (3.40)$$

$$\beta = \beta_0 e^{-bt'} \quad (3.41)$$

Equation (3.40) gives y_0 as a function of β_0 , t' , and a fitting constant, b, which depends on only the $\{K_i\}$. Before applying this equation to problems in correlation and design, it is informative to compare the time-dependence of the concentrations of the various components in the reaction mix as predicted by this model with the time-dependences that are known to characterize the true solutions of the differential equations.

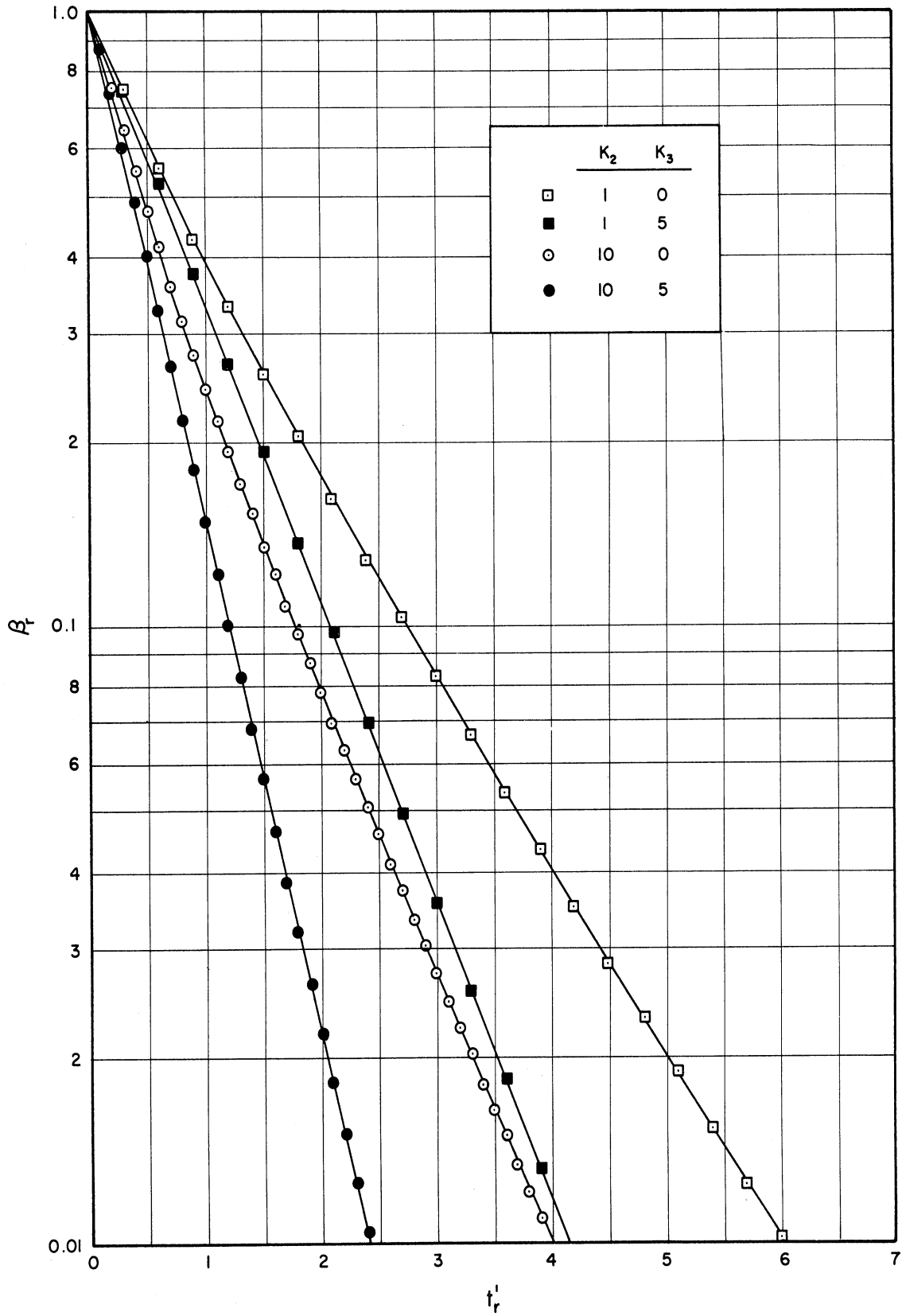


Figure 3.3 Dimensionless Concentration of B versus Dimensionless Time -- High K_2 Reference Runs.

The rate of disappearance of A is obtained by differentiating y_0 , as given by Equation (3.40), with respect to t' .

$$r_0 = -\frac{dy_0}{dt'} = y_0 \beta_0 e^{-bt'} = y_0 \beta \quad (3.42)$$

This is in agreement with Equation (3.18a). If β_0 is less than three, all the B will eventually be consumed and there will be no further reaction.

Therefore y_0 should approach an asymptotic positive value for large time.

From Equation (3.40),

$$y_{0\infty} = e^{-\frac{\beta_0}{b}} \quad (3.43)$$

It is also known that if y_1 is plotted against time, a maximum and a point of inflection are indicated if β_0 is large enough. From Equation (3.20a),

$$y_1 \propto (y_0 - y_0^{K_2}) \quad (3.44)$$

Then, differentiating, and using Equation (3.42),

$$\frac{dy_1}{dt'} \propto -y_0 \beta_0 e^{-bt'} + K_2 y_0^{K_2} \beta_0 e^{-bt'} \quad (3.45)$$

Further differentiation of Equation (3.42) gives

$$\frac{d^2 y_0}{dt'^2} = y_0 \beta_0^2 e^{-2bt'} + y_0 \beta_0 e^{-bt'} \quad (3.46)$$

Differentiating Equation (3.45), and using Equations (3.42) and (3.46),

$$\frac{d^2 y_1}{dt'^2} \propto y_0 \beta_0^2 e^{-2bt'} + y_0 \beta_0 e^{-bt'} - K_2 y_0^{K_2} \beta_0 e^{-bt'} - K_2 y_0^{K_2} \beta_0^2 e^{-2bt'} \quad (3.47)$$

At the inflection point,

$$\frac{d^2 y_1}{dt'^2} = 0 \quad (3.48)$$

By substituting Equation (3.41) into (3.47) and simplifying, the inflection point is found to occur when

$$y_0^{K_2-1} = \frac{\beta + b}{K_2^2 \beta + K_2 b} \quad (3.49)$$

As the reaction proceeds, y_0 and β decrease continuously. The right-hand side of Equation (3.49) also varies in a continuous fashion, as can be seen from Equation (3.50)

$$\frac{d\left[\frac{\beta+b}{K_2^2\beta+K_2b}\right]}{dt'} = \frac{d\left[\frac{\beta+b}{K_2^2\beta+K_2b}\right]}{d\beta} \frac{d\beta}{dt'} = -b\beta \left[\frac{b(K_2-K_2^2)}{(K_2^2\beta+K_2b)^2} \right] \begin{matrix} \equiv < 0, K_2 < 1 \\ \equiv > 0, K_2 > 1 \end{matrix} \quad (3.50)$$

As time goes from zero to infinity, $y_0^{K_2-1}$ goes from unity to $\exp(-(K_2-1)\beta_0/b)$ and $\frac{\beta+b}{K_2^2\beta+K_2b}$ varies from $\frac{\beta_0+b}{K_2^2\beta_0+K_2b}$ to $1/K_2$. If K_2 is less than one, β_0 is large enough to allow the inflection point to be reached if

$$e^{-\frac{(K_2-1)\beta_0}{b}} \geq \frac{\beta_0+b}{K_2^2\beta_0+K_2b} \quad (3.51)$$

The inequality sign is reversed if K_2 is greater than one.

From Equation (3.45), a maximum value of y_1 obtains when

$$y_0^{K_2-1} = \frac{1}{K_2} \quad (3.52)$$

This agrees with Equation (2.13), as reported by Riggs. The relationship between the maximum and inflection point of y_1 is shown more clearly in Figures 3.4.

If an inflection in y_1 is observed, it occurs beyond the maximum; this is in agreement with theory. Similar considerations apply to y_2 , which exhibits two inflections, but the mathematics is considerably more complex and will not be given here.

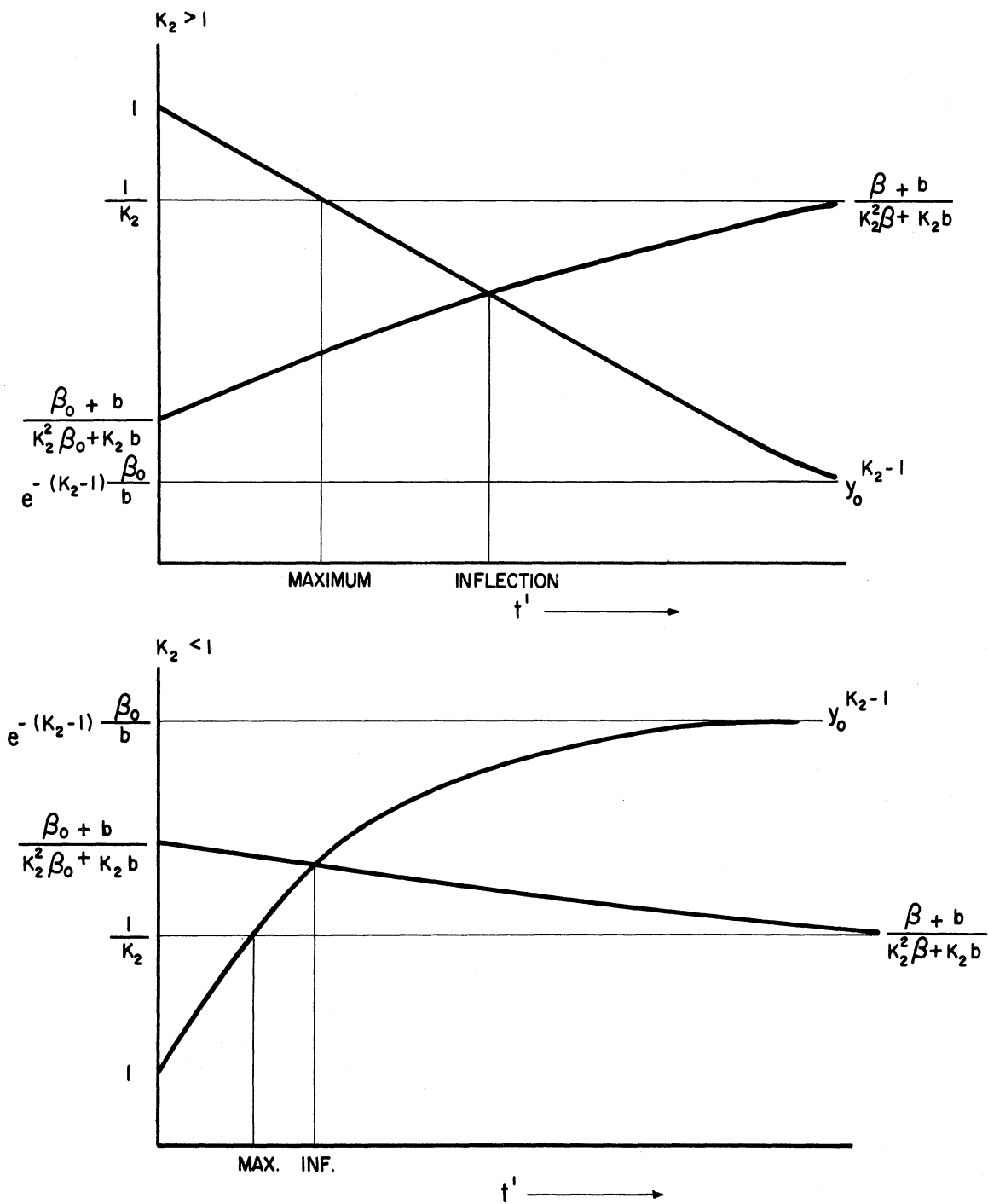


Figure 3.4 Relationship of Maximum and Inflection Point of the Dimensionless Concentration of the First Product.

3. Fitting the Explicit Solution to the Numerically-Integrated Solution

In the derivation of the approximate solution given by Equation (3.40), only one curve fitting constant, b , was proposed. This parameter is a function of only the $\{K_i\}$. The nature of this dependence was found by fitting the data of Appendix B and additional data, for $K_2 = 3$, to Equation (3.40) by using the Method of Least Squares, as described in Appendix F. Program 3, in Appendix A, was used for this purpose. The deviation was defined by

$$D = \sum_{\substack{\text{all} \\ \text{data}}} (\hat{y}_0 - y_{0P})^2 \quad (3.53)$$

where \hat{y}_0 = datum obtained by numerical integration
 y_{0P} = datum obtained from Equation (3.40) .

The zero of $\partial D / \partial b$ was found by using Newton's method as detailed in Appendix F. The first guesses at b for each set of $\{K_i\}$, were estimated from semilogarithmic plots of β versus t' , of which Figures 3.3 are typical. Program 3 was written for the IBM 704 Data Processing System; the output from Program 1 was in the form of punched cards, coded in a fashion suitable for IBM 650, and not 704, input. These cards were used as data for a second 650 program, which read in the Program 1 output, and punched out a new set of cards compatible with the input format used by Program 3. This reformulation program is described in greater detail as Program 2 in Appendix A. Figure 3.5 shows the variation of b with K_2 for K_3 -values of zero, three and five. The values of b computed by Program 3 for $K_2 \geq 0.1$ were correlated by a second-degree multinomial in K_3 and $\log K_2$. This is an example of the functional fit approach described in Appendix F. There is no theoretical basis for this correlation; its value lies solely in the accuracy with

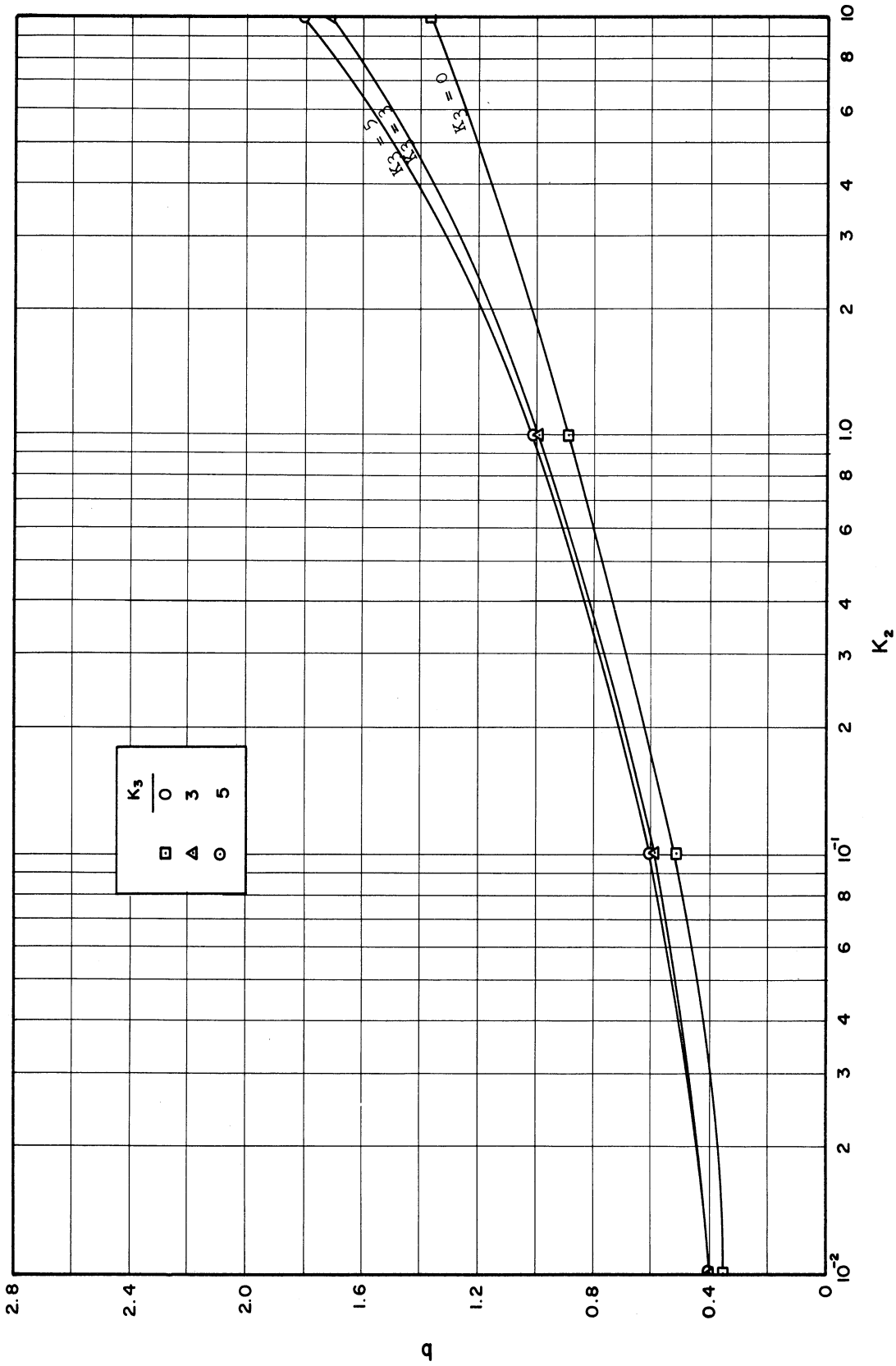


Figure 3.5 Parameter of the Approximation versus K_2 , the Ratio of the Rate Constant for the Second Reaction to That for the First Reaction.

which it represents the dependence of b on the $\{K_i\}$.

$$\begin{aligned}
 b = & 0.897 + 0.429 \log K_2 + 0.053 \log^2 K_2 \\
 & + (0.0736 + 0.0632 \log K_2 + 0.0273 \log^2 K_2) \times K_3 \\
 & - (0.0072 + 0.00545 \log K_2 + 0.00262 \log^2 K_2) \times K_3^2
 \end{aligned}
 \tag{3.54}$$

4. Accuracy of the Explicit Solution

a. Range of Applicability. The least squares program for b also computed the standard error of prediction, σ_{pred} , of y_0 .

$$\sigma_{\text{pred}} = \sqrt{\frac{D}{N+1}}
 \tag{3.55}$$

where N = number of y_0 data used .

The output from Program 2 was given to Program 4, which computed the standard error of prediction introduced by using the low- K_2 correlation given by Equations (3.22). The resulting standard errors, and the computed b -values, are listed in Table III.3. Figure 3.6 is a plot of σ_{pred} versus K_2 for two values of K_3 and for the two correlation schemes. The low- K_2 correlation can be used when K_2 is less than 0.12, for $K_3 = 0$; or less than 0.04, when $K_3 = 5$.

For very large K_2 , the solution should be asymptotic to a termolecular reaction with unit rate constant.



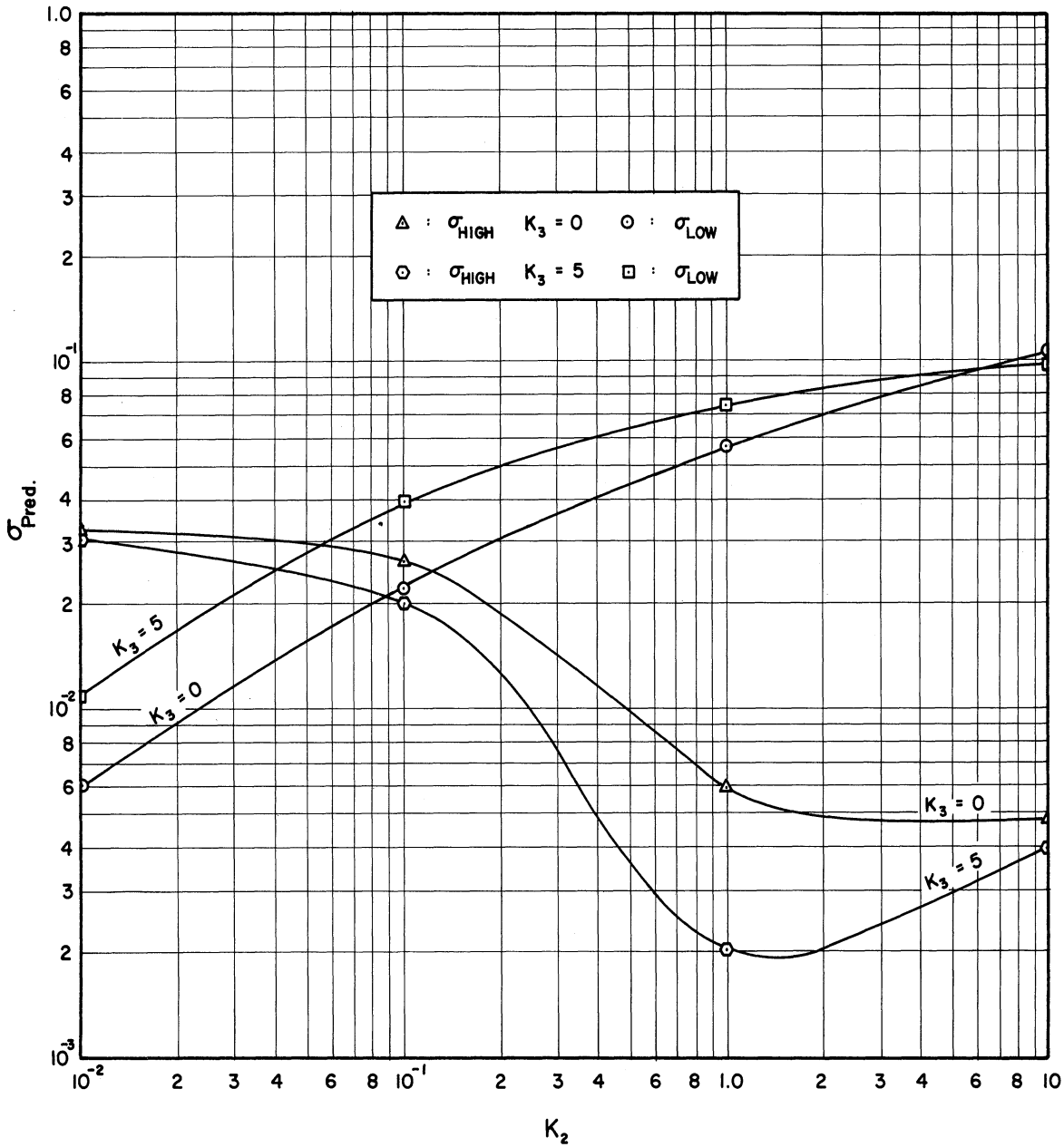


Figure 3.6. σ_{pred} vs. K_2 for High- K_2 and Low- K_2 Correlations.

Integration of the rate equation gives⁽²²⁾

$$t' = \frac{1}{1-\beta_0} \left[\frac{2(1-y_0)}{\beta_0(\beta_0-2+2y_0)} + \frac{1}{\beta_0-2} \ln \left(\frac{\beta_0 y_0}{\beta_0-2+2y_0} \right) \right] \quad (3.57)$$

TABLE III.3. COMPARISON OF HIGH- K_2 AND LOW- K_2 CORRELATION SCHEMES

K_2	K_3	$\sigma_{\text{low } K_2}$	$\sigma_{\text{high } K_2}$	b
0.01	0	0.006	0.033	0.355
0.01	5	0.011	0.032	0.387
0.1	0	0.022	0.026	0.521
0.1	3			0.593
0.1	5	0.039	0.020	0.601
1	0	0.056	0.006	0.897
1	3			1.053
1	5	0.074	0.002	1.085
10	0	0.106	0.005	1.379
10	3			1.734
10	5	0.099	0.004	1.818

y_0 cannot be solved for as an explicit function of time; it was therefore decided not to use this correlation in the study. As the largest value of K_2 indicated in Table III.1 is six, further correlation work for large K_2 seems unwarranted.

b. Error Propagation

The maximum standard error of prediction of y_0 is about 0.03; let us look for a moment at the average error induced in the y_i , which we shall call $\bar{\epsilon}_i$. For small errors in y_0 ,

$$\epsilon_i = \epsilon_0 \frac{dy_i}{dy_0} \quad (3.58)$$

where ϵ_0 is the error in y_0 , and ϵ_i the corresponding error in y_i . Define $\bar{\epsilon}_i$ as ϵ_i averaged over y_0 .

$$\bar{\epsilon}_i = \frac{1}{1-y_{0\infty}} \int_0^{y_{1\infty}} \epsilon_i dy_0 \quad (3.59)$$

Substituting Equation (3.58) into (3.59), and replacing y_0 by y_i as the variable of integration,

$$\bar{\epsilon}_i = \frac{\epsilon_0}{1-y_{0\infty}} \int_0^{y_{1\infty}} dy_i = \frac{\epsilon_0 y_{1\infty}}{1-y_{0\infty}} \quad (3.60)$$

or

$$\frac{\bar{\epsilon}_i}{\epsilon_0} = \frac{y_{1\infty}}{1-y_{0\infty}} \quad (3.61)$$

As only A and B are initially present,

$$1-y_{0\infty} = y_{1\infty} + y_{2\infty} + y_{3\infty} = \sum_{i=1}^3 y_{i\infty} \quad (3.62)$$

and

$$\frac{\bar{\epsilon}_i}{\epsilon_0} = \frac{y_{i\infty}}{\sum_{i=1}^3 y_{i\infty}} \quad (3.63)$$

The right-hand side of Equation (3.63) is clearly less than unity, so the average error induced in y_i is less than that in y_0 .

B. Data Correlation

It is possible, using the product distribution equations described in Chapter II and the approximate time-dependent solution introduced in the first half of this chapter, to 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. By using 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 empirical and theoretical models is obtained. Glaring difficulties in fit, beyond those indicated in Table III.3, can be evidence of poor experimental method or a deviation between the true reaction mechanism and that required by Equations (3.1).

Two methods will be used to find the rate constants from experimental data: a differential approach, and an integral method. In Part 1 below, experimental rate data will be differenced and fit to Equations (3.19). In Part 2, the $\{K_i\}$ will be found by fitting product distribution data to Equations (3.20); Part 3 describes the fitting of time-composition data to the empirical model derived above. An integral fit is used in these last two methods, as integrated solutions or approximations to the solutions of the rate equations are employed.

1. Differential Treatment of the Rate Equations to Find Rate Constants

Three 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.

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

t_j to t_{j+1} , by

$$\bar{r}_{cij} = -\frac{\Delta[P_i]}{\Delta t} = \frac{[P_i]_j - [P_i]_{j+1}}{t_{j+1} - t_j} \quad (3.64)$$

where

r_{cij} = defined rate
 $\bar{\quad}$ = average value .

When dimensionless concentrations are used, this average rate is given by

$$\bar{r}_{mij} = -\frac{\Delta y_i}{\Delta t} = \frac{y_{ij} - y_{i,j+1}}{t_{j+1} - t_j} \quad (3.65)$$

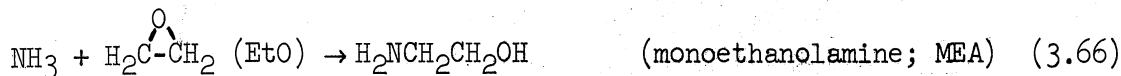
- b. Plot \bar{r}_{ij} against t . If \bar{r}_i is the ordinate, this plot consists of a set of horizontal lines of height r_{ij} , each extending from t_j to t_{j+1} .
- c. Draw a smooth curve through this difference plot. This curve is a graph of the true reaction rate, r_{ci} or r_{mi} , versus time. Construct reaction rate plots for each reacting component.
- d. At each experimental point, use Equations (3.1) to obtain the rate constants.

a. 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. Potter⁽³⁵⁾, when studying the production of ethanamine from ethylene oxide and ammonium hydroxide at 20°C, mixed the two

reactants and withdrew samples at intervals. The chemical reactions are



The experimental data on this system are given in Appendix E.

From Equations (3.1), (3.15) and (3.17),

$$r_{m0} = -\frac{dy_0}{dt} = k_1 [A]_0 y_0 \beta. \quad (3.69)$$

$-\Delta y_0/\Delta t$ is plotted against t in Figure 3.7, and the smoothed curve is also indicated. The $\{t_j\}$ were chosen to minimize the effects of experimental error on the difference plot. The $\{r_{m0}\}$ were found from the smoothed curve and, at each experimental point, k_1 was computed from Equation (3.69). Equation (3.70) was used to estimate the best value of k_1 ; the indicated summations were taken to minimize the effects of errors in y_0 late in the reaction.

$$\bar{k}_1 = \frac{\sum_j r_{m0j}}{[A]_0 \sum_j y_{0j} \beta_j} \quad (3.70)$$

r_{m1} is given by

$$r_{m1} = -\frac{dy_1}{dt} = [A]_0 k_2 y_1 \beta + \frac{dy_0}{dt}. \quad (3.71)$$

To find k_2 , Equation (3.72) was used.

$$\bar{k}_2 = \frac{-\sum_j \left(\frac{dy_{0j}}{dt} + \frac{dy_{1j}}{dt} \right)}{[A]_0 \sum_j y_{1j} \beta_j} \quad (3.72)$$

The plots of $-\Delta y_1/\Delta t$ and $-dy_1/dt$ against time are included as Figure 3.8.

Figure 3.9 shows the difference and derivative plots for y_2 . Equation (3.73)

was used to find k_3 .

$$\bar{k}_3 = \frac{-\sum_j \left(\frac{dy_{1j}}{dt} + \frac{dy_{0j}}{dt} + \frac{dy_{2j}}{dt} \right)}{[A]_0 \sum_j y_{2j} \beta_j} \quad (3.73)$$

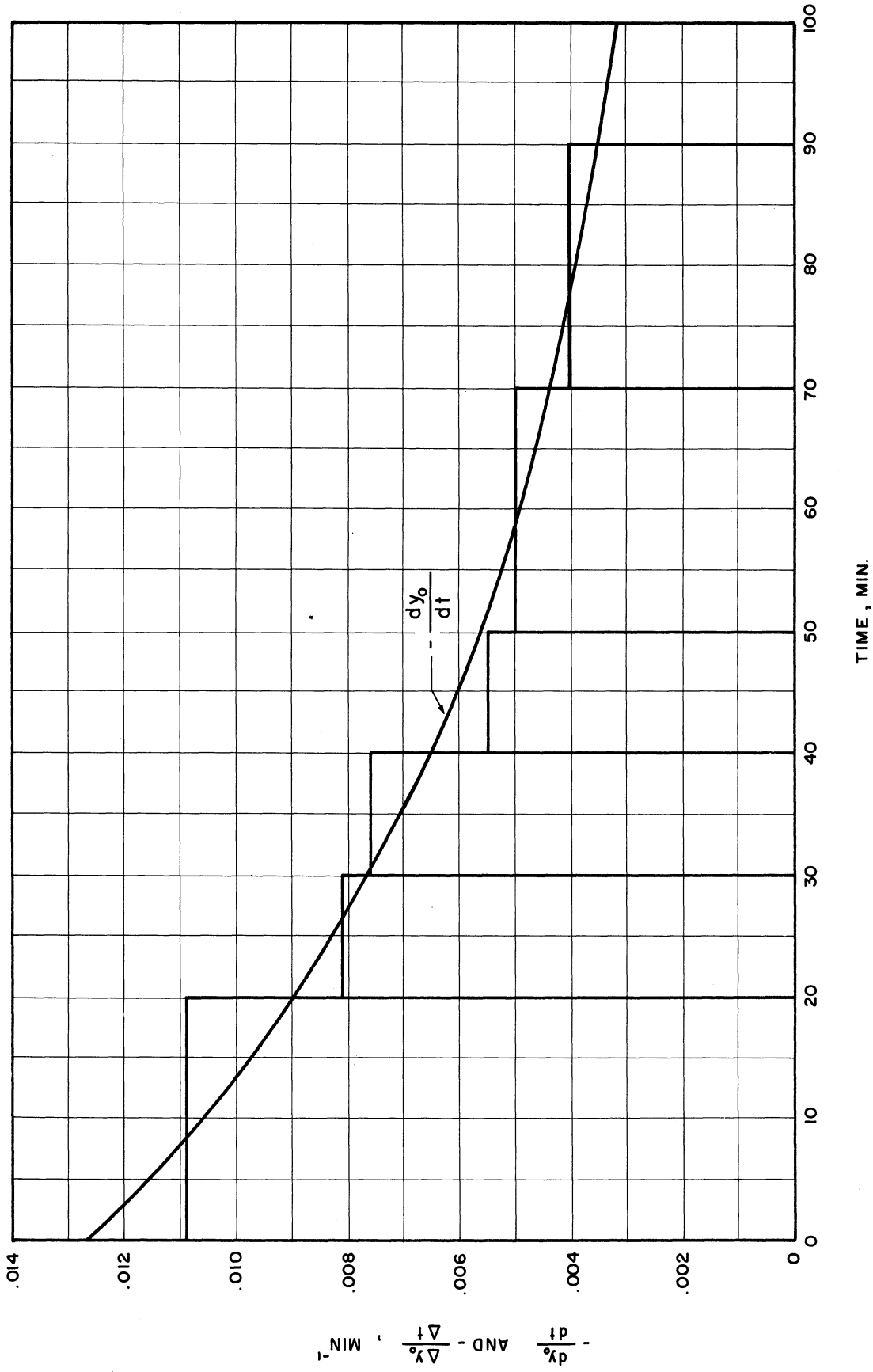


Figure 3.7. Difference Plot for First Reaction in Ethanolamine Synthesis at 20°C.

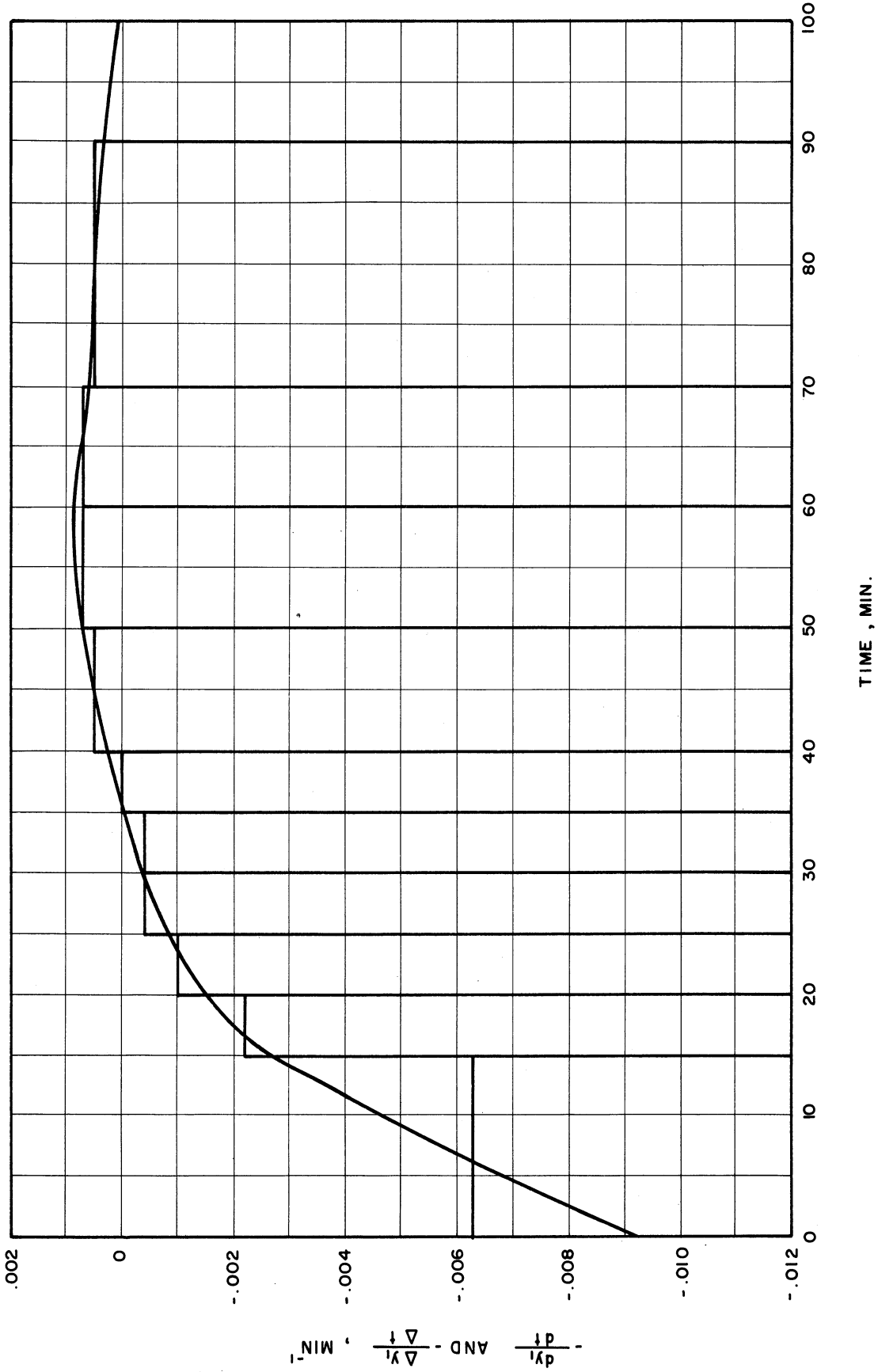


Figure 3.8. Difference Plot for Second Reaction in Ethanolamine Synthesis at 20°C.

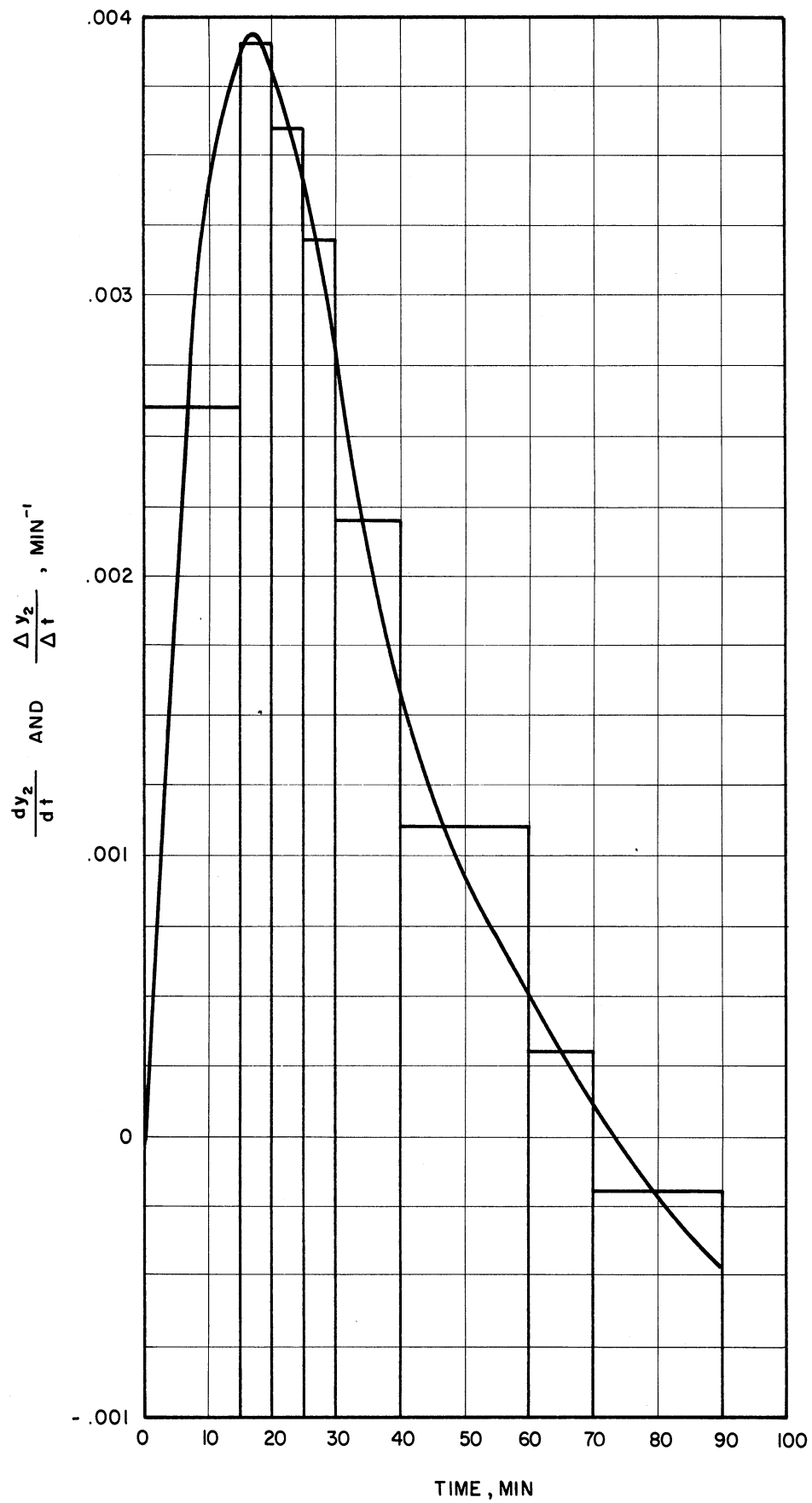


Figure 3.9. Difference Plot for Third Reaction in Ethanolamine Synthesis at 20°C.

The values of the $\{k_i\}$ found in this way are listed in Table III.5.

b. Approximate Treatment when Data Are Based on Various Initial Conditions

The usefulness of Equations (3.64) and (3.65) for estimating average reaction rates is based on the assumption that the differences between the compositions of two reaction mixes, taken at different times after the reactants have been mixed, are due solely to the greater amount of reaction which has taken place in the sample withdrawn at the later time. But this is only true if the initial conditions, particularly β_0 , for the two runs are the same. If it is desired to correlate a set of data, obtained at various times, from reaction mixes not having common initial conditions, we cannot simply list the runs in order of increasing time and apply the difference equations. A correction must be applied, taking into account the β_0 associated with each run.

When the $\{\beta_0\}$ are not identical throughout, the times at which each sample is taken are changed to the times at which the same product distribution would obtain if β_0 were equal to some reference value. For a reference value of β_0 equal to unity, Equation (3.36) applies.

$$t'_n = -\frac{1}{b} \ln \left[\beta_0 e^{-bt'} - \beta_0 + 1 \right] \quad (3.36)$$

The procedure to be employed is:

- a. Start with a set of guesses at the $\{k_i\}$, given by $k_1^{(1)}$, $K_2^{(1)}$ and $K_3^{(1)}$.
- b. Compute $b^{(1)}$ from Equation (3.54).
- c. Compute $t'^{(1)}$ for each run from Equation (3.8), using $k_1^{(1)}$ and the initial conditions for each run.

d. Compute t_r' for each run, using Equation (3.36).

e. Compute $\beta_r^{(1)}$ for each run.

$$\beta_r^{(1)} = 1 - (\beta_0 - \beta) \quad (3.74)$$

where β_0 = initial molar ratio for the run in question
 β = dimensionless concentration of B for the run in question, at the sampling time.

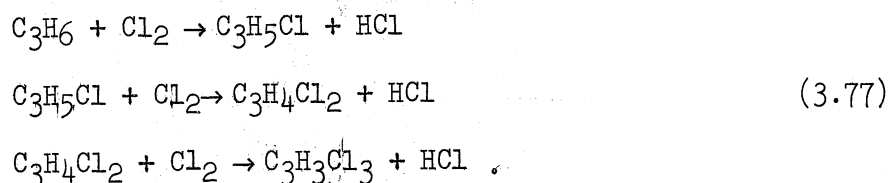
f. Proceed as in the exact differential treatment described above, using t_r' instead of t as the independent variable. The rates to be determined by difference will be the dimensionless ones defined by Equation (3.23). The equations for $k_1^{(2)}$, $K_2^{(2)}$, and

$$k_1^{(2)} = \frac{\sum_j \left(\frac{dy_1}{dt_r'} \right)_j^{(1)}}{\sum_j y_{1j} \beta_{rj}^{(1)}} k_1^{(1)} \quad (3.75) \quad K_2^{(2)} = \frac{\sum_j \left(\left(\frac{dy_1}{dt_r'} \right)_j^{(1)} + \left(\frac{dy_0}{dt_r'} \right)_j^{(1)} \right)}{\sum_j y_{1j} \beta_{rj}^{(1)}} \quad (3.76a)$$

$$K_3^{(2)} = \frac{\sum_j \left(\left(\frac{dy_1}{dt_r'} \right)_j^{(1)} + \left(\frac{dy_0}{dt_r'} \right)_j^{(1)} + \left(\frac{dy_2}{dt_r'} \right)_j^{(1)} \right)}{\sum_j y_{2j} \beta_{rj}^{(1)}} \quad (3.76b)$$

The best estimates of the rate constants have been found when $k_1^{(2)}$ equals $k_1^{(1)}$, $K_2^{(2)}$ equals $K_2^{(1)}$, and $K_3^{(2)}$ equals $K_3^{(1)}$. 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 derived earlier, and used to reduce the times to the reference case.

This method of solution was applied to the data of Groll and Hearne⁽¹⁷⁾ on the substitutive chlorination of propylene at 525°C; these data are given in Appendix E. The reactions are



Four guesses were made at the $\{k_i\}$, and four sets of $\{k_i^{(2)}\}$ obtained. As the guesses were rather close together, a first-degree functional fit was assumed to define the dependence of the computed $\{k_i\}$ on the guessed values.

The equations arrived at were

$$k_1^{(2)} = 0.248k_1^{(1)} + 230K_2^{(1)} + 29.2K_3^{(1)} + 307 \quad (3.78)$$

$$K_2^{(2)} = -0.001425k_1^{(1)} + 0.390K_2^{(1)} + 0.1211K_3^{(1)} + 1.740 \quad (3.79a)$$

$$K_3^{(2)} = 0.000438k_1^{(1)} + 3.97K_2^{(1)} - 0.268K_3^{(1)} - 3.31 \quad (3.79b)$$

where k_1 = rate constant for the first reaction, l/gmol-sec.

The rate constants found by equating $\{k_i^{(1)}\}$ to $\{k_i^{(2)}\}$ in the equations above are listed in Table III.5.

c. Exact Treatment when a Portion of the Data Is Based on the Same Initial Conditions

In the inexact method described in Part b above, data obtained from runs for which the β_0 were not all the same were rendered differentiable by reducing the sampling times, through Equation (3.36), to the corresponding times for a reference run. Equation (3.36) is, as indicated earlier, an approximation to an exact integral relationship between t' and t_r' , given by Equation (3.29). For this reason, only approximate rate data are differentiated when Equation (3.36) is used and the estimates of the $\{k_i\}$ are inexact. If a fair amount of data has been obtained for a given value of β_0 , say β_{0c} , the integral in Equation (3.29) can be graphically evaluated and the data for β_0 not equal to β_{0c} can be exactly reduced to this common molar ratio. Using real time,

$$t_c = \frac{[A]_{oc}}{[A]_o} \int_0^{t_c} \frac{\beta_c dt_c}{\beta_0 - \beta_{0c} + \beta_c} \quad (3.80)$$

where \hat{c} = conditions for the common run.

It is a simple, but lengthy, matter to reduce the reaction times for those runs in which β_0 is not equal to β_{0c} to the equivalent times for the modal molar ratio. For each value of β_0 different from β_{0c} , the integral in Equation (3.80) is graphically evaluated at a set of values of t_c . Then

$$\int_0^{t_c} \frac{\beta_c dt_c}{\beta_0 - \beta_{0c} + \beta_c} \text{ is plotted against } t_c. \text{ The value of } t_c \text{ for which}$$

$$\int_0^{t_c} \frac{\beta_c dt_c}{\beta_0 - \beta_{0c} + \beta_c} = \frac{[A]_0 t}{[A]_{0c}} \quad (3.81)$$

is the reference time to be used in the differential solution. When all the data have been reduced to the reference case, they are differenced as in Part a.

The amount of work required when this method is employed is frequently more excessive than is justified by the results. If there are enough data for $\beta_0 = \beta_{0c}$ to allow the evaluation of the integral in Equation (3.80), these data alone could be differentiated directly as in Part a. On the other hand, the use of the additional data provides a check on the assumption that the rate constants are independent of composition.

2. Determination of Relative Magnitudes of Rate Constants from Product Distribution Data

The product distribution equations (3.20) can be used to find best values of K_2 and K_3 from experimental data even when the reaction time is unspecified. Frequently, product distributions are given only for the steady state which obtains when all the B in the reaction mix has been consumed; here, time is infinite and k_1 cannot be found. Furthermore, the distribution of converted A among the several products is independent of β_0 , and if only rate constant ratios are to be evaluated, the integral fit to experimental data is considerably simpler than the differential methods described above.

Program 5, in Appendix A, was written to determine rate constant ratios from product distribution data; y_0 , the fraction of A unreacted, is the independent variable, and the $\{K_i\}$ are the parameters of the approximation. The overall deviation was defined by

$$D = \sum_{\text{all data}} \sum_{i=1}^j (\hat{y}_i - y_{iP})^2 \quad (3.82)$$

where y_{iP} = value of y_i predicted by Equation (3.20)
 j = number of reactions .

D is composed of two sums: a constant positive quantity, which is a function of only the $\{y_0\}$ and the $\{\hat{y}_i\}$; and a variable sum, dependent on the values of the $\{K_i\}$. The function to be minimized, called C , was defined as one-half the variable sum of squares

$$C = \sum_{\text{all data}} (y_{1P}^2 + y_{1P}(\hat{y}_3 + y_0 - \hat{y}_1 - 1) + y_{2P}^2 + y_{2P}(y_0 + \hat{y}_3 - \hat{y}_2 - 1) + y_{2P}y_{1P}) \quad (3.83)$$

At the minimum,

$$\frac{\partial C}{\partial K_i} = 0 \quad (i=2, j) \quad (3.84)$$

Newton's method was used to obtain the best values of the $\{K_i\}$; the required second derivatives of C were approximated by difference quotients, as defined in Equation (F.16).

The best $\{K_i\}$ and the associated standard errors of prediction, defined by Equation (3.85), are given in Table III.4, for several different experimental systems.

$$S_e = \sqrt{\frac{D}{j^m - j + 1}} \quad (3.85)$$

where m = number of compositions correlated .

A more complete tabulation of the results is in Appendix C.

The accuracies of the rate constant ratios in Table III.4 vary from system to system and are dependent on many factors. The number of pieces of data employed, the levels of the dimensionless concentrations which are fitted to the product distribution equations, and the experimental error

TABLE III.4. CORRELATION OF PRODUCT DISTRIBUTION DATA

Reaction A B	Conditions	Pieces of Data (m)	K_2 K_3	s_e	Reference
Methanol Propylene Oxide	NaOH catalyst 45°C	12	0.12**** --	0.001	(26,34)
1-methoxy-2-propanol Propylene oxide	NaOH catalyst 60°C	5	1.01**** 1.03****	0.009	(26)
1,3-butanediol Acetic acid	50°C	8	0.62	0.003	(33)
1,4-butanediol Acetic acid	50°C	8	0.50	0.008	(33)
Monoethanolamine Ethylene oxide	10°C	12	0.75 --	0.022	(35)
Ammonium hydroxide Ethylene oxide	10-30°C	36	5.7* 4.3*	0.011	(35)
Carbon tetrachloride Hydrogen fluoride	290-305°C Vapor phase FeCl ₃ -activated carbon catalyst	5	0.56	0.190	(27)
Propylene Chlorine	510-528°C** Atmospheric pressure Flow reactor	5	1.02 1.01	0.011	(17)
Benzene Chlorine	440-450°C** Flow reactor Atmospheric pressure	18	0.48 0.00***	0.015	(30)

* Investigator reported $K_2 = 6$, $K_3 = 4$

** Chlorination found to be entirely substitutive

*** Found by fitting observed trichlorobenzene concentrations

**** Lay⁽²⁶⁾ found values for the rate constant ratios to be, respectively, 0.10, 1.00 and 1.00.

itself, are most important. The accuracy of K_3 depends on these factors and the precision with which K_2 is measured as well.

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 (3.1). The only reaction set which occasions a large s_e is the hydrofluorination of carbon tetrachloride. In the next section, where time is re-introduced as an independent variable, the standard error of prediction will again be computed; the differences between those values and the ones given in Table III.4 are measures of the inability of the approximate model to describe the rate equations.

The rate constant ratios presented in Table III.4 are useful not only for correlation purposes, but also for the insight they lend into the mechanisms of the reactions themselves.

The rate constant ratios for the alkylene oxide additions agree closely with the values obtained by the individual experimenters. Both Potter and Lay used the same product distribution equations as were used in Program 5, so the agreement is not surprising. Potter used a graphical method to estimate the rate constant ratios for the ethanolamine syntheses, so a greater difference between the present and previous work is evident here. The results for the set of reactions initiated by monoethanolamine are consistent with those obtained when ammonia was used as the starting material. No such agreement was observed by Lay, and he postulated a dependence of the rate constants on the methanol concentration; no corresponding argument appears to be required for the ethylene oxide addition.

The study of the reaction between chlorine and benzene indicates that succeeding halogenations of chlorobenzene are increasingly difficult.

This is in agreement with theory^(8A). The rate constant for the acetic acid esterification of the second carboxyl group on the butanediols is about one-half of that for the first reaction, as there are half as many reactive groups on the intermediate product as on the starting material.

A free-radical mechanism is responsible for the propylene-chlorine reactions. Whereas the Freon synthesis cannot be represented by the product distribution equations, the former system appears to fit them quite well. This may be attributed to the relative rates of the steps in the chain mechanism or the use of a catalyst in the latter case. In addition, some question can be raised about the experimental accuracy of the hydrofluorination results. At any rate, the tentative conclusion that all the chlorine atoms add to the three-carbon skeleton with equal ease, is tenable. The electronic effect of the halogens on the number three carbon is minor, in view of the free-radical mechanism of the reaction.

3. Determination of Absolute Magnitudes of Rate Constants from Product Distributions with Times Given

Equations (3.40), (3.41) and (3.20), which describe the approximate solution of the rate equations, can be fitted to experimental data when sampling times, as well as the compositions of the reaction mixes, are given. In Part 2, where these times were not specified, only the rate constant ratios K_2 and K_3 could be determined; when the sampling times are given, k_1 can be found and all the rate constants can be estimated.

a. Choice of Proper Time-Dependence of the Common Reactant

Equations (3.22) and (3.40) approximate the conversion of A for small and large values of K_2 , respectively. When y_0 and the $\{K_i\}$ are

known, Equations (3.20) can be used to find the concentrations of the several products. It now remains to study the equations to be used to describe the amount of B in the reaction mix at any time. The most obvious answer is the material balance equation (3.24). However, the problem is more complex than it might seem; different approaches are required, depending on the size of K_2 .

Low K_2 : When K_2 is small, the yield of products heavier than P_1 is low. If $K_2 = 0$, stoichiometrically equivalent quantities of A and B are consumed.

Then,

$$\beta = \frac{\beta_0^2 - \beta_0}{\beta_0 - e^{t'(1-\beta_0)}} \quad (\beta_0 \neq 1) \quad (3.86)$$

$$\beta = \beta_0 - 1 + \frac{1}{t'+1} \quad (\beta_0 = 1) \quad (3.87)$$

The difference between this value and that obtained from the material balance is given by

$$\Delta\beta = \sum_{i=2}^j i y_i \quad (3.88)$$

When K_2 is small, $\Delta\beta$ is negligible, and Equation (3.86) is a sufficiently accurate representation of the time-dependence of the concentration of B. Furthermore, if Equation (3.86) is used, any solutions derived for this case are directly applicable to the study of a single second-order reaction.

High K_2 : We have already derived an equation relating β to β_0 , t' , and the $\{K_i\}$.

$$\beta = \beta_0 e^{-bt'} \quad (3.41)$$

As this equation is quite different from the material balance equation, use of it would render any results internally inconsistent. If material balance consistency is demanded, Equation (3.24) is to be preferred to (3.41).

However, in describing the consumption of B, we 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 data in Appendix B: one from each run. At each point, β was computed from a material balance, and either from Equation (3.87) or (3.41), depending on the size of K_2 . These values were compared with the true solutions of the differential equations and squared deviations were calculated. The results of an F-test showed that, at ninety per cent confidence, the material balance does not predict β as well as the shorter equations above. For this reason, in the discussion to follow, Equations (3.86) and (3.41), rather than the material balance, will be used to correlate the literature values of β .

b. Correlation of Literature Data

Program 6 was written to determine the best set of rate constants to describe published and experimental kinetic data on systems of consecutive competitive reactions. A detailed description of its operation is given in Appendix A. In the data correlated here, reaction times are given and the absolute magnitudes of the rate constants are estimated. For a given set of rate constants, Equation (3.54) is used to find b ; (3.86) or (3.41) determine β ; (3.22) or (3.40) give y_0 ; and (3.20) is used to compute the product distribution. The creep method described in Appendix F is used to minimize the overall deviation, defined by

$$D = \sum_{\substack{\text{all} \\ \text{data}}} \left((\hat{y}_0 - y_{0p})^2 + (\hat{\beta} - \beta_p)^2 + \sum_{i=1}^j (\hat{y}_i - y_{ip})^2 \right) \quad (3.89)$$

The predicted and observed compositions of the reaction mixes are given in Appendix E; Table III.5 contains a summary of these results. When rate constants have also been computed by differential methods or reported by the experimenter, these values are also included for comparison. A standard error of prediction is also reported; here it is defined by

$$S_e = \sqrt{\frac{D}{m(j+2)-j}} \quad (3.90)$$

The rate constants and rate constant ratios presented in Table III.5 vary in accuracy from system to system for the same reasons that the kinetic data given in Table III.4 possessed differing degrees of exactness. A further inaccuracy is introduced in the present case by the fact that not only are the product distribution equations fitted, but the approximate time-dependent solutions for y_0 and β as well. The rate constant ratios given in the preceding section correlate the product distributions with a much smaller deviation than is observed here and, if the differential rate equations are assumed to hold, are more kinetically significant. The reason for this is simple. The only function of the K_1 in the earlier study was to correlate the product distribution equations, which are exact consequences of the rate equations; in the present case, the $\{K_1\}$ are adjusted not only to describe the product concentrations, but also to give a value of b , through Equation (3.54), which describes as well as possible the time-dependence of the concentrations of the initiating reactants. A compromise is reached in the present correlation between the best values of the rate constant ratios to perform each of these duties and it is not surprising that the compromise values do not fit the product distribution data as well as the values found for that purpose alone.

TABLE III.5 ESTIMATION OF ALL RATE CONSTANTS FOR SELECTED CONSECUTIVE COMPETITIVE REACTIONS

Reaction A B	Temperature*	Pieces of Data (m)	Number of Reactions (j)	Units	k_1 K_2 K_3	s_e	Refer- ence
Benzene Chlorine	450°C	13	2	(1)	11600 0.68	0.032	(30)
					890.**		
Propylene Chlorine	525-528°C	4	3	cgs	1.10 1.446	0.019	(17)
Carbon tetrachloride Hydrogen fluoride	290-300°C	4	2	(2)	227000 1.01	0.162	(27)
Methanol Propylene oxide	45°C	8	2	(2)	0.0174 0.88	0.011	(34)
Ammonium hydroxide Ethylene oxide	10°C	6	3	(1)	0.001254*** 5.7 4.6	0.014	(35)
	20°C	10	3	(1)	0.003872*** **** 6.048 4.529	0.013	(35)
	30°C	3	3	(1)	0.00914*** 5.4 4.5	0.022	(35)

NOTES

Units

- (1): centimeter-gram-minute
- (2): centimeter-gram-hour

Footnotes

- * Other conditions the same as in Table III.4
- ** Values obtained by differentiation: 828, 1.19, 1.40
- *** k_1 reported by investigator: 10°C, 0.001351; 20°C, 0.003880; 30°C, 0.00946
- **** Values obtained by differentiation: 0.00380, 6.2, 4.7
Fourth significant figure kept for reactor design

It might be noted here that there are methods of obtaining estimates of individual rate constants, but these are either inexact or preclude the measurement of other constants in the set. The use and limitations of a single effective second-order rate constant for the study of a pair of consecutive competitive reactions have been described in Chapter II. Another method mentioned earlier involves the use of one of the reaction products as the initiating reactant for the study of the later reactions in the set. Such a method was employed by Potter, who included the reactions of monoethanolamine and diethanolamine with ethylene oxide in his study of the complete set of three reactions. If there are j reactions in the set or if $k_{j+1} \ll k_j$, P_{j-1} can be reacted with B to find k_j . Then P_{j-2} can be reacted and the effects of the j -th reaction can be subtracted, using the known value of k_j , to give k_{j-1} . This procedure could be continued indefinitely if the rate constants were determined with sufficient accuracy; however, the propagation of errors in the determination of the rate constants for the later reactions would make this method quite inaccurate for more than a few reactions, although it can sometimes be extended considerably if the rate constants for each step are substantially less than those for the preceding reactions in the series.

If a large excess of A or P_i is used and if the rate constants for the subsequent reactions are not considerably greater than that for the first, essentially only one reaction, pseudo-first order, will take place. The rate constant computed in this way may not be applicable when more realistic molar ratios are used if there is any composition effect whatsoever. Furthermore, a study of this sort would have to be made for every reaction in the set, as the initiating reactant is not distributed among several products.

The results of the correlations presented in Tables III.4 and III.5 can be used to estimate the validity of the differential rate equations as well as that of the approximation to them. The variances whose square roots are listed in Table III.5 are composed of three components:

- (1). v_e , the variance due to experimental error;
- (2). v_d , the variance occasioned by the inaccuracy of the assumption that the differential equations describe exactly the physical system;
- (3). v_a , the variance caused by the inability of the integral approximation to describe strictly the true solution of the postulated rate equations.

The variances which can be computed from Table III.4 contain only the first two of these components. If v_e were known, v_d could be found by subtracting the error variance out of the variance occasioned by the product distribution fitting; or by subtracting v_e and v_a , the latter obtained from Figure 3.6, from the variances consequent of the complete integral fit. An F-test could be used to see if the variance, v_d , were significant. If the first method were used, only the differential equations obtained by dividing one rate equation into another would be checked; if the reactions were all of order n in B ($n \neq 1$), this would not be evidenced by the results. The value of the second method is somewhat diminished because the confidence limits of the final conclusion would be less stringent, owing to the additional step of the subtraction of v_a . Individual rate equations can be studied by computing v_d , using several higher products as initiating reactants, and assuming that the variances due to the inability of the individual rate equations to

represent the true system are additive. Differential methods are also available for checking individual rate equations; the constancies of the $\{k_i\}$ determined in this way are measures of the adherence of the chemical system to the differential model which it is supposed to fit.

As there was a large body of data available on ethanolamine synthesis, this system was treated in greater detail than were the others. Rate constants were estimated at three temperatures: 10°C, 20°C, and 30°C-- so that the activation energies could be calculated for each ethylene oxide addition. Figure 3.10 shows Arrhenius plots for the three reactions. The literature values of k_1 and those obtained from Program 6 are shown. The plots are nearly linear; the activation energies and frequency factors for the three reactions are listed in Table III.6. As all the data at each temperature are based on the same set of initial conditions, it is a simple matter to plot the experimental data and compare it with the predicted compositions at the sampling times. A graphical representation is not only more lucid than a table; it is useful in detecting any "drifts" or non-random error in the approximate representation of the course of the reaction. As can be seen from Figures 3.11 through 3.13, the approximate solution fits excellently the experimental data from which the rate constants were found.

c. Correlation of Experimental Work

Potter's data on ethanolamine synthesis, although extensive, was based on only a single run at each temperature. It was decided to confirm the values of the $\{k_i\}$ obtained above by carrying out the reaction using a different value of β_0 .

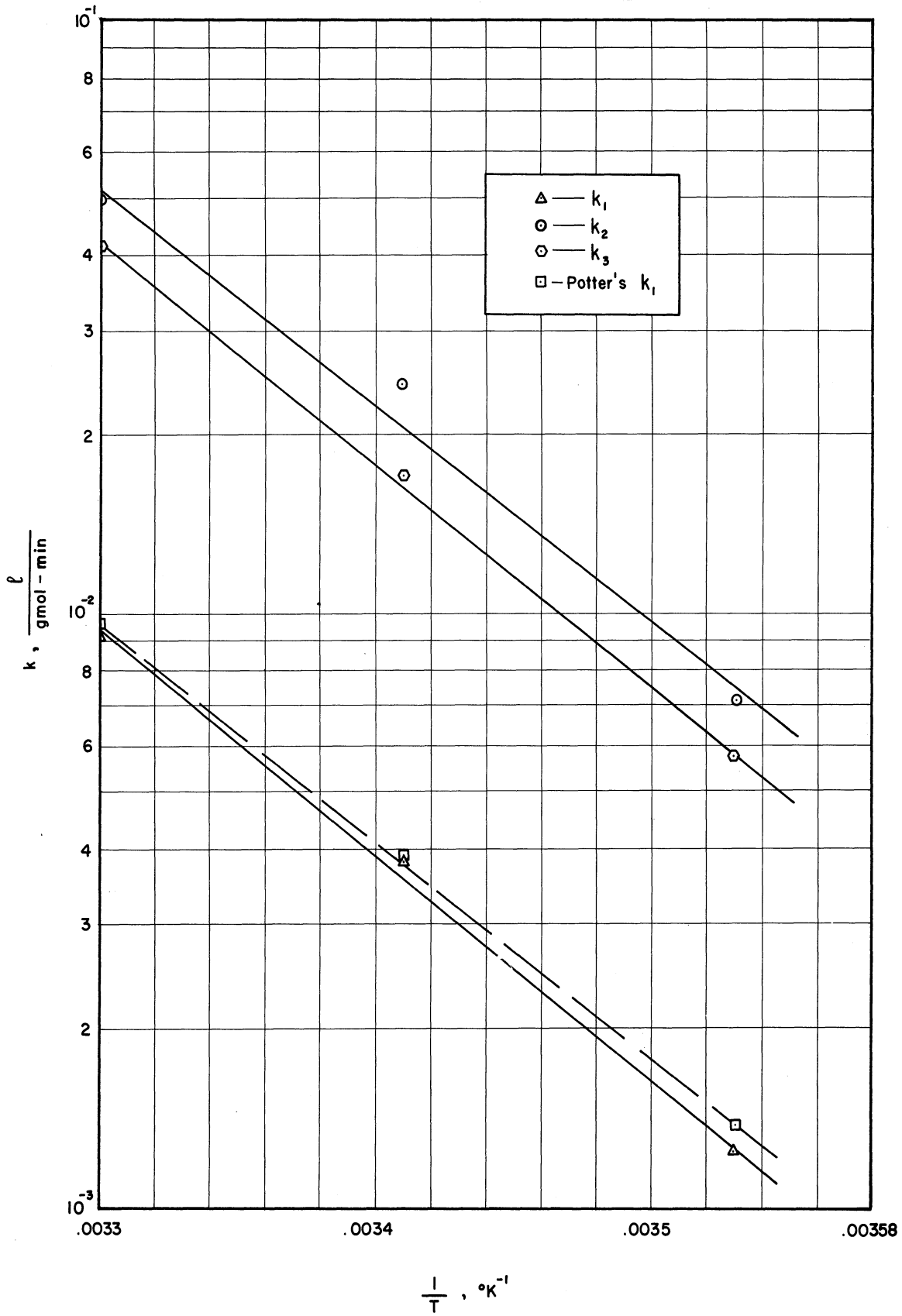


Figure 3.10. Arrhenius Plot for Ethanolamine Synthesis.

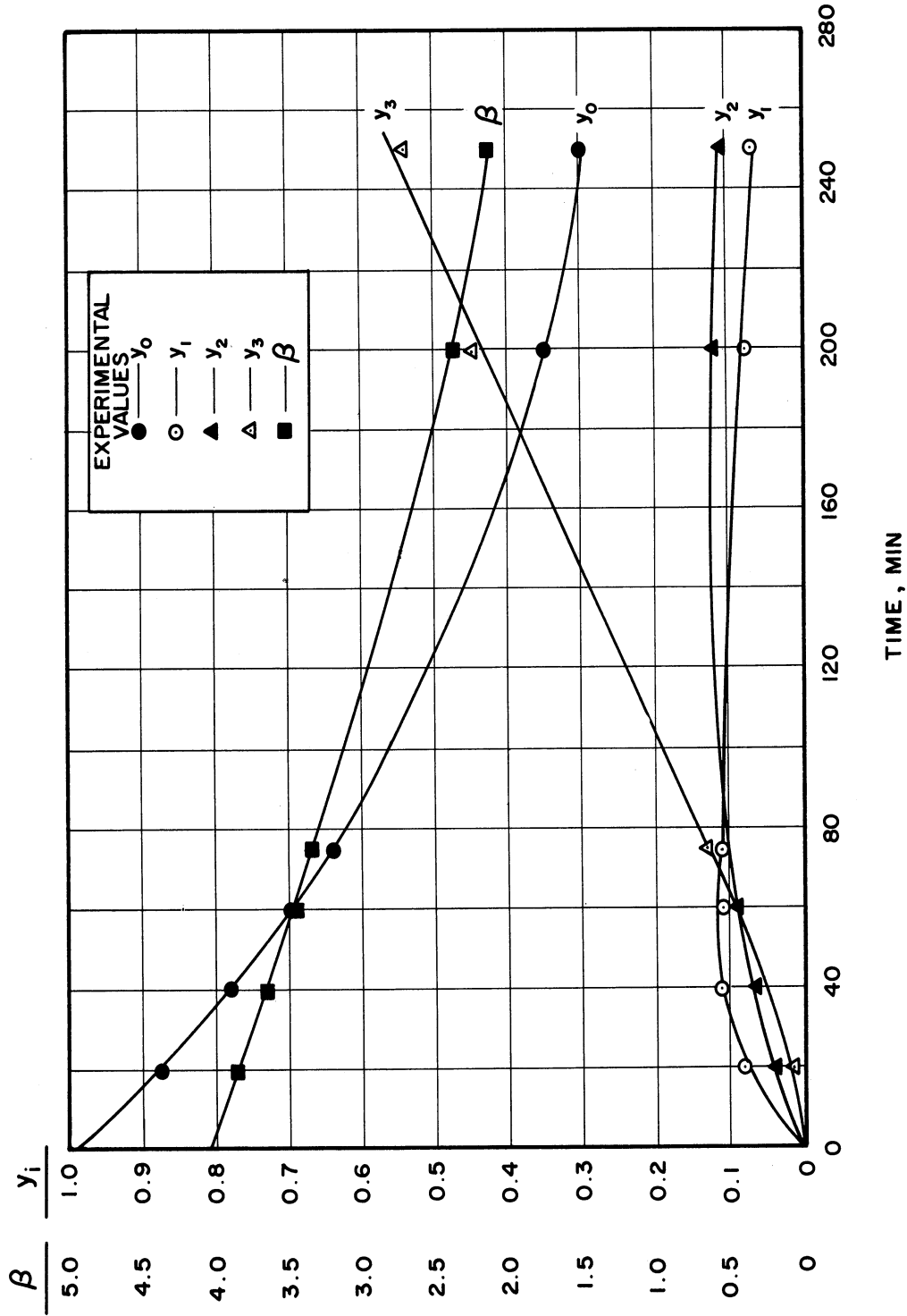


Figure 3.11. Concentration-Time Profiles for Ethanolamine Synthesis at 10°C. (Curves are computed from calculated rate constants and approximate model.)

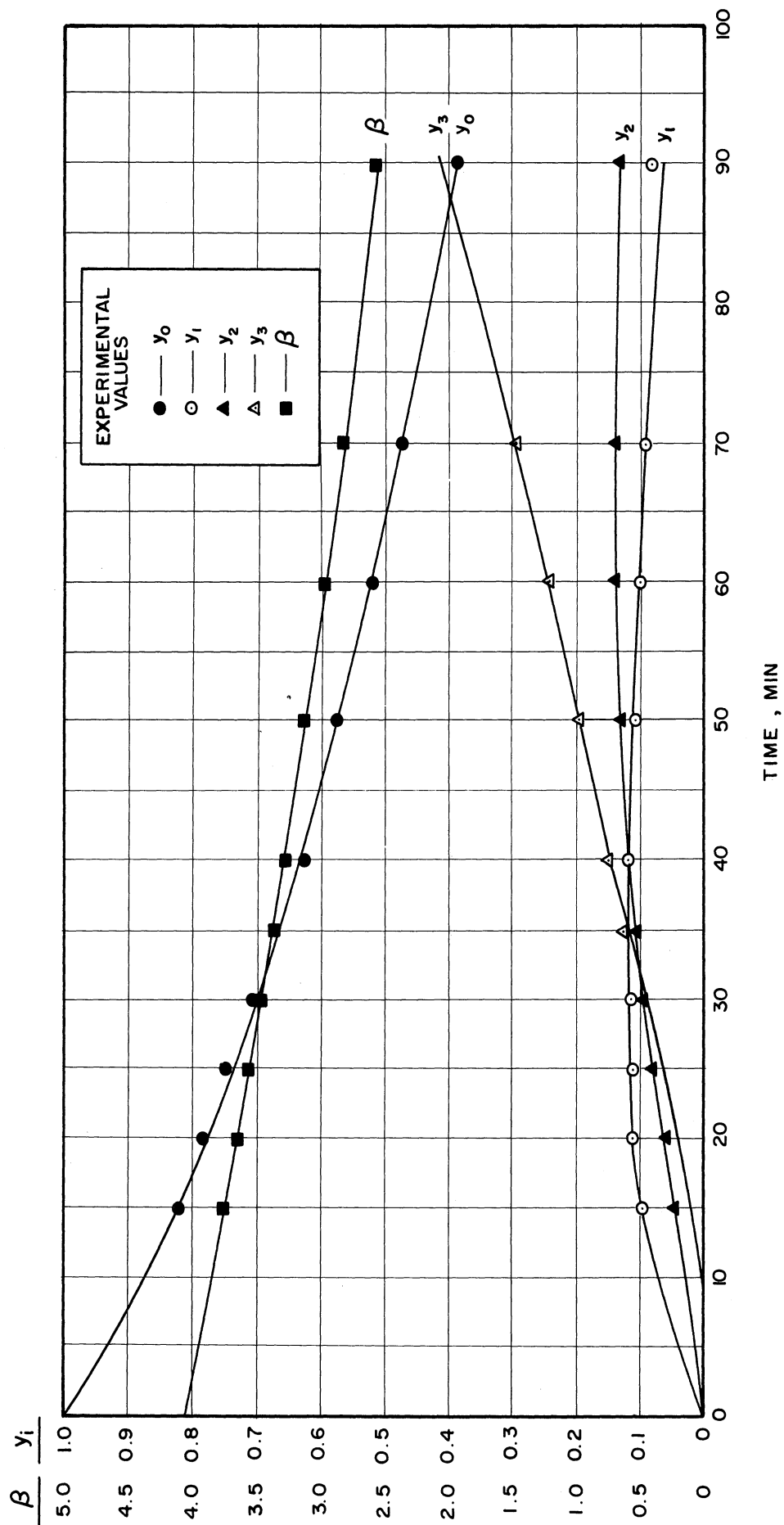


Figure 3.12. Concentration-Time Profiles for Ethanolamine Synthesis at 20°C. (Curves are computed from calculated rate constants and approximate model.)

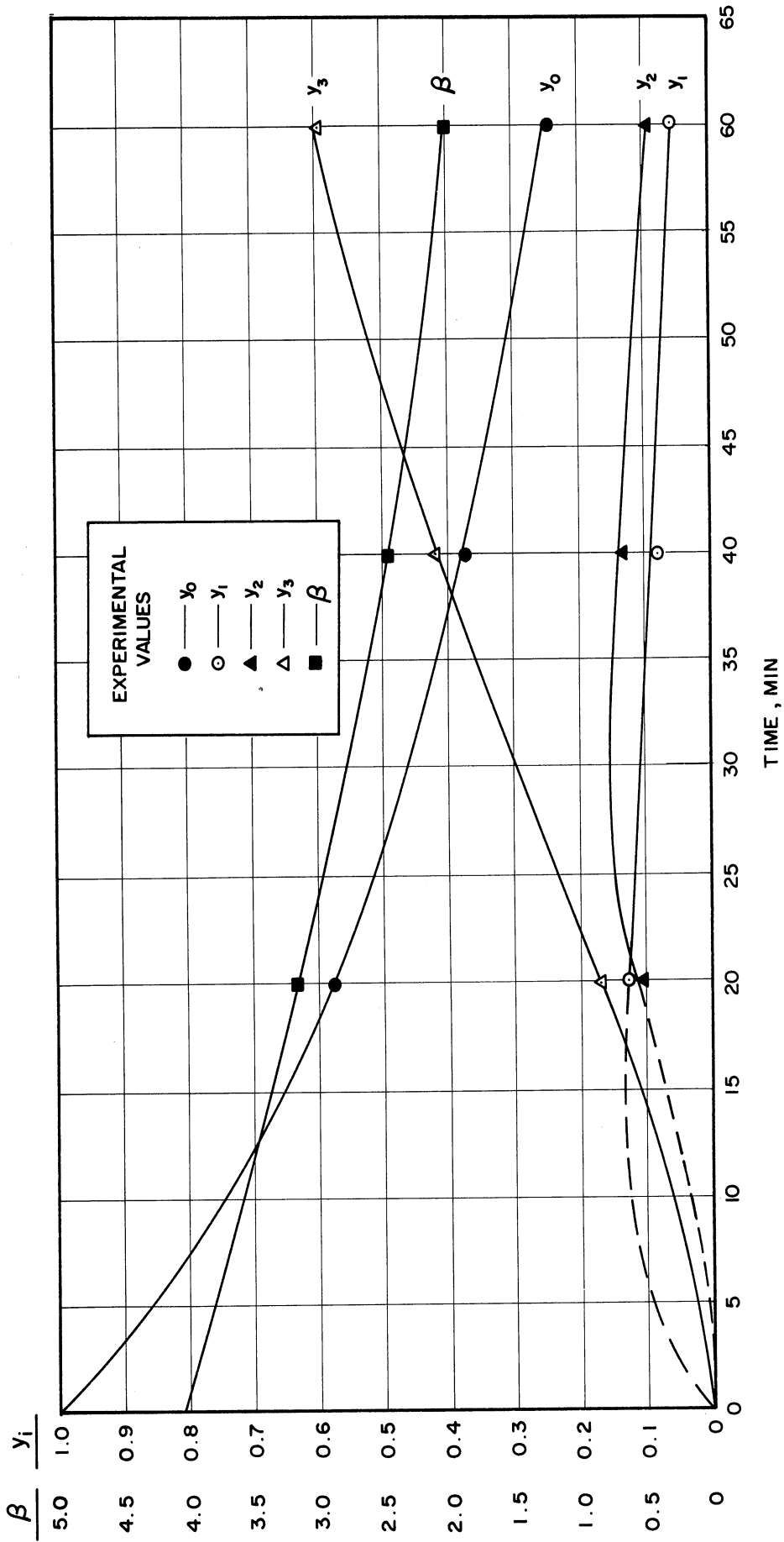


Figure 3.13. Concentration-Time Profiles for Ethanolamine Synthesis at 30°C. (Curves are computed from calculated rate constants and approximate model.)

TABLE III.6. ACTIVATION ENERGIES AND FREQUENCY FACTORS FOR ETHANOLAMINE SYNTHESIS

<u>Formation of</u>	<u>Activation Energy, cal/gmol*</u>	<u>Frequency Minimum Value*</u>	<u>Factor, Best Value</u>	<u>1/gmol-minx10⁻¹⁰ Maximum Value*</u>
Monoethanolamine	17,300+1700	1.1	1.8	2.8
Diethanolamine	16,700+1700	6	10	17
Triethanolamine	17,000+1700	4	8	14

* at 50% confidence

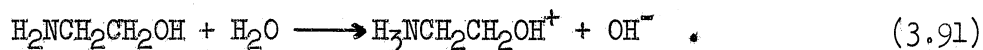
(1). Experimental Method. The reactions were performed at 20°C in the liquid phase. Two stock solutions were prepared--one of each reactant. Approximately 89 cc of 30% ammonium hydroxide were added to 310 cc of distilled water to make the ammonia stock. An Acculute was used to prepare one liter of 1N sulfuric acid. Fifty cc aliquots of the standard acid were titrated to a brom thymol blue endpoint with the ammonium hydroxide; from three determinations of the normality of the base, a value of 2.94 was obtained. To prepare the ethylene oxide solution, 106 grams of distilled water, chilled in a beaker to just above freezing, were put on the pan of a 0.01-gram three-beam balance. The ethylene oxide was removed from the freezer and an excess added to the beaker. Oxide was allowed to evaporate until the desired weight, 43 grams, remained; the contents of the beaker were then poured into a chilled glass-stoppered reagent bottle, which was stored in the freezer.

When a run was to be made, the ethylene oxide stock solution was removed from the freezer and thawed in cold water, to reduce the oxide loss. The constant temperature bath was turned on; this consisted of an outer water bath, fitted with an electric stirrer, in which was set a 12" x 12" battery jar. A mercury switch, a 200-watt immersion heater, and an air stirrer were mounted in the inner bath. The mercury switch was set at 20°C. As this was less than the ambient temperature while the runs were being made, ice was added to the outer bath and cold water was passed through copper coils in the inner bath. The desired amount of ammonium hydroxide was added from a burette to a 25 x 300 Pyrex test tube, which was then stoppered and placed in the battery jar. The ethylene oxide stock was weighed out and immediately added to the ammonia. The test tube was stoppered tightly and shaken frequently during the run.

When the desired time had elapsed, the test tube was unstoppered, allowing the unconverted oxide to escape, thus terminating the reaction. The reaction mix was stripped of unreacted ammonia by placing the test tube in boiling water for twenty minutes, and then in a 56°C bath until the vapor above the mix showed no basicity in contact with a piece of moist pHydron paper. The volumes of the reaction mixes were then measured and the cooled solutions were stored in screw-cap bottles.

(2). Experimental Results. Three intensive properties of the reaction mixes were determined; these, combined with a knowledge of the total volume of the reaction mix, gave the total number of mols of each amine produced by the reaction. A material balance was used to find y_0 and β .

Amine Normality: The ethanolamines behave as weak bases in aqueous solution; for instance,



Three aqueous solutions of mixtures of the three amines were prepared, and aliquots titrated with a dilute hydrochloric acid solution prepared by adding 430 cc of distilled water to 2 cc of 38 per cent hydrochloric acid. As the normalities of these amine solutions were known, the normality of the acid could be determined; it was found to be 0.0682. This acid was used to titrate two of the three reaction mixes. The third mix was titrated with 6.53N hydrochloric acid. All three titrations were taken to a pH of seven as indicated by a Beckmann pH meter. These results were confirmed by titration of a second aliquot of each reaction mix with the 1N sulfuric acid used to titrate the ammonia stock. The results obtained here, as

well as the conditions for each run and the remaining analytical data, are given in Appendix D. It was feared that some residual ammonia had contributed to the measured basicity of the reaction mixes. For this reason, mixtures of amines and ammonia resembling in composition the experimental reaction mixes were subjected to the ammonia stripping procedure described above. At the times corresponding to those at which the reaction mixes were withdrawn, aliquots of the control were titrated with 1N sulfuric acid. The results of these titrations were used to correct the observed amine normalities to their true values.

pH: The ionization constants of aqueous ethanolamine solutions have been reported in the literature (3,7,47). For monoethanolamine

$$K_{b1} = \frac{[\text{OH}^-][\text{HMEA}^+]}{[\text{H}_2\text{O}][\text{MEA}]} = 3.18 \times 10^{-5} \text{ at } 25^\circ\text{C} \quad (3.92)$$

where K_{b1} = ionization constant of monoethanolamine .

For diethanolamine,

$$\rho K_a = 18.082 - \frac{561.2}{T} - 0.02427T + (4501.15 - (20120990 + 739.513T + T^2)^{1/2})\mu \quad (3.93)$$

where ρK_a = apparent ionization constant for deprotonation of HDEA⁺
 T = absolute temperature, °K
 μ = ionic strength

or,

$$K_{b2} = \frac{[\text{OH}^-][\text{HDEA}^+]}{[\text{H}_2\text{O}][\text{DEA}]} = 9.35 \times 10^{-6} \text{ at } 25^\circ\text{C} \quad (3.94)$$

For triethanolamine,

$$\rho K_a = 2.524 + \frac{1563}{T} + 0.806\mu \quad (3.95)$$

or

$$K_{b3} = \frac{[\text{OH}^-][\text{HTEA}^+]}{[\text{H}_2\text{O}][\text{TEA}]} = 5.93 \times 10^{-7} \text{ at } 25^\circ\text{C} \quad (3.96)$$

The pH's of the three known mixtures were determined. The concentration of water is essentially constant and is given by its molar density. Three material balances and one charge balance can be written; for the last, the hydronium ion concentration is neglected.

$$[\text{MEA}]_T = [\text{MEA}] + [\text{HMEA}^+] \quad (3.97a)$$

$$[\text{DEA}]_T = [\text{DEA}] + [\text{HDEA}^+] \quad (3.97b)$$

$$[\text{TEA}]_T = [\text{TEA}] + [\text{HTEA}^+] \quad (3.97c)$$

$$[\text{OH}^-] = [\text{HMEA}^+] + [\text{HDEA}^+] + [\text{HTEA}^+] \quad (3.98)$$

where \hat{T} = total normality, ionized and unionized .

Equations (3.92), (3.94), (3.96), (3.97) and (3.98) comprise seven equations in the unknowns $[\text{OH}^-]$, $[\text{HMEA}^+]$, $[\text{MEA}]$, $[\text{HDEA}^+]$, $[\text{DEA}]$, $[\text{HTEA}^+]$ and $[\text{TEA}]$. From them, the hydroxide ion concentration was found for each known mixture and was plotted against the measured pH on semilogarithmic paper. This graph is given as Figure 3.14.

The pH's of the reaction mixes were also measured, and in each case Figure 3.14 was used to convert these measurements to hydroxide ion concentrations. The ammonium ion concentration was computed, assuming the ammonium hydroxide to be negligibly dissociated.

$$K_{\text{bNH}_3} = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_4\text{OH}]_T} = 1.8 \times 10^{-5} \text{ gmole/l.} \quad (18) \quad (3.99)$$

Denote the primary, secondary, and tertiary amines by A_1 , A_2 , and A_3 , and define

$$K'_{bi} = K_{bi} [\text{H}_2\text{O}] \quad (i=1,2,3) \quad (3.100)$$

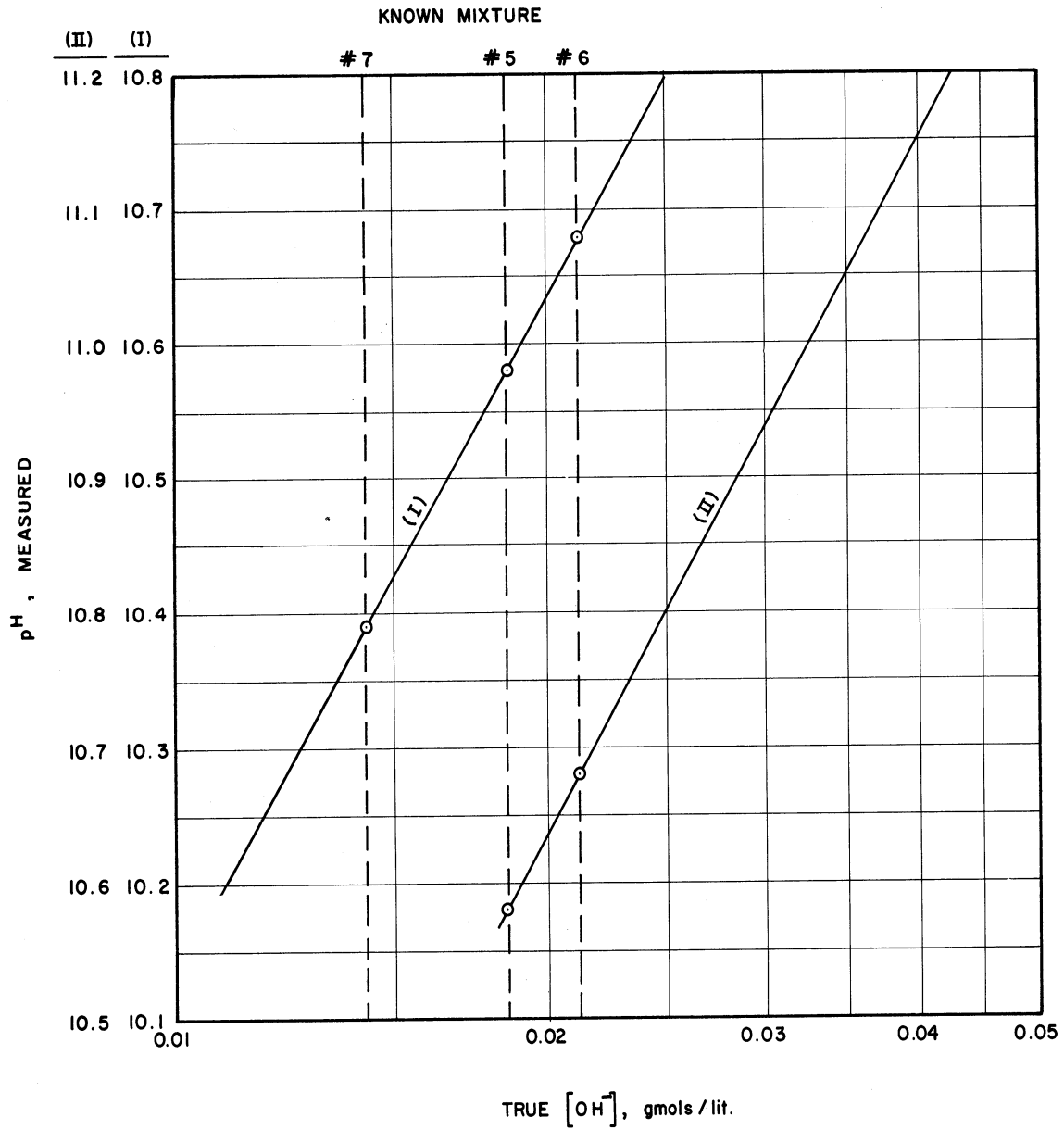


Figure 3.14. pH Calibration Curve for Ethanolamine Mixtures.

By substituting material balances on each amine into Equations (3.92), (3.94), (3.96) and (3.100),

$$\frac{[A_i H^+]}{[A_i]_T - [A_i H^+]} = \frac{K'_{bi}}{[OH^-]} \quad (i=1,2,3) \quad (3.101)$$

Rearranging,

$$[A_i H^+] = [A_i]_T \left\{ \frac{K'_{bi}}{K'_{bi} + [OH^-]} \right\} \quad (i=1,2,3) \quad (3.102)$$

Furthermore,

$$\sum_{i=1}^3 [A_i H^+] = [OH^-] - [NH_4^+] \quad (3.103)$$

By substituting Equations (3.102) into (3.103), a linear equation in the $\{[A_i]_T\}$ is obtained.

$$\sum_{i=1}^3 [A_i]_T \left\{ \frac{K'_{bi}}{K'_{bi} + [OH^-]} \right\} = [OH^-] - [NH_4^+] \quad (3.104)$$

Density: The densities of the three known mixtures were measured in a 10 ml uncorrected specific gravity bottle. From these densities, corrected to 28.5°C, partial weights of the three amines were calculated. These weights were defined so that Equation (3.105) held for each mixture.

$$\text{Weight of bottleful of mixture at } 28.5^\circ\text{C} = \text{Weight of bottleful of water at } 28.5^\circ\text{C} + \sum_{i=1}^3 v_i [A_i]_T \quad (3.105)$$

As the $\{[A_i]_T\}$ were known, the $\{v_i\}$ could be computed. This, incidentally, is another example of a first-degree functional fit. Then, for the reaction mixes,

$$\text{Weight of bottleful of reaction mix at } 28.5^\circ\text{C} = \text{Weight of bottleful of ammonium hydroxide of normality indicated by control at } 28.5^\circ\text{C} + \sum_{i=1}^3 v_i [A_i]_T \quad (3.106)$$

As the $\left\{ \sum_{i=1}^3 [A_i]_T \right\}$ were known from the hydrochloric acid titrations, Equations (3.104) and (3.106) could be used to compute the total amount of each amine produced in each run. These data are given in Appendix E.

(3). Correlation of Results. Program 6 was used to estimate rate constants from the experimental data described above. The data were correlated twice; first, with Potter's data for 20°C, and second, alone. The results are presented in Table III.7. Reasonable agreement is achieved, except that the value of K_3 determined experimentally is low. This is of little concern, however, at the low conversions obtained by the present experimentation.

TABLE III.7. ESTIMATED RATE CONSTANTS FOR ETHANOLAMINE SYNTHESIS AT 20°C

<u>Rate Constant or Rate Constant Ratio</u>	<u>Potter's Data Alone</u>	<u>Present ex- perimentation</u>	<u>All Data</u>
k_1 , l/gmol-min	0.003872	0.003489	0.003857
K_2	6.048	5.275	6.042
K_3	4.529	1.819	4.556
s_e	0.013	0.019	0.017
s_e using results on Potter's data	0.013	0.027	0.017

NOTE: Fourth significant figure retained on rate constants for reactor design.

IV. ENGINEERING APPLICATIONS TO OPTIMAL REACTOR DESIGN

If the differential rate equations governing the course of a system of reactions are known and no integrated solutions are available, it is a lengthy job to design a chemical reactor for the production of a desired amount of a given product. Guesses must be made at the values of the design and operating variables, the rate equations must be integrated numerically, and the costs evaluated for the chosen design and method of operation. This procedure is repeated until a combination of variables is found which provides the desired results at the minimum cost. Considerably simpler design methods can be used when integrated solutions of the rate equations are available, for then the most time-consuming part of the design, the numerical integration, is unnecessary. If an explicit solution of the rate equations has been found, the cost of production can be described as an explicit function of the design and operating variables and design equations can be derived. These equations, in addition to simplifying the optimization procedure, indicate the fashion in which the several cost factors affect the final design, and can be used to show how the operating conditions should be varied in response to changes in costs and demand.

A. Description of the Reactor to be Optimized

The basic design problem to be solved in this chapter may be stated as follows: Given the rate constants for a set of consecutive competitive reactions and the necessary cost factors, design a flow reactor with a specified diameter to produce Z mols of P_1 per hour, at the minimum cost.

To simplify the derivation of the design equations, certain assumptions will be made regarding the operation of the flow reactor. The reaction mix is assumed to have a constant density. This is frequently true for liquid-phase reactions, and particularly so if the reactants are diluted with some inert solvent. For gas-phase reactions, the compressibility of the reaction mix should not change much as the reaction proceeds, and the molar flow rate must be constant; this means that unless there is a diluent gas, the $\{n_i\}$, as defined by Equations (2.1), should all be equal to unity. The flow in the tube is assumed to be fully developed turbulent, so that the fluid velocity is the same everywhere in the pipe. Longitudinal diffusion will be neglected, so that slug flow is obtained throughout. Then reaction time will be directly proportional to reactor length

$$dt = \frac{AdL}{V} \quad (4.1)$$

where t = reaction time
 A = cross-sectional area of pipe
 L = reactor length
 V = volumetric flow rate at L

The absence of radial temperature or concentration gradients is assumed, and the reactor is to operate isothermally, with the rate constants independent of composition. If the activation energies for all reactions are the same, reaction time, and hence reactor length may be scaled, taking into account the degree of nonisothermality, but this poses an additional design problem, which will not be treated here. The scaling equation is

$$\ln \frac{t_1}{t_2} = \frac{\Delta E}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right) \quad (4.2)$$

where $\hat{\Delta}$ = datum at temperature for which reactor was designed
 $\hat{\Delta}$ = datum at the true temperature
 ΔE = common activation energy
 R = gas constant
 T = absolute temperature

Mixing is assumed to be perfect everywhere. Hence, there are to be no temperature fluctuations at the inlet when the reactants first contact one another. For part of the discussion to follow, we will consider the design of a reactor in which additional B is added at a downstream point; perfect and instantaneous mixing are assumed to obtain here, so that a material balance may be used to relate the injection volume and the concentrations of the reaction mixes immediately preceding and following injection.

B. Definition of the Cost Function

The following cost factors will be considered in designing the flow reactor described above:

- P: value of product, $\$/\text{lbmol } P_1$
- R: cost of removing A, B and P_1 from reaction mix, $\$/\text{lbmol A or B or } P_1$. The reaction mix is assumed to be separated with complete recovery of the starting materials; this ideal is nearly reached in many present-day operations. The recovered A and B are recycled to the reactor inlet.
- M: reactor operating cost, $\$/\text{ft-hr}$. This term includes a fixed fraction of the capital cost of the reactor.
- W: value of byproduct, $\$/\text{lbmol } P_2$. It is assumed that P_3 is worthless; if this is not true, K_2 can be raised slightly above its true value to take the sales of P_3 into account.
- A: cost of fresh A, $\$/\text{lbmol}$
- B: cost of fresh B, $\$/\text{lbmol}$.

Of these cost figures, all but P usually affect the design of the reactor. As the production rate of P_1 is given, the value associated with P; that is, PZ , is fixed. However, it is important to know P, to ascertain whether, in the light of the other cost figures, the process being studied is, in fact, economically feasible.

There are four independent operating and design variables whose best values will be determined by the optimization procedures below; initial molar ratio of the initiating reactants, feed rate, injection rate, and injection point; the last is the distance from the inlet at which the injection is made. As Z is stipulated, the reactor length required to produce the desired amount of product is determined by the independent variables above. These variables are subject to some restrictions, as not every combination of feed rate and feed composition will provide enough product, regardless of the reactor length; we will deal only with those values of the parameters which are theoretically feasible. Define

$$v = \frac{1}{N_A x_{A0} + N_B - N_B x_{A0}} \quad (4.3)$$

where v = molar volume
 \hat{A} = of A
 x = mol fraction
 \hat{B} = of B

Then the hourly production cost of P_1 is given by

$$\gamma = ML + V_f v (A x_{A0} + B(1-x_{A0})) + (V_i + V_f) \left(R[A]_f + R[B]_f - A[A]_f - B[B]_f \right) + \frac{BV_i}{N_B} + RB' - WB' \quad (4.4)$$

where V = volumetric flow rate
 \hat{f} = of the feed (for V_f); final (for concentrations)
 \hat{i} = of the injection stream
 b' = byproduct rate
 γ = hourly production cost

The results obtained from the flow reactor design can be applied directly to batch reactor optimization. The reactants are added to a well-stirred pot and, at some later time, more B is added. The reaction mix is separated and the recovered A and B are used in the next batch. The differential

batch reactor operating cost is defined by

$$dT_{opB} = M' V_B dt \quad (4.5)$$

where T_{opB} = operating cost
 = for batch operation
 M' = batch reactor operating cost, \$/hr-ft³
 V_B = batch reactor volume .

Equation (4.5) is realistic if the capital cost of the reactor is small compared to the mixing expense or if there is little or no injection. From Equation (4.4), the differential operating cost of a flow reactor is

$$dT_{opF} = M dL \quad (4.6)$$

where \hat{F} = for flow operation .

Substituting Equation (4.1) into (4.6),

$$dT_{opF} = \frac{M V dt}{A} \quad (4.7)$$

Let us suppose that, in time θ , one batch of product is produced from an initial batch volume, V_{B0} . Further, assume that the optimum design of the batch reactor requires a variation with time of the reaction volume, given by

$$V_B = V_{B0} \eta(t) \quad (4.8)$$

For a constant-density system, when a single injection is made, η is a step function.

$$\eta = 1 \quad (0 \leq t < t_i) \quad (4.9a)$$

$$\eta = \frac{V_{B0} + V_{Bi}}{V_{B0}} \quad (t_i \leq t) \quad (4.9b)$$

where V_{Bi} = injection volume in batch operation
 t_i = time at which injection is made .

To obtain the same amount of product from the flow reactor in the same time, a feed rate of V_{B0}/θ must be used, and the required reactor length is given by

$$L = \int_0^\theta \frac{V dt}{A} = \int_0^\theta \frac{V_{B0} \eta dt}{A \theta} = \frac{V_{B0}}{A \theta} \int_0^\theta \eta dt \quad (4.10)$$

The hourly operating cost of the flow reactor is

$$\tau_{opF} = ML = \frac{MV_{B0}}{A\Theta} \int_0^{\Theta} \eta dt, \quad (4.11)$$

Substituting Equation (4.8) into (4.5) and integrating, the operating cost per batch of the batch reactor is

$$\tau_{opBB} = \int_0^{\Theta} M'V_{B0}\eta dt = M'V_{B0} \int_0^{\Theta} \eta dt \quad (4.12)$$

and the hourly cost is

$$\tau_{opB} = \frac{MV_{B0}}{\Theta} \int_0^{\Theta} \eta dt = \tau_{opF} \frac{AM'}{M}. \quad (4.13)$$

The hourly operating cost of the batch reactor is directly proportional to that of the flow reactor, if Equation (4.5) is used to describe the former charge; it follows, from (4.13), that design equations derived for a flow reactor may be applied to batch reactor design if M is replaced by AM'.

C. The Concept of Downstream Injection

1. Literature References

In the chemical industry, staged reactors are not uncommon. Often quantities of reactant are added after some degree of conversion has been attained, to quench the system and obtain more nearly isothermal operation. The quench converter⁽⁵²⁾ for the production of sulfuric acid exemplifies this mode of operation. A French patent⁽⁴²⁾ describes an apparatus similar to a rotating-disc contactor, in which reactant is injected on to each of several coaxial discs, which are rotated rapidly to homogenize the mix. Jones⁽²⁵⁾ describes an apparatus, similar in design to a Votator, where downstream injection is used to approximate isothermality during the exothermic combination of viscous reactants. Baumann⁽⁴⁾ discusses a staged ammonia reactor, where quenching is obtained by several additions of cooled gas during the later stages of reaction.

Downstream injection not only affects the temperature profile in the reactor; it affects the concentration profile as well. In the sections to follow, the effect of injection on yield and cost will be considered and the derived relations will be used to develop equations to solve the design problem postulated above.

2. Explicit Solution of the Rate Equations for a Reactor with a Single Injection

In this study, it will be assumed that only a single injection, of pure B, is made. The composition of the reactor product will then depend on the feed rate and composition; the injection rate and location of the injection point; and the reactor length. Equations describing the dependence of the product composition on these five variables will be derived, one set for each of the two approximate solutions of the rate equations developed in Chapter III.

a. A Single Second-Order Reaction

When K_2 is small, the $\{y_i\}$ ($i > 1$) are negligible, and essentially only a single reaction takes place. It will be assumed here that $K_2 = 0$, and that no higher products are formed; the design equations eventually derived will then be those for a reactor in which a single second-order reaction is to be carried out.

Replacing the dimensionless variables in Equation (3.22a) with real quantities, as given by Equations (2.32), (3.8) and (3.17),

$$\frac{[A]}{[A]_0} = \frac{\left(\frac{[B]_0}{[A]_0} - 1\right) \exp\left\{[A]_0 k_1 t \left(1 - \frac{[B]_0}{[A]_0}\right)\right\}}{\frac{[B]_0}{[A]_0} - \exp\left\{[A]_0 k_1 t \left(1 - \frac{[B]_0}{[A]_0}\right)\right\}} \quad (4.14)$$

The mol fraction of A in the feed is found from the initial concentrations of A and B.

$$x_{A0} = \frac{[A]_0}{[A]_0 + [B]_0} \quad (4.15)$$

Substituting Equation (4.15) into (4.14),

$$[A] = \frac{\frac{[A]_0(1-2x_{A0})}{x_{A0}} \exp\left[\frac{[A]_0 k_1 t \left(\frac{2x_{A0}-1}{x_{A0}}\right)}{x_{A0}}\right]}{\frac{1-x_{A0}}{x_{A0}} - \exp\left[\frac{[A]_0 k_1 t \left(\frac{2x_{A0}-1}{x_{A0}}\right)}{x_{A0}}\right]} \quad (4.16)$$

If the value of t used in Equation (4.16) is the residence time in the portion of the reactor preceding the injection point, the calculated value of [A] is the concentration of A immediately prior to injection. This residence time is given by

$$t' = \frac{\pi D^2 L'}{4V_f} \quad (4.17)$$

where D = tube diameter
L' = distance of injection point from inlet .

Then, from Equations (4.16) and (4.17),

$$[A]' = \frac{\frac{[A]_0(1-2x_{A0})}{x_{A0}} \exp\left[\frac{[A]_0 k_1 \pi D^2 L' (2x_{A0}-1)}{4V_f x_{A0}}\right]}{\frac{1-x_{A0}}{x_{A0}} - \exp\left[\frac{[A]_0 k_1 \pi D^2 L' (2x_{A0}-1)}{4V_f x_{A0}}\right]} \quad (4.18)$$

where [A]' = concentration of A immediately prior to injection .

The residence time in the second portion of the reactor is

$$t'' = \frac{\pi D^2 (L-L')}{4(V_f + V_i)} \quad (4.19)$$

Substituting Equation (4.3) into (4.18),

$$[A]' = \frac{v(1-2x_{A0})e^{\epsilon}}{\frac{1-x_{A0}}{x_{A0}} - e^{\epsilon}} \quad (4.20)$$

where $\epsilon = \frac{v k_1 \pi D^2 L' (2x_{A0}-1)}{4V_f}$. (4.20a)

As $K_2 = 0$, equimolar amounts of A and B are consumed during the reaction; therefore

$$[B]' = [A]' - [A]_0 + [B]_0 \quad (4.21)$$

where $[B]'$ = concentration of B immediately prior to injection .

Let the double-prime superscript denote properties of the reaction mix immediately after injection. From a material balance around the injection point,

$$[A]'' = \frac{V_f [A]'}{V_i + V_f} \quad (4.22)$$

and

$$[B]'' = \frac{\frac{V_f v (2x_{A0} - 3 + \frac{1}{x_{A0}})}{1 - x_{A0} - \epsilon} + \frac{V_i}{v_B}}{V_i + V_f} \quad (4.23)$$

Equation (4.16) can be used to find $[A]_f$.

$$[A]_f = \frac{([B]'' - [A]'') e^H}{\frac{[B]''}{[A]''} - e^H} \quad (4.24)$$

where $H = \frac{k_1 \pi D^2 (L - L') ([A]'' - [B]'')}{4(V_f + V_i)} \quad (4.24a)$

and Equations (4.23), (4.21) and (4.19) are used to find the double-primed quantities. The rate of consumption of B must equal that of A. Therefore

$$[B]_f = \frac{V_f v v_B (1 - 2x_{A0}) + V_i}{v_B (V_f + V_i)} + [A]_f \quad (4.25)$$

The production rate, Z, is given by

$$Z = V_f x_{A0} v - (V_i + V_f) [A]_f \quad (4.26)$$

b. A Set of Consecutive Competitive Reactions

Here, the approximate solution of the complete set of rate equations, derived in Chapter III, will be used to relate the composition

of the reactor effluent to the five variables listed above. Substituting real parameters into the dimensionless Equation (3.40),

$$\frac{[A]_0}{[A]_0} = \exp \left[\frac{[B]_0}{b[A]_0} \left(e^{-b[A]_0 k_1 t} - 1 \right) \right] \quad (4.27)$$

As

$$[A]_0 = v \alpha_{A0} \quad (4.28)$$

substitution of Equation (4.17) into (4.27) gives

$$[A]' = \alpha_{A0} v \exp \left[\frac{(1-\alpha_{A0})}{b \alpha_{A0}} \left(\exp \frac{-b \alpha_{A0} k_1 \pi D^2 L' v}{4V_f} - 1 \right) \right] \quad (4.29)$$

Similarly, Equation (3.41) becomes

$$[B]' = v(1-\alpha_{A0}) e^{-\frac{b \pi D^2 L' \alpha_{A0} v}{4V_f}} \quad (4.30)$$

[A]" is given by Equation (4.22) and [B]" is computed from Equation (4.31).

$$[B]'' = \frac{V_f [B]' + \frac{V_i}{N_B}}{V_i + V_f} \quad (4.31)$$

The approximate solution derived in Chapter III is applicable only when A and B alone are present initially. For this reason, the course of the reaction after injection cannot be followed by applying the approximation directly, using the double-primed quantities as initial conditions. However, the product distribution equations are satisfied everywhere in the reactor, so that a mix composition identical to that found immediately after injection would be obtained without injection if the proper choice of $[B]_0$ and the residence time were made. If these equivalent values, $[B]_{0e}$ and t_e , can be computed, the composition of the final product can be found by solving the approximate equations for a feed composition given by $[B]_{0e}$ and a reaction time of $t_e + t''$. Immediately after injection, the flow rate in the reactor is $V_f + V_i$ and the molar flow rate of A, free and combined,

is $V_f[A]_0$. Therefore, the apparent, or equivalent, initial concentration of A is given by

$$[A]_{oe} = \frac{V_f[A]_0}{V_i + V_f} \quad (4.32)$$

where \hat{e} = equivalent value .

The equivalent volume fraction of A in the feed is then

$$V_{Ae} = \frac{V_f[A]_0 \nu_A}{V_i + V_f} \quad (4.33)$$

and that of B is

$$V_{Be} = 1 - V_{Ae} = \frac{V_i + V_f - V_f[A]_0 \nu_A}{V_i + V_f} \quad (4.34)$$

From Equation (4.28), $[B]_{oe}$ is given by

$$[B]_{oe} = \frac{V_i + V_f - V_f \nu_{A0} \nu_A}{\nu_B (V_i + V_f)} \quad (4.35)$$

From Equations (3.41), (3.8) and (3.17),

$$\frac{[B]''}{[B]_{oe}} = e^{-b[A]_{oe} k_1 t_e} \quad (4.36)$$

Substituting (4.28) and (4.32) into (4.36), and solving for t_e ,

$$t_e = -\frac{V_i + V_f}{b \nu_{A0} \nu_f k_1} \ln \frac{[B]''}{[B]_{oe}} \quad (4.37)$$

Using Equations (4.30), (4.31) and (4.35) to find the argument of the logarithm in (4.37),

$$t_e = -\frac{V_i + V_f}{b \nu_{A0} \nu_f k_1} \ln \left[\frac{V_f \nu_B (1 - \nu_{A0}) \nu \exp\left(-\frac{b \pi D^2 L' k_1 \nu_{A0} \nu}{4 V_f}\right) + V_i}{V_i + V_f - V_f \nu_{A0} \nu_A} \right] \quad (4.38)$$

The equivalent mol fraction of A in the feed is found by substituting the equivalent initial concentrations of the reactants into Equation (4.15).

$$\nu_{A0e} = \frac{V_f \nu_{A0} \nu_B \nu}{V_i + V_f \nu_B \nu} \quad (4.39)$$

The reaction time and product compositions are given by

$$t_f = t_e + t'' \quad (4.40)$$

$$[B]_f = [B]_{oe} e^{-b[A]_{oe} k_1 t_f} \quad (4.41)$$

$$[A]_f = [A]_{oe} \exp \left[\frac{1-x_{Aoe}}{b x_{Aoe}} (\exp(-b[A]_{oe} k_1 t_f) - 1) \right] \quad (4.42)$$

t_e , t'' , $[B]_{oe}$, $[A]_{oe}$ and x_{Aoe} are found, respectively, from Equations (4.38), (4.19), (4.35), (4.32) and (4.39). When $[A]_f$ is known, y_0 can be found, and the product distribution may be computed.

D. Numerical Design Methods

As equations to describe the composition of the reactor product as a function of the design and operating variables are now available, it is a simple matter to substitute the results obtained above into Equation (4.4) and write the production cost of P_1 in terms of these variables. As we are stipulating the production rate which the reactor is to meet, one of these five parameters is not truly independent. In this study, reactor length was considered to be the dependent variable although, in theory, any of the five are suitable.

Three numerical design procedures are described below. In the first two, values of the feed rate and composition, the injection rate and injection point are chosen, and the reactor length and total cost computed, using the equations derived earlier in this chapter. The values of the four independent variables are adjusted until the cost is minimized. In the third method, a flow reactor is simulated on a digital computer and a descent method, similar to those currently employed in industrial optimization studies, is used to find the best design.

1. Optimal Design of a Reactor to Carry Out a Single Second-Order Reaction

The definition of the cost function is, in this case, slightly simpler than that given by Equation (4.4).

$$T = ML + V_f v (A \alpha_{A0} + B(1 - \alpha_{A0})) + (V_i + V_f) (R[A]_f + R[B]_f - A[A]_f - B[B]_f) + \frac{BV_i}{N_B} \quad (4.43)$$

The last two terms in the earlier equation are not used in the present definition because no by-product is formed. The dependences of $[A]_f$ and $[B]_f$ on the independent variables are given by Equations (4.24) and (4.25); it remains only to find the reactor length required to achieve the desired production rate.

Substituting Equation (4.24) into (4.26) and rearranging,

$$\frac{([B]'' - [A]'') e^{\mathcal{H}}}{[B]'' - e^{\mathcal{H}}} = \frac{V_f \alpha_{A0} v - Z}{V_f + V_i} \quad (4.44)$$

By using Equations (4.20), (4.22) and (4.23), Equation (4.44) can be rewritten in terms of the independent variables. Solving for $e^{\mathcal{H}}$

$$e^{\mathcal{H}} = \frac{(V_f v N_B (2\alpha_{A0} - 3 + \frac{1}{\alpha_{A0}}) + V_i (\frac{1 - \alpha_{A0}}{\alpha_{A0}} - e^{\mathcal{E}})) (V_f \alpha_{A0} v - Z)}{V_f (1 - 2\alpha_{A0}) v e^{\mathcal{E}} (v(1 - \alpha_{A0}) V_f N_B + V_i - Z N_B)} \quad (4.45)$$

Similarly, \mathcal{H} itself can be written as a function of the independent variables.

$$\mathcal{H} = - \frac{k_p \pi D^2 (L - L') (V_f v N_B (1 - 2\alpha_{A0}) + V_i)}{4 (V_f + V_i)^2 N_B} \quad (4.46)$$

Substituting Equation (4.45) into (4.46) and rearranging,

$$L = L' - \frac{4 (V_f + V_i)^2 N_B}{k_p \pi D^2 [V_f v N_B (1 - 2\alpha_{A0}) + V_i]} \ln \left[\frac{(V_f v N_B (2\alpha_{A0} - 3 + \frac{1}{\alpha_{A0}}) + V_i (\frac{1 - \alpha_{A0}}{\alpha_{A0}} - e^{\mathcal{E}})) (V_f \alpha_{A0} v - Z)}{V_f (1 - 2\alpha_{A0}) v e^{\mathcal{E}} (v(1 - \alpha_{A0}) V_f N_B + V_i - Z N_B)} \right] \quad (4.47)$$

As Z is specified, Equation (4.26) can be used to give $[A]_f$.

$$[A]_f = \frac{V_f \kappa_{A0} V - Z}{V_i + V_f} \quad (4.48)$$

Substituting Equation (4.25) into (4.48), and simplifying,

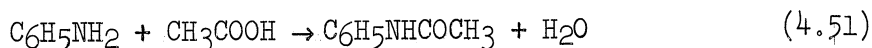
$$[B]_f = \frac{V_f V \kappa_B (1 - \kappa_{A0}) + V_i - Z \kappa_B}{\kappa_B (V_f + V_i)} \quad (4.49)$$

Substituting Equations (4.48) and (4.49) into the coefficients of A and B in (4.43),

$$\gamma = ML + (V_i + V_f)R([A]_f + [B]_f) + Z(A+B) \quad (4.50)$$

The last term above is constant. It is not surprising that the costs of A and B are irrelevant to the design of the reactor, because the consumption rate of the reactants is fixed when the production rate is set, as there are no reactant losses and no byproducts are formed.

Program 7 uses a creep method to find that combination of independent variables which will produce most cheaply P_1 at the required rate. A more complete description of the program is in Appendix A. The total cost is given by Equation (4.50); the reactor length and the effluent composition are found from (4.47) through (4.49). A typical bimolecular reaction is that used to produce acetanilide.



The reaction is normally carried out batchwise, in the liquid phase, at about $150^\circ C$ ⁽¹¹⁾. Rees⁽³⁸⁾ found that the reaction obeyed second-order kinetics; if a 100 per cent excess of acetic acid is used, the change in density accompanying complete conversion of the aniline is only 6.5 per cent. Program 7 was used to design a flow reactor to produce 300,000 lbs of acetanilide annually. The physical properties of the reactants, the cost factors used⁽²⁾ and the rate constant for the reaction are given in

Table IV.1. The product was assumed to be separated from the unconverted reactants by cooling and crystallization, and R was based on the cost of the required heat-exchange equipment and the crystallizer. The results of the design computation are in Table IV.2. Additional design runs were made with R increased by several orders of magnitude; the results of these runs are also in Table IV.2. As we would expect, as the importance of the reactor cost diminishes, the optimum conversion increases and the best feed

TABLE IV.1. PARAMETERS FOR DESIGN OF ACETANILIDE REACTOR

Molar volume of A, v_A (aniline)	1.649 ft ³ /lbmol
Molar volume of B, v_B (acetic acid)	1.072
Production rate, Z	0.308 lbmols/hr
Rate constant, k_1	5.64 ft ³ /hr-lbmol
Reactor diameter, D	0.01 ft
Recycle cost, R	\$1805 hr/yr-lbmol
Reactor operating cost, M	\$3.75/yr-ft

composition approaches equimolarity.

It appears, from these results, that regardless of the initial guess at the injection volume, the contribution of injection to optimal reactor operation is not significant. Although non-zero design values of the variables V_i and L' were found, it is likely that zero values were not attained only because the effects of small adjustments of the values of these parameters occasioned an insignificant change in the computed cost. The

TABLE IV.2. OPTIMUM REACTOR DESIGNS FOR A SECOND-ORDER REACTION

All Conditions as for Table IV.1, excepting R

Part 1--with Injection

Run	1	2	3	4	5	6
R, \$/yr-lbmol	1805	1805	1805	18050	180500	1805000
<u>Initial guesses</u>						
L', ft	3320	3320	3320	3320	3320	3320
V _i , ft ³ /hr	1.680	16.80	0.168	0.168	0.168	0.168
V _f , ft ³ /hr	1.680	1,680	1.680	1.680	1.680	1.680
x _{Ao}	0.400	0.400	0.400	0.400	0.400	0.400
<u>Design values</u>						
L'	5	5	18	15	22	0
V _i	0.4787	0.3920	0.1876	0.0934	0.0849	0.0892
V _f	3.710	3.805	4.001	1.811	1.093	0.8576
x _{Ao}	0.483	0.470	0.440	0.474	0.528	0.563
L, ft	6151	6148	6151	8821	17320	44160
[A] _f , lbmols/ft ³	0.2434	0.2437	0.2435	0.1735	0.0946	0.0399
[B] _f , lbmols/ft ³	0.3717	0.3718	0.3717	0.2555	0.1239	0.0458
<u>Production cost, \$/yr*</u>						
	27,720	27,720	27,720	47,830	111,400	312,100
Run	1	2	3	4	5	6

* exclusive of raw material cost

Part 2--no injection

Run	7	8	9	10
R	1805000	180500	18050	1805
<u>Initial guesses</u> ($L_i = V_i = 0$)				
V_f	1.680	1.680	1.680	1.680
x_{Ao}	0.400	0.400	0.400	0.400
<u>Design values</u>				
V_f	0.9472	1.179	1.902	4.186
x_{Ao}	0.496	0.480	0.446	0.415
L	44080	17300	8831	6152
$[A]_f$	0.0401	0.0946	0.1734	0.2432
$[B]_f$	0.0457	0.1241	0.2551	0.3720
<u>Production cost, \$/yr*</u>				
	312,100	111,400	47,880	27,720

changes made in all the variables were defined as percentages of their current values; therefore, as the injection point approached the reactor inlet, increasingly smaller modifications were made. As the independent variables were adjusted by multiplicative factors, Program 7 could be used directly to design reactors operating without injection, simply by guessing zero values for the injection volume and point. The results of these calculations, for the same values of R, are also in Table IV.2. By comparing the two sets of results, it would seem to be a valid conclusion that downstream injection cannot be used to decrease production costs when only one reaction takes place.

2. Optimal Design of a Reactor to Carry Out a Set of Consecutive Competitive Reactions

The procedure required to design a reactor to produce P_1 at a specified rate is somewhat more complex when K_2 is large, because byproduct formation must be taken into account and because the required reactor length cannot be written as an explicit function of the independent variables. From Equations (3.15), (3.20a) and (4.28), the value of y_1 which obtains at the reactor outlet is

$$y_{1f} = \frac{Z}{V_f \kappa_{A0} \nu} = \frac{y_{0f} - y_{0f}^{K_2}}{K_2 - 1} \quad (4.52)$$

where y_{if} = final value of y_i .

From Equation (3.20b),

$$y_{2f} = \frac{K_2^2 y_{0f} - K_2 K_3 y_{0f} + K_2 K_3 y_{0f}^{K_2} - K_2 y_{0f}^{K_2}}{(1-K_3)(1-K_2)(K_2-K_3)} + \frac{K_2 y_{0f}^{K_3}}{(K_3-1)(K_3-K_2)} \quad (4.53)$$

y_{0f} is related to the final composition by

$$y_{0f} = \frac{(V_i + V_f)[A]_f}{V_f \kappa_{A0} \nu} \quad (4.54)$$

Substituting Equations (3.15), (4.28) and (4.54) into (4.53), the byproduct rate is given by

$$b' = (V_i + V_f) [A]_f (C_1 + C_2 \gamma_0^{K_2-1} + C_3 \gamma_0^{K_3-1}) \quad (4.55)$$

where

$$C_1^{-1} = \frac{(1-K_3)(1-K_2)}{K_2} \quad (4.56a)$$

$$C_2^{-1} = -\frac{(1-K_2)(K_2-K_3)}{K_2} \quad (4.56b)$$

$$C_3^{-1} = \frac{(K_3-1)(K_3-K_2)}{K_2} \quad (4.56c)$$

Substituting Equations (4.28), (4.32) and (4.39) into (4.42),

$$[A]_f = \frac{V_f N_{A0} v}{V_i + V_f} \exp \left[\frac{V_i + V_f v_B - V_f N_{A0} v}{b V_f N_{A0} v_B} \left(\exp \frac{-b V_f N_{A0} k_1 t_f v}{V_i + V_f} - 1 \right) \right] \quad (4.57)$$

Equations (4.19), (4.38) and (4.40) are used to find t_f ; by substituting them into (4.57), (4.58) is obtained.

$$[A]_f = \frac{V_f N_{A0} v}{V_i + V_f} \exp \left[\frac{V_i + V_f v_B v (1-N_{A0})}{b v V_f N_{A0} v_B} \left(\frac{e^{\alpha} (V_i + V_f v_B v (1-N_{A0}) e^{\beta})}{V_i + V_f v v_B (1-N_{A0})} - 1 \right) \right] \quad (4.58)$$

where

$$\alpha = -\frac{b V_f N_{A0} k_1 v \pi D^2 (L-L')}{4(V_i + V_f)^2} \quad (4.59a)$$

$$\beta = -\frac{b \pi D^2 L' k_1 N_{A0} v}{4 V_f} \quad (4.59b)$$

By similar substitutions, the exit concentration of B is found to be

$$[B]_f = \frac{V_f v (1-N_{A0}) e^{\beta} + \frac{V_i}{v_B}}{V_i + V_f} \exp \left(\alpha \exp \left[\frac{(1-N_{A0})}{b N_{A0}} (e^{\beta} - 1) \right] \right) \quad (4.60)$$

Let the exponent in Equation (4.58) be called B .

$$B = \frac{V_i + V_f v_B v (1-N_{A0})}{b v V_f N_{A0} v_B} \left(\frac{e^{\alpha} (V_i + V_f v_B v (1-N_{A0}) e^{\beta})}{V_i + V_f v v_B (1-N_{A0})} - 1 \right) \quad (4.61)$$

From Equations (4.54) and (4.58),

$$B = \ln y_{of} \quad (4.62)$$

After a set of values of the independent variables is chosen, Equation (4.52) must be solved implicitly for y_{Of} . Equations (4.54) and (4.55) are then used to compute the byproduct rate. As B is known from Equation (4.62), substitution of (4.59a) into (4.61) and rearrangement gives the reactor length, L .

$$L = L' - \frac{4(V_f + V_i)^2}{bV_f \kappa_{A0} k_1 v \pi D^2} \ln \left[\frac{V_i + V_f \sqrt{B} v (1 - \kappa_{A0}) + b v V_f \kappa_{A0} \sqrt{B}}{V_i + V_f \sqrt{B} v (1 - \kappa_{A0}) e^3} \right] \quad (4.63)$$

Equations (4.54) and (4.60) give the concentrations of the reactants in the effluent; then the total cost is computed from Equation (4.4).

Program 8, described in greater detail in Appendix A, uses the equations derived above to find the best values of the design and operating variables to produce P_1 at a molar rate, Z . A creep method is used for optimization and Newton's method is employed to find y_{Of} . Defining H by rearrangement of Equation (4.52),

$$H = \frac{1}{K_2 - 1} (y_{Of} - y_{Of}^{K_2}) - \frac{Z}{V_f \kappa_{A0} v} \quad (4.64)$$

It is desired to find that value of y_{Of} for which $H = 0$. The required derivative is

$$\frac{dH}{dy_{Of}} = \frac{1}{K_2 - 1} \left(1 - \frac{K_2 y_{Of}^{K_2}}{y_{Of}} \right) \quad (4.65)$$

The program was applied to the ethanolamine system, for which the greatest amount of data is available. The reactants were assumed to be pure ethylene oxide and 30% ammonium hydroxide, as reported in the literature⁽⁴⁶⁾. Twenty million pounds of monoethanolamine were to be produced annually; the product separation was to be performed in a 28"-diameter distillation column with thirteen plates. Illustrative cost factors and physical properties of the feed are given in Table IV.3; Table IV.4 contains a summary of the optimum design with and without injection.

TABLE IV.3. PARAMETERS FOR DESIGN OF MONOETHANOLAMINE REACTOR

Molar volume of A, v_A (ammonium hydroxide)			1.019 ft ³ /lbmol
Molar volume of B, v_B (ethylene oxide)			0.795
Production rate, Z			34.2 lbmols/hr
Reactor diameter, D			0.206 ft
Rate constants	Potter	Present <u>work</u>	Both <u> </u>
k_1 , ft ³ /lbmol-hr	3.73	3.36	3.72
K_2	6.048	5.275	6.042
K_3	4.529	1.819	4.556
b	1.629	1.431	1.616
Product separation cost, R			\$ 232.50 hr/lbmol-yr
Reactor operating cost, M			113.90 /yr-ft
Value of A, A			2.63 hr/lbmol-yr
Value of B, B			6.81 hr/lbmol-yr
Value of byproduct, W (diethanolamine)			25.70 hr/lbmol-yr

TABLE IV.4. OPTIMUM DESIGNS FOR MONOETHANOLAMINE REACTOR

All conditions as in TABLE IV.3

Run	1	2	3	4	5
<u>Initial guesses</u>					
V_i , ft ³ /hr	87.0	0	0	0	0
V_f , ft ³ /hr	815	815	5000	684.4	684.4
x_{Ao}	0.476	0.476	0.900	0.557	0.557
L, ft	1921	1450	8000	1679	1679
L', ft	960	0	0	0	0
<u>Rate Constants</u>	Potter	Potter	Potter	Both	Present work
<u>Design Values</u>					
V_i	19	0	0	0	0
V_f	665.4	684.4	684.2	683.7	644.8
x_{Ao}	0.575	0.557	0.557	0.557	0.550
L	1678	1679	1679	1682	1769
L'	0	0	0	0	0
$[A]_f$	0.5335	0.5334	0.5335	0.5334	0.5251
$[B]_f$	0.3563	0.3566	0.3564	0.3574	0.3763
b' , lbmols/hr	12.50	12.48	12.48	12.46	12.57
<u>Production cost, \$/yr</u>					
	336,600	336,100	336,100	336,400	339,800
Run	1	2	3	4	5

As in the single-reaction case, injection of pure B offers no cost advantage. This observation was confirmed by repeating the optimization for other values of the relevant costs. The fact that the same best design is reached from widely differing initial guesses at the values of the independent variables is strong evidence that the optimum combination of design parameters found here is unique. Three sets of rate constants were taken as characterizing the reaction set: Potter's; those gotten by correlating the data obtained from the present experimental work, as described in Chapter III; and a set obtained by fitting both Potter's and the present data simultaneously. The optimum designs based on these three sets of $\{k_i\}$ are very similar, indicating that, for practical purposes, the results of the present experimentation are consistent with the more complete earlier work.

3. Optimal Design by Means of Reactor Simulation on the IBM 704 Digital Computer

When no integrated solution of the rate equations is available, the functional dependence of those dependent variables which figure in the cost equation--reactor length and the product composition--on the independent operating and design variables, cannot be written, even implicitly. This is frequently the case in industry, when the mechanism of a process is unknown, and the yield is to be maximized by choosing the proper operating conditions. The approach most often taken is empirical--the response surface is studied from point to point and no theoretically founded equations are proposed to describe it.

This type of approach was used to confirm the results obtained by Program 8. A chemical reactor was simulated on the IBM 704; the simulation program is Program 9 in Appendix A. This reactor "operated" by integrating the differential equations (2.2) in a fashion similar to that used by Program 1. Auxiliary portions of the program provided for ten consecutive competitive reactions, ten injections of any mixture of reactants and products, and ten recycles. The concentration profiles in the reactor were checked against those predicted by Program 1, and essentially perfect agreement was obtained. For each set of values of the independent variables, the computer printed the compositions of the reaction mix at ten-foot intervals along the length of the reactor; the required value of L was that for which $[F_L]$ satisfied Equation (4.66).

$$[P_i] = \frac{Z}{V_f + V_i} \quad (4.66)$$

The composition of the reaction mix at the exit could be read from the computer output and the cost of production calculated. The Method of Steepest Descent, described in Appendix F, was used to find the region of minimum cost. The required partial derivatives were approximated by difference quotients, so five reactor simulations had to be run in the neighborhood of each point along the descent. Program 10 was written to read in the several lengths and compositions, compute the costs associated with each run, and find the next point in the descent by the methods outlined in Appendix F. The program also punched out the data cards for Program 9.

The progress of the descent is traced in Table IV.5. It was assumed at first that the best values of the injection length and rate were positive; for the first six points, both of the variables decreased. Before either of them had fallen to zero, a point was reached where a feed of pure A

TABLE IV.5 - COURSE OF DESCENT IN DESIGN OF MONOETHANOLAMINE REACTOR

All data as in Table IV.3; Potter's rate constants are used.

Point	V_i , ft ³ /hr L', ft	V_f , ft ³ /hr x_{Ao} L, ft	$[A]_f$, lbmols/ ft ³ $[B]_f$ $[P_1]_f$ $[P_2]_f$	η , \$/yr	$\alpha(n)$
0	815.0 618	815.0 0.4760 1581	0.2343 0.8798 0.02098 0.007220	605100	--
1	534.8 644	940.0 0.6045 1259	0.3854 0.6925 0.02319 0.004895	514600	210.0
2	440.5 636	751.8 0.7464 1424	0.4532 0.5871 0.02868 0.006432	452700	76.95
3b	403.7 610	687.4 0.6807 1435	0.4111 0.6246 0.03134 0.008804	428700	113.6
4	336.7 590	596.9 0.7181 1551	0.4297 0.5753 0.03663 0.01184	397600	167.6
5a	224.2 540	480.7 0.7458 1844	0.4533 0.4720 0.04852 0.02123	365400	171.7
6a*	180.6 480	636.1 1.2165			

* This point was not run, as $x_{Ao} > 1$. Effective values computed for point 5a give 5b, which is used to continue the descent without injection.

TABLE IV.5 (cont'd)

Point	V_f x_{Ao}	L	$[A]_f$ $[B]_f$	$[P_1]_f$ $[P_2]_f$	T	$\alpha(n)$
5b	709.9 0.4760	1844	0.4533 0.4720	0.04852 0.02123		48.9
6b	753.8 0.6107	1534	0.5952 0.3407	0.04537 0.01277	341300	24.4
7	729.4 0.5395	1522	0.5227 0.4137	0.04689 0.01617	335200	36.7
8	692.7 0.5929	1606	0.5703 0.3475	0.04937 0.01626	333600	13.75
9b	679.0 0.5417	1624	0.5168 0.3976	0.05037 0.01938	332700	
Program 8	684.3 0.557	1679	0.5335 0.3565	0.0500 0.01822	336100	

was demanded. In this case, no reaction takes place in the pre-injection portion of the reactor. This results was taken as an indication that injection was being rejected as a means of lowering cost; in continuing the descent, only the feed rate and composition were varied, and only three simulations were made in the neighborhood of each point. The decrease of the step size, α , as the solution proceeds, indicates that the minimum is being approached. The results of Program 8 for the same rate constants and cost factors are indicated in Table IV.5 for comparison.

Equation (4.39) was used to find x_{AOe} for the first six points; the effective feed rate was found by summing V_f and V_i . These effective variables and the true ones for the later points are plotted in Figure 4.1. The descent is indicated by dotted lines through the effective points, and then by solid lines.

From Chapter II, the maximum conversion of A to P_1 is given by

$$[P_1]_{max} = [A]_0 K_2 \frac{K_2}{1-K_2} \quad (2.12)$$

Therefore, the feed rate must be large enough so that

$$V_f [A]_0 K_2 \frac{K_2}{1-K_2} \geq Z \quad (4.67)$$

When the two sides of Equation (4.67) are equal, just enough A is being fed to the reactor to produce P_1 at a molar rate, Z . Therefore, the minimum allowable feed rate is

$$V_{fmin} = \frac{Z}{[A]_0 K_2 \frac{K_2}{1-K_2}} \quad (4.68)$$

When x_{AO} is close to unity, it must be ascertained that the feed rate of B is high enough to meet the desired production rate, but this is unnecessary

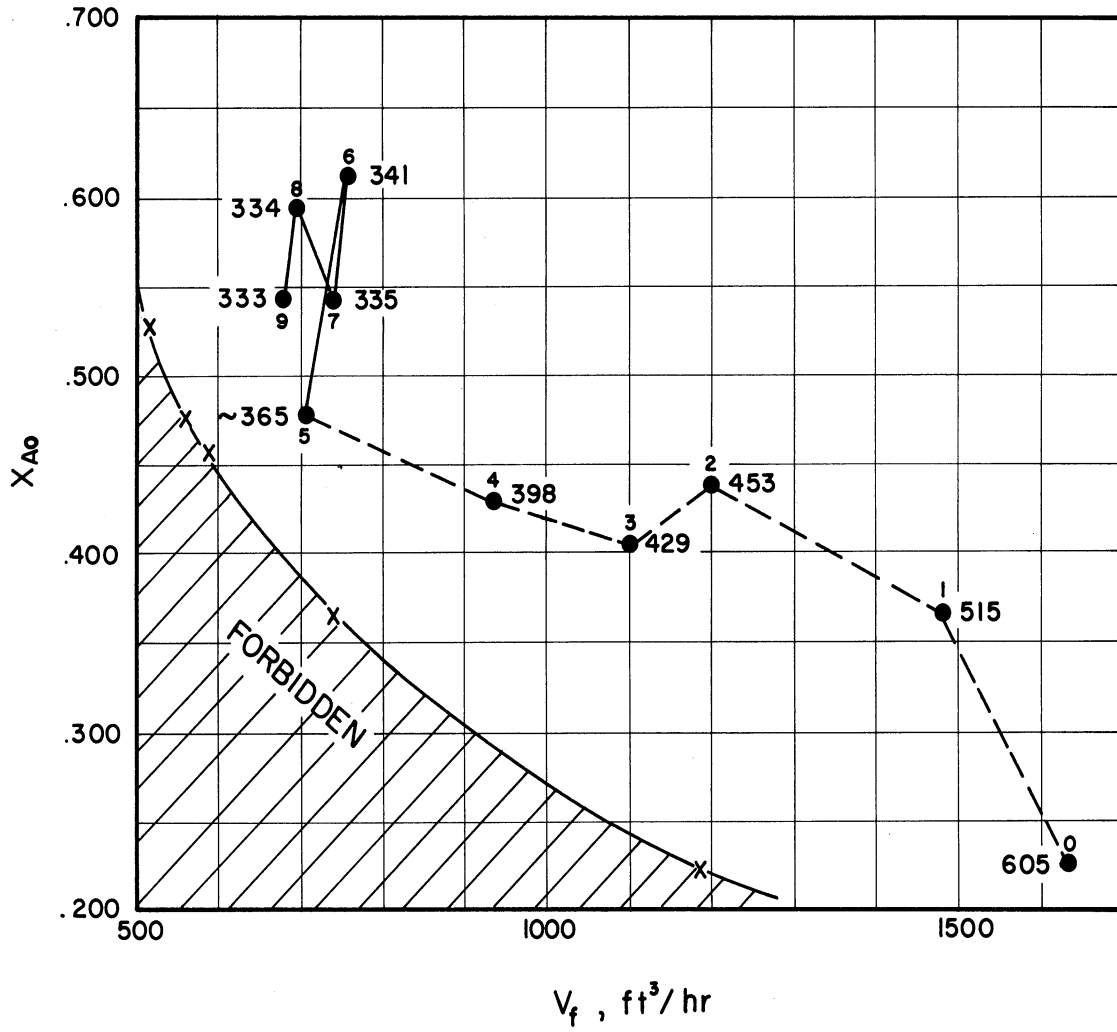


Figure 4.1 Steepest Ascent Design of Monoethanolamine Reactor at 20°C (Costs given in \$1000) .

in the region studied here. The plot of $V_{f_{\min}}$ against x_{A0} in Figure 4.1 outlines a forbidden region; if the independent variables of feed rate and mol fraction of A are chosen in this area, the production requirements cannot be met.

From the results of the steepest descent procedure, the point of minimum cost was estimated to lie in the rectangle

$$\begin{aligned} 0.500 < x_{A0} < 0.600 \\ 500 < V_f < 750 \text{ ft}^3/\text{hr} \end{aligned} \quad (4.69)$$

Nine additional simulation runs were made in this region and the operating costs were computed by Program 10. The results of this study are in Table IV.6. These points are plotted with the later points of the descent in Figure 4.2. Lines of constant cost are drawn to aid in the estimation of the design values of V_f and x_{A0} . The best operating conditions appear to be bounded by

$$0.540 < x_{A0} < 0.580 \quad (4.70)$$

and

$$660 < V_f < 710 \text{ ft}^3/\text{hr}.$$

The optimum design obtained from Program 8 satisfies Equation (4.70); the corresponding point in V_f - x_{A0} space is indicated in Figure 4.2. The results obtained here serve as additional confirmation of the ability of the approximate solution of the rate equations to represent the true solutions. For an engineer, this practical evidence of the usefulness of the explicit equations can be expected to be considerably more meaningful than the earlier comparisons of the results obtained by using the two methods, as summarized in Table III.3.

TABLE IV.6 - ADDITIONAL POINTS FOR MONOETHANOLAMINE REACTOR DESIGN

Point	Feed rate, ft ³ /hr	x _{A0}	Production Cost, \$/yr
1	600	0.596	335700
2	700	0.575	332600
3	741	0.525	337200
4	700	0.475	344700
5	600	0.454	464900
6	570	0.475	432700
7	521	0.525	452100
8	500	0.575	410100
9	600	0.525	345200

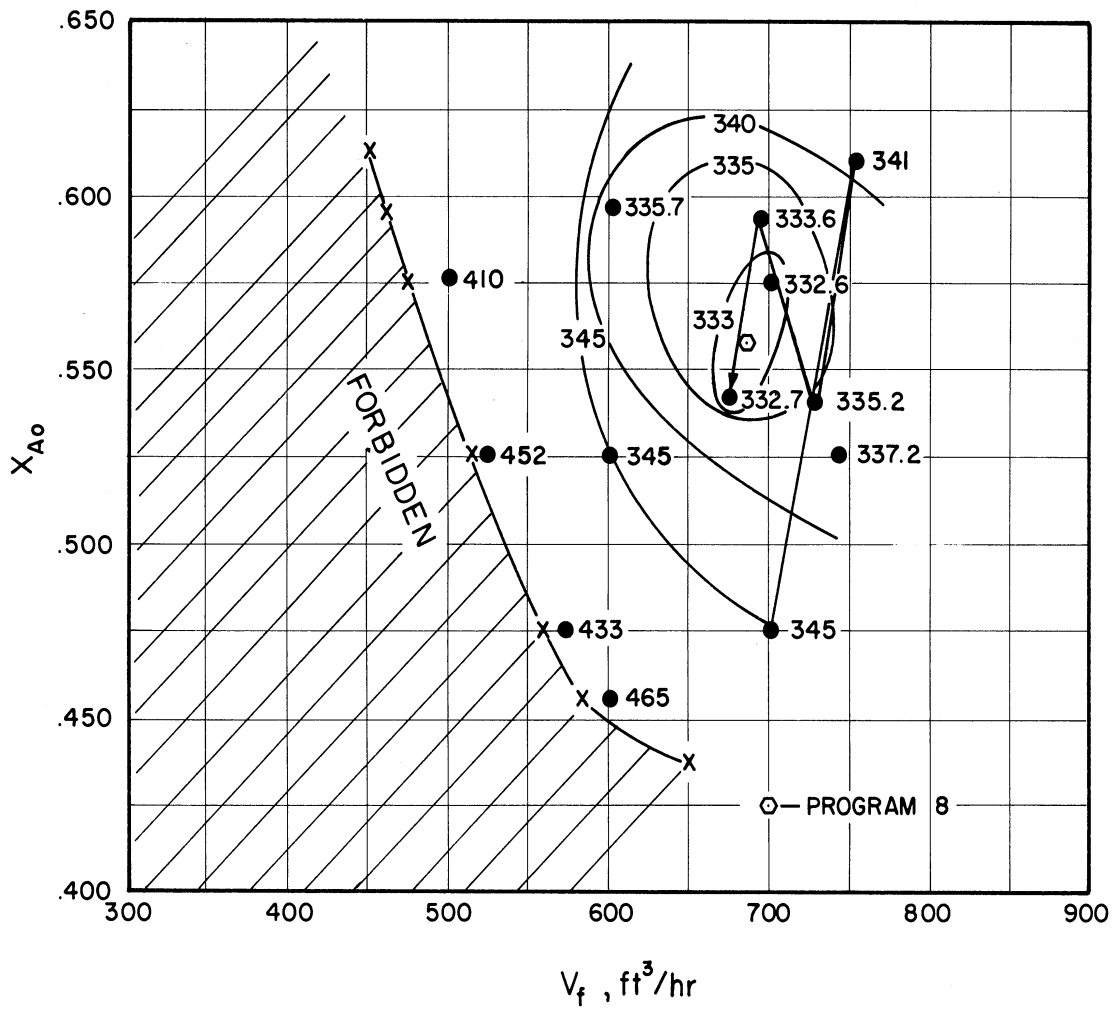


Figure 4.2 Detail of Minimum Region of Monoethanolamine Reactor at 20°C.

E. Analytical Design Methods

The equations derived earlier in this chapter to describe the total production cost as a function of the design and operating variables were exceedingly complex, and unsuited to analytical treatment. For this reason, methods such as creep and steepest descent, which required computation of the cost response only at isolated points, were used to solve the design problem posed earlier. These studies indicated that the problem was not as complex as it was at first thought, because injection was rejected as an economizing design feature. In this section, we will treat the problem of designing a simple flow reactor, without injection, and with only two important design variables--feed rate and feed composition. Mathematical relationships between the optimum values of these parameters which can be solved directly to give the best design will be derived. In the discussion to follow, the volumetric feed rate will be signified by V , as there is now no ambiguity in the definition.

1. To Carry Out a Second-Order Reaction

The cost function used here is obtained from that used earlier by setting $V_i = 0$.

$$\tau = ML + VR([A]_f + [B]_f) + Z(A+B) \quad (4.71)$$

As before, $[A]_f$ and $[B]_f$ are found from the material balance equations (4.48) and (4.49); these simplify, when $V_i = 0$, to

$$[A]_f = \frac{Vr_{A0}V - Z}{V} \quad (4.72)$$

and

$$[B]_f = \frac{rV(1 - r_{A0}) - Z}{V} \quad (4.73)$$

From Equations (4.18) and (4.28), the final concentration of A can be written as a function of the operating variables and reactor length.

$$[A]_f = \frac{v(1-x_{A0})e^D}{\frac{1-x_{A0}}{x_{A0}} - e^D} \quad (4.74)$$

where $D = \frac{vk_1\pi D^2 L(2x_{A0}-1)}{4V}$ (4.75)

Equations (4.72), (4.74) and (4.75) can be solved for L.

$$L = \frac{4V}{vk_1\pi D^2(2x_{A0}-1)} \ln \frac{(1-x_{A0})Z - Vv x_{A0}(1-x_{A0})}{Zx_{A0} - Vv x_{A0}(1-x_{A0})} \quad (4.76)$$

From Equations (4.15) and (4.28), the argument of the logarithm in (4.76) can be written as $\frac{(1-x_{A0})(Z-V[A]_0)}{x_{A0}(Z-V[B]_0)}$. As the mol fractions lie between zero and one, the argument is positive only if the molar feed rates of both--or neither, but this is absurd--A and B exceed Z. This is an obvious requirement, and one confirmed by the mathematics. Substituting Equations (4.72) and (4.73) into (4.71),

$$\mathcal{T} = ML + (A+B-2R)Z + RVv \quad (4.77)$$

The minimum production cost obtains when

$$\frac{\partial \mathcal{T}}{\partial V} = 0 = M \frac{\partial L}{\partial V} + Rv \quad (4.78)$$

and

$$\frac{\partial \mathcal{T}}{\partial x_{A0}} = 0 = M \frac{\partial L}{\partial x_{A0}} + RV \frac{\partial v}{\partial x_{A0}} \quad (4.79)$$

Substituting the value of \mathcal{T} given by Equations (4.3), (4.76) and (4.77) into (4.78) and (4.79), respectively,

$$\frac{\partial \mathcal{T}}{\partial V} = 0 = \frac{4M}{vk_1\pi D^2(2x_{A0}-1)} \ln \frac{(1-x_{A0})Z - Vv x_{A0}(1-x_{A0})}{Zx_{A0} - Vv x_{A0}(1-x_{A0})} - \frac{4MVZ}{k_1\pi D^2[Z^2 - ZVv + V^2v^2x_{A0}(1-x_{A0})]} + Rv \quad (4.80)$$

TABLE IV.7. COMPARISON OF ACETANILIDE REACTOR DESIGNS

All data except R as in Table IV.1

	Program 7 <u>injection</u>	Program 7 <u>no injection</u>	Program 11 <u></u>
<u>R = 1805\$-hr/yr-lbmol</u>			
V, ft ³ /hr	4.192	4.186	4.183
x _{A0}	0.416	0.415	0.417
L, ft	6150	6152	6146
<u>R = 18050</u>			
V	1.904	1.902	1.902
x _{A0}	0.444	0.446	0.446
L	8821	8831	8833
<u>R = 180500</u>			
V	1.178	1.179	1.177
x _{A0}	0.480	0.480	0.480
L	17320	17300	17360

$$\text{and } \frac{\partial \mathcal{T}}{\partial x_{A0}} = 0 = \frac{4MVZ}{v k_1 \pi D^2 (2x_{A0} - 1)} \left[\frac{-Z + v \tau^2 (N_A x_{A0}^2 + N_B (1 - x_{A0})^2)}{x_{A0} (1 - x_{A0}) [Z^2 - v \tau Z + v^2 \tau^2 x_{A0} (1 - x_{A0})]} \right] \quad (4.81)$$

$$- \frac{4VM(N_A + N_B)}{k_1 \pi D^2 (2x_{A0} - 1)^2} \ln \frac{(1 - x_{A0})Z - v \tau x_{A0} (1 - x_{A0})}{Z x_{A0} - v \tau x_{A0} (1 - x_{A0})} + RV(N_B - N_A) \tau^2$$

The roots of Equations (4.80) and (4.81), if unique, are the optimum values of x_{A0} and V . Program 11, described in Appendix A, was used to solve the two equations, using the data of Table IV.1 for acetanilide synthesis. The second-order partials of \mathcal{T} were estimated from the printout, and the Hessian was evaluated at the presumed optimum; the existence at this point of at least a local minimum of the production cost response was indicated. Several values of the molar recovery cost, R , were assumed; the designs obtained by Program 11 are compared in Table IV.7 with those given by Program 7. The results of the latter program for the runs in which

positive injection rates and lengths were assumed were converted to a no-injection basis by assuming the feed and injection streams to be mixed immediately before being fed to the reactor inlet; a negligible change is occasioned in the dependent variables of cost, reactor length and product composition by this assumption that $L' = 0$. The agreement between the results of these two methods of design is excellent.

2. To Carry Out a Set of Consecutive Competitive Reactions

The analytical design problem here is more difficult than that for a single reaction, for the same reasons that the numerical procedure was more involved: byproducts must be taken into account and the required reactor length cannot be written explicitly. The cost function is given by Equation (4.4), setting $V_i = 0$.

$$\tau = ML + V_r(A\alpha_{A0} + B(1 - \alpha_{A0})) + V(R-A)[A]_f + (R-B)[B]_f + (R-W)b' \quad (4.82)$$

From Equation (4.29),

$$[A]_f = \alpha_{A0} v \exp \left[\frac{(1 - \alpha_{A0})}{b\alpha_{A0}} \left(\exp \frac{-b\alpha_{A0} k_1 \pi D^2 L v}{4V} - 1 \right) \right] \quad (4.83)$$

Similarly, from Equation (4.30),

$$[B]_f = v(1 - \alpha_{A0}) e^{\frac{b\pi D^2 L k_1 \alpha_{A0} v}{4V}} \quad (4.84)$$

Define f by

$$f = \frac{-b\pi D^2 L k_1 \alpha_{A0} v}{4V} \quad (4.85)$$

and B by

$$B = \frac{(1 - \alpha_{A0})(e^f - 1)}{b\alpha_{A0}} \quad (4.86)$$

Then

$$[A]_f = \alpha_{A0} v e^B \quad (4.87)$$

and

$$[B]_f = v(1 - \alpha_{A0}) e^f \quad (4.88)$$

Substituting Equation (4.28) into (4.87)

$$e^{\theta} = y_0 \quad (4.89)$$

Substituting Equations (4.87), (4.88), (4.89) and (4.55) into (4.82),

$$\begin{aligned} \gamma = ML + Vv(A\alpha_{A0} + B(1-\alpha_{A0})) + V((R-A)\alpha_{A0}ve^{\theta} + (R-B)v(1-\alpha_{A0})e^{\theta}) \\ + (R-W)V\alpha_{A0}v(C_1e^{\theta} + C_2e^{K_2\theta} + C_3e^{K_3\theta}) \end{aligned} \quad (4.90)$$

Equation (4.90) gives the production cost as a function of the feed rate and composition and the reactor length. This last variable is implicitly defined by Equation (4.91).

$$y_1 = \frac{1}{K_2 - 1} \left\{ e^{\theta} - e^{K_2\theta} \right\} = \frac{Z}{V\alpha_{A0}v} \quad (4.91)$$

As this equation cannot be solved for L, the optimum design cannot be found by setting equal to zero the derivatives of the cost function with respect to the independent variables, as was done above. The problem here is more conveniently phrased as follows: Find those values of reactor length and feed rate and composition which minimize the production cost, subject to the restraint given by Equation (4.91).

This problem is solved by using the Method of Undetermined Multipliers. Require Equation (4.91) to hold, and also that

$$\frac{\partial \gamma}{\partial L} + \lambda \frac{\partial h}{\partial L} = 0 \quad (4.92a)$$

$$\frac{\partial \gamma}{\partial \alpha_{A0}} + \lambda \frac{\partial h}{\partial \alpha_{A0}} = 0 \quad (4.92b)$$

$$\frac{\partial \gamma}{\partial v} + \lambda \frac{\partial h}{\partial v} = 0 \quad (4.92c)$$

where λ = the undetermined multiplier, a function of the constants and the independent variables

$$h = \frac{1}{K_2 - 1} \left\{ e^{\theta} - e^{K_2\theta} \right\} - \frac{Z}{V\alpha_{A0}v} \quad (4.93)$$

$\partial h/\partial L$ and $\partial T/\partial L$ can be computed and used to find λ from Equation (4.92a).

$$\frac{\partial h}{\partial L} = \frac{1}{K_2 - 1} \left\{ e^B - K_2 e^{K_2 B} \right\} \frac{\partial B}{\partial L} \quad (4.94)$$

$$\frac{\partial T}{\partial L} = M - \frac{\pi D^2 k_1 \lambda_{A0} v^2 (1 - \lambda_{A0}) e^{\frac{r}{2}}}{4} \left\{ (R-A)e^B + (R-B)b + (R-W)(C_1 e^B + C_2 K_2 e^{K_2 B} + C_3 K_3 e^{K_3 B}) \right\} \quad (4.95)$$

where $\frac{\partial B}{\partial L} = - \frac{(1 - \lambda_{A0}) e^{\frac{r}{2}} \pi D^2 k_1 v}{4V}$ (4.96)

Then Equation (4.92b) becomes

$$\begin{aligned} \frac{\partial T}{\partial \lambda_{A0}} - \frac{\partial T/\partial L}{\partial h/\partial L} \cdot \frac{\partial h}{\partial \lambda_{A0}} = 0 = v [A \lambda_{A0} + B(1 - \lambda_{A0})] + (R-A) \lambda_{A0} v e^B + (R-B) v (1 - \lambda_{A0}) e^{\frac{r}{2}} + \frac{LM}{V} \\ + (R-W) \lambda_{A0} v (C_1 e^B + C_2 e^{K_2 B} + C_3 e^{K_3 B}) + \frac{4(K_2 - 1) Z \frac{\partial T}{\partial L}}{V \lambda_{A0} v^2 (e^B - K_2 e^{K_2 B}) (1 - \lambda_{A0}) e^{\frac{r}{2}} \pi D^2 k_1} \end{aligned} \quad (4.97)$$

where $\partial T/\partial L$ is computed from Equation (4.95). Similarly, from Equation

(4.92c),

$$\begin{aligned} \frac{\partial T}{\partial \lambda_{A0}} - \frac{\partial T/\partial L}{\partial h/\partial L} \cdot \frac{\partial h}{\partial \lambda_{A0}} = 0 = V A \lambda_{A0} v^2 - V B \lambda_{A0} v^2 + V(R-A) e^B \lambda_{A0} v^2 - V(R-B) e^{\frac{r}{2}} (1 - \lambda_{A0}) v^2 \\ + \frac{4M(1 - e^{\frac{r}{2}}) V}{b \lambda_{A0}^2 (1 - \lambda_{A0}) e^{\frac{r}{2}} \pi D^2 k_1 v} + \frac{4(K_2 - 1) Z \lambda_{A0} \frac{\partial T}{\partial L}}{\lambda_{A0}^2 (e^B - K_2 e^{K_2 B}) (1 - \lambda_{A0}) e^{\frac{r}{2}} \pi D^2 k_1 v} - \frac{LM \lambda_{A0} v}{\lambda_{A0}} \\ - \frac{(R-B) V v (1 - e^{\frac{r}{2}})}{\lambda_{A0}} + (R-W) V \lambda_{A0} v^2 (C_1 e^B + C_2 e^{K_2 B} + C_3 e^{K_3 B}) \end{aligned} \quad (4.98)$$

Equations (4.91), (4.97) and (4.98) constitute three equations in three unknowns: the best design values of V , λ_{A0} and L . Multiplying Equation (4.98) by $\frac{\lambda_{A0}}{V \lambda_{A0} v}$ and subtracting (4.97),

$$\frac{4M(1 - e^{\frac{r}{2}})}{b \lambda_{A0} (1 - \lambda_{A0}) e^{\frac{r}{2}} \pi D^2 k_1 v^2 \lambda_{A0}} - \frac{2LM}{V} - \frac{R}{\lambda_{A0}} = 0 \quad (4.99)$$

Equation (4.99) can be used in place of (4.97) or (4.98) to simplify the solution. Unfortunately, no further simplifications are possible. The results obtained from Program 8 and presented in Table IV.4 were substituted

into Equations (4.91), (4.97) and (4.99) to see if the numerical solutions were consistent with the analytical equations. The numbers involved, showing the quality of the check, are in Table IV.8. The equations derived above appear to be valid.

It should be mentioned that the value of the analytical solutions presented here and in Equations (4.80) and (4.81) is diminished only slightly by the fact that they do not admit of explicit solution. Graphical methods are available to find the roots, and the equations simplify to soluble expressions when certain cost factors are neglected. It is much more informative--and here even more convenient, in the long run--to simplify a general expression, than to try to generalize from a host of trivial solutions.

TABLE IV.8 - CHECK OF ANALYTICAL DESIGN EQUATIONS FOR MONOETHANOLAMINE REACTOR

Numbers to be substituted into analytical equations:

V	648	K ₂	6.05
x _{A0}	0.557	K ₃	4.53
L	1679	D	0.206
v _A	1.019	b	1.629
v _B	0.795	R	232.5
Z	34.2	A	2.63
k ₁	3.73	W	25.7
M	113.9	B	6.81

Calculated functions:

v	1.089
φ	-0.300
e ^φ	0.742
φ ₀	-0.1260
e	0.882
C ₁	0.340
C ₂	0.783
C ₃	-1.120
∂T/∂L	100.5

<u>Equation</u>	(4.99)	(4.91)	(4.97)
Positive terms*	841		492
Negative terms*	852	0.6	484
Calculated Z _{total}	1.3	34.0	1.6

* left-hand side of equation

V. CONSIDERATIONS ON THE METHOD AND RECOMMENDATIONS FOR FUTURE WORK

A. The Approximate Solution of Complex Rate Equations

The procedures used in the last two chapters to treat systems of consecutive competitive reactions are applicable not only to the cases discussed, but rather are an application of a more general algorithm to a particular reaction system. In this section, the steps used in the treatment of consecutive competitive reactions will be described in a most general sense, so that the applications of the method to other systems which defy exact solution will be evident.

If a reaction mechanism has been proposed, differential equations can be written to describe the course of reaction. If these equations are soluble, the procedure to be followed is straightforward: the equations are solved and the resulting integral expressions are used for correlation and design, as was done above for a single second-order reaction. If, on the other hand, the equations cannot be integrated to relate explicitly the values of the composition variables to time and the initial conditions, the solution procedure is considerably more complex.

The first step in the development of an approximate solution of the rate equations is the numerical integration of the equations for a wide range of values of the reaction parameters and initial conditions. Fewer integrations will be required if the rate equations are first put into dimensionless form. Analog computation may prove useful here, both for the speed with which the solutions can be found and because of the visual nature of the solution. Frequently, some properties of the solution can be found, even if the

complete solution cannot be obtained. If, for instance, two concentration profiles can be related in terms of the initial conditions for each run, the amount of numerical integration required can be considerably reduced. Time-independent solutions, obtained by solving the quotient of two rate equations, can reduce the number of concentrations whose time-dependence will have to be described empirically.

Eventually, it will be necessary to make some sort of empirical correlation. The choice of the dependent variable to be represented in this way is very important. If possible, only one variable should be approximated and in such a way that its values at least at zero and infinite time are consistent with theory. Before the variable is chosen, many questions must be answered satisfactorily: can the values of the other dependent variables be explicitly solved for, using the approximation? Is the value of the variable sensitive to changes in time and initial conditions so that errors in fit will not cause gross deviations when inverse functions are used? Can an approximating expression be found which is simple and uses few empirical parameters yet is accurate for a wide range of initial conditions and values of the rate constants? Does having an explicit equation for this variable offer any additional bonuses--for example, the ability to relate results obtained from different sets of initial conditions, or to reduce to a known exact solution if certain of the rate constants are set equal to zero? It may be impossible to find a variable which satisfies all these requirements. Compromises will often have to be made, but it can not be overemphasized that the choice of the variable to be represented explicitly is one that should be made only after some consideration.

When the variable and its empirical representation have been chosen, the rate equations are solved, using the approximation, to find the functions describing the concentrations of the other components. The asymptotic values of all the dependent variables should agree with theory and other facts known to be true of the unattainable exact solutions should be confirmed. If equations have been derived to relate solutions of the rate equations through their initial conditions, these should be introduced here to put the approximate solution into its most generally applicable form.

In the derivation of the approximate solution, some arbitrary parameters are generally involved. These may be functions of the initial conditions, the rate constants, or both. The parameters are estimated by fitting the approximate solution of the rate equations to the exact solution, the latter having been found from the numerical integration. The best values of the parameters may be expressed as functions of the variables on which they are defined, or their dependence may be put in graphical form. The former method, if feasible, is to be preferred because the approximate solution may then be written completely in closed form.

B. Advantages of the Integral Method and Recommendations for Future Work

Before completing this discussion of the approximate treatment of complex reaction systems, it is worthwhile to consider the advantages offered by the integral solution, in spite of its approximate nature.

It was pointed out earlier that the integral solution of the rate equations is considerably more convenient than the equations themselves for the correlation of literature data and for the development of design

equations. The most frequent criticism which might be made of this procedure is that it is inexact. This fact cannot be denied, but its importance can easily be overestimated. It cannot be claimed that differences between experimental results and those predicted by the approximate model are due solely to the manner in which the model was derived. First of all, there is no reason to expect the experimental system to adhere rigorously to the differential equations written to represent it. Even if it did, experimental error would preclude any positive confirmation of this. The proposed approximate model fits the experimental results within experimental error and the rate constants computed using the integral solution are consistent with those obtained by more direct means, such as the differential treatments of Chapter III. It would be interesting to see whether the assumed differential rate equations fit the data as well as the model proposed here; it is not unlikely that they might not.

A similar line of reasoning applies to reactor design. The definition of the production cost is approximate; many of the cost responses are really non-linear, and some of the cost factors change from day to day. If a wholly accurate cost picture were to be written, it would have to include pumping cost, amortization, down time, supply-demand interaction and a host of other variables. The most important factors are included in Chapter IV, but the expression for the total cost is still inexact. If such is the case, nothing is to be gained by refining the integral solution to absurd extremes. In addition, it should not be rejected because it is approximate, for it is no more approximate than the cost function into which it is substituted. It is clear from Table IV.5 and Figure 4.2, that there

is no significant difference between the optimum designs obtained from the approximate solution and those gotten from the differential equations themselves. The former method consumed perhaps a minute of 704 computer time and a minimum amount of human effort, whereas the latter took about 90 minutes on the computer and perhaps 10 hours of pencil work. For the IBM 650, whose speed is perhaps eighty times slower than the 704, the differences in computer time become alarmingly great. And if it is desired to adjust continuously the operation of the reactor to respond to changes in the magnitudes of the cost factors, only with the use of an integrated solution could this be done.

For the engineer, the true test of the approximation lies not in its ability to satisfy the differential rate equations, which are theoretically-grounded assumptions, but rather in its ability to correlate real data and solve real design problems. It seems reasonable then that the algorithm described above might be used for the solution of practical problems without the intermediate step of postulating a set of rate equations. A flowsheet for this type of operation is given in Figure 5.1. Though the several functions of the blocks in the diagram can be performed by man or machine, the discussion to follow is based on the assumption that the entire procedure is programmed.

The input to the computer consists of: 1) the body of available data, if any, on the experimental system; 2) any analytical formulae which have been derived relating the values of the several dependent variables to one another or to the initial conditions; 3) any values which the dependent variables must have at zero or infinite time and 4) any functions which, it

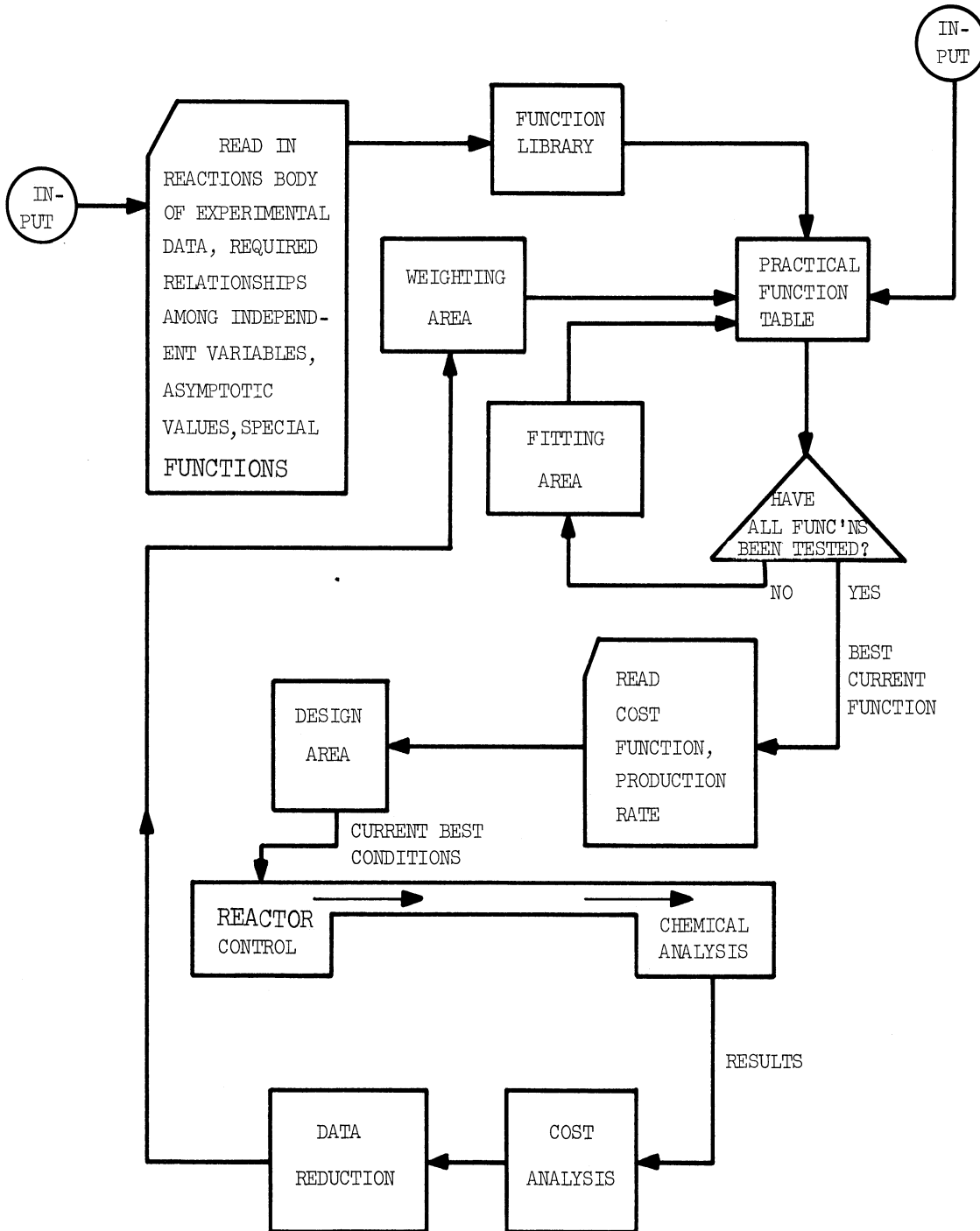


Figure 5.1 Generalized Reactor Design System.

is hoped, will aid in the correlation. The computer searches a programmed library of other possible functions and prepares a list of functions which satisfy the requirements in the input and are most promising. The current available data are fitted to the functions in this table and the best approximation is chosen. The desired production rate and current values of the several cost factors are read in and the optimum operating conditions for the reactor are derived.

If a real reactor is being optimized, these conditions are achieved through the instrumentation of the apparatus and output in the form of digitized analytical results are fed back to the computer. For a more rapid and thorough study, the reactor may be simulated on the computer with a random error superimposed on the output. In either event, a cost can be computed and more experimental data obtained from the reactor output. These data are then combined with the original data and a weighting procedure is employed. In general, recent data will be weighted more heavily than old results. The practical function table is again entered and the procedure repeated. Provision should be made for additional inputs to this table as new useful functions become evident. Such a study would be most informative. Of interest would be the stability and rate of convergence of the system in response to changes in the cost factors, desired production rate and experimental error amplitude.

C. Conclusions

The contributions of this study to the fields of chemistry and engineering are:

- (1). For the first time, equations explicit in concentration have been derived which describe to within two per cent 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.
- (2). These formulae have been used to correlate experimental and literature data on consecutive competitive reaction systems. The standard deviation between the experimental and calculated compositions of the reaction mixes was always less than four per cent and usually less than two per cent of the initial concentration of A. The values of the rate constants which were used to obtain the best fit to the published data agreed closely with the values found by more direct means, such as data differentiation and graphical integration.
- (3). From the correlations described by (2), insight was gained into the mechanisms of the following reactions:
 - (a). Esterification of butanediols
 - (b). Substitutive chlorination of propylene
 - (c). Hydrofluorination of carbon tetrachloride .
- (4). From the correlations described by (2), earlier results on the following systems were confirmed:
 - (a). Addition of ethylene oxide to ammonia
 - (b). Chlorination of benzene
 - (c). Addition of propylene oxide to methanol .

- (5). The integrated rate equations have been used to develop numerical and analytical methods of finding the optimum design of batch and flow reactors in which consecutive competitive reactions or single second-order syntheses are to be carried out.
- (6). Computer programs have been written for reactor simulation and design purposes, and they have been applied to the design of reactors for the productions of monoethanolamine and acetanilid.
- (7). Downstream injection of the common reactant was found to be useless for economizing operation.

APPENDICES

APPENDIX A

DESCRIPTION OF COMPUTER PROGRAMS

Program 1: Program to Integrate Differential Rate Equations

Purpose: A set of consecutive competitive reactions is represented by Equations (2.1). The rate of formation of the i -th product is given by

$$\frac{d[P_i]}{dt} = k_i [B][P_{i-1}] - k_{i+1} [B][P_i] \quad (i=0, \dots, j) \quad (3.1b)$$

For the methanol-propylene oxide system, Lay⁽²⁶⁾ found that the specific reaction rate constant showed an exponential dependence on methanol (A) concentration. This program solves the differential equations above, for $j = 3$, allowing the use of an exponential dependence as mentioned above. When the exponential term is not desired, e may be replaced by unity. Five differential equations are solved simultaneously--the four implied by $i = 0, 1, 2$ and 3 , and the differential equation for the disappearance of B.

$$-\frac{d[B]}{dt} = [B] \sum_{i=0}^j k_{i+1} [P_i] \quad (3.1c)$$

The program takes thirteen pieces of data as input, in three groups. The first group is that data which is normally constant for any particular study; it consists of the molar density of A, the maximum allowable error per time interval, the three rate constants and the fractional conversion of B required before the problem is completed and the next set of data read. The second set is generally varied, and consists of the initial time, t_0 ,

the base of the exponentiation and the time interval at which results are desired, Δt . The last set contains the initial values of the concentrations of all the reactants and products. The output format consists of the concentration profiles and the number of halvings of Δt necessary to obtain the desired accuracy.

Logic: The data are read in and the program uses the Runge-Kutta subroutine, with time interval Δt , to get the new concentration profile at time $t_0 + \Delta t$. Δt is halved and the RKSUB is repeated twice with this smaller interval; the concentration profile arrived at in this fashion is compared with the previous one. If the error is less than the specified amount, the second set of values of $[A]$, ..., $[P_3]$, and $[B]$ is punched out, and taken as the initial values for the concentration profile at $t_0 + 2\Delta t$. If the error is too great, the time interval is again halved, the RKSUB pursued four times, and the comparison made. The procedure is repeated until sufficient agreement is reached and then the most accurate values of concentration are used for the next time step. After each punchout, the program checks to see if enough of the B originally present has been consumed; when such is the case, the program reads a new set of data and repeats the process.

Computer: IBM 650 with indexing

Language: GAT (Generalized Algebraic Translator)

Subroutines needed: FIX (change from floating-point mode to fixed-point)
FLOAT (change from fixed-point mode to floating-point)
READ (input)
PUNCH (output)
P (exponentiation) (listed as GEXP)
RKSUB (Runge-Kutta)

Storage requirements: 1147 words

Running time: .66 minutes x number of reactions x number of time intervals

Correspondence of variables:

Y0 : t_0
Y1 : $[A]_0$
Y2 : $[B]_0$
Y3 : $[P_1]_0$
Y4 : $[P_2]_0$
Y5 : $[P_3]_0$
X0 : molar density of A
X1 : base of the exponentiation
X2 : Δt
X4 : maximum allowable error per time interval
Z0 : required fraction conversion of B
Z1 : $-k_1$
Z2 : $-k_2$
Z3 : $-k_3$

Z(6*J3+4) : t
Z(6*J3+5) : [A]
Z(6*J3+6) : [B]
Z(6*J3+7) : [P₁]
Z(6*J3+8) : [P₂]
Z(6*J3+9) : [P₃]

J3 : number of halvings required

J0 : counter for storage of time and concentrations
in Z-field*

J1 : required number of passes through RKSUB*

J2 : counter on number of passes through RKSUB*

J4 : counter for calculation of difference between
results of previous and present passes*

J5 : counter for temporary storage of time and con-
centrations in C-field*

J6 : counter for extracting time and concentrations
from Z-field*

C0 : stored value of t*

C1 : stored value of [A]*

C2 : stored value of [B]*

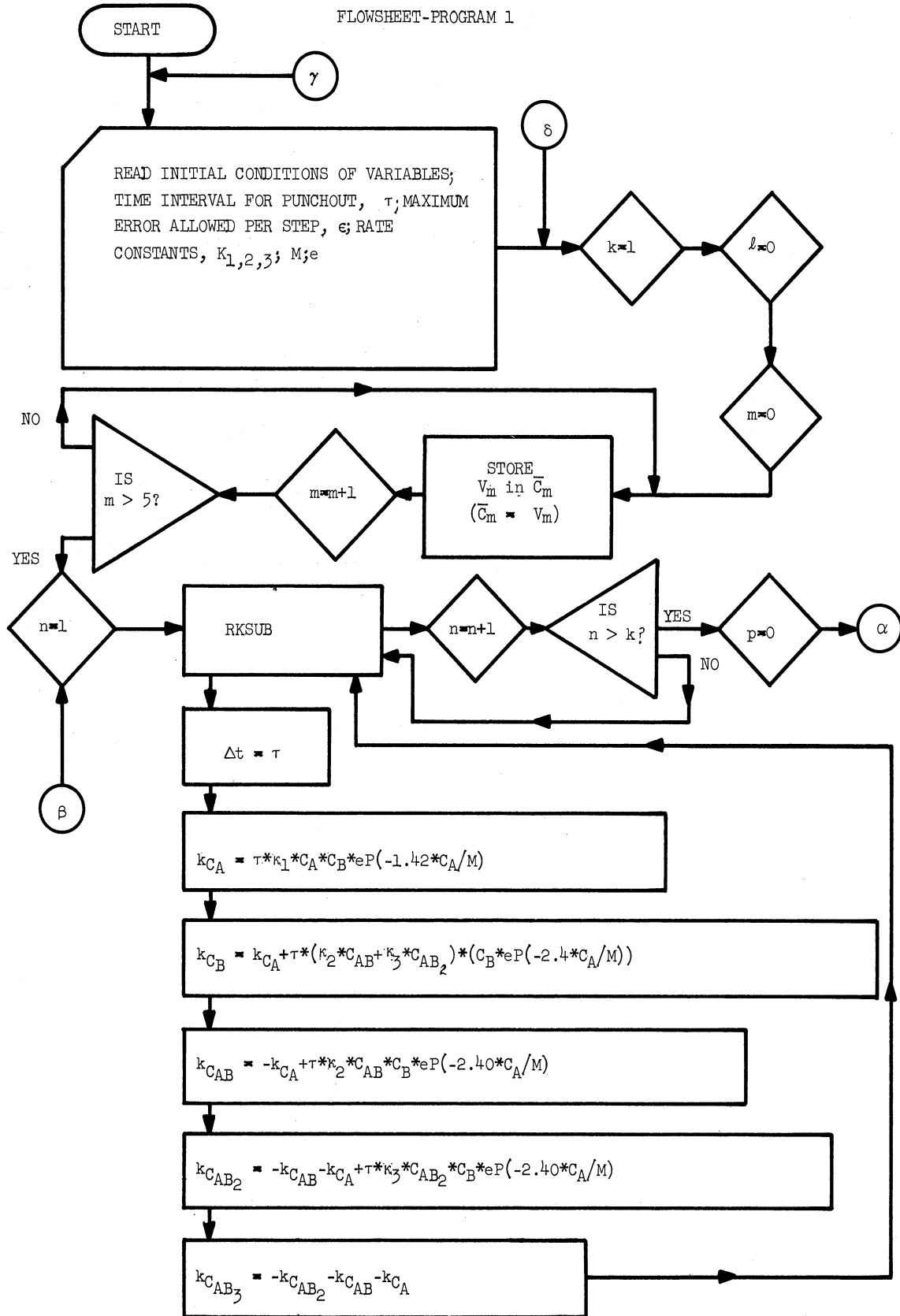
C3 : stored value of [P₁]*

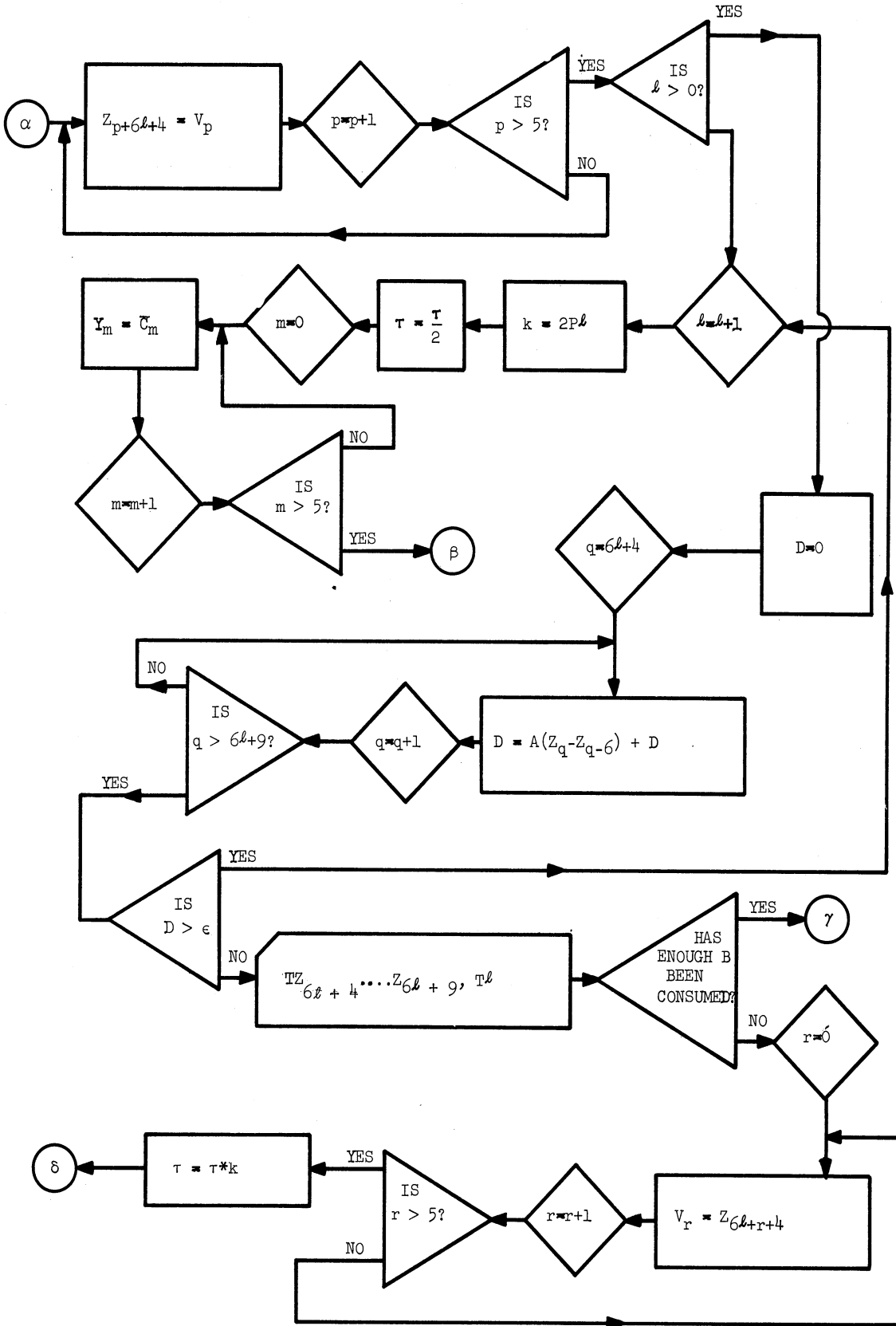
C4 : stored value of [P₂]*

C5 : stored value of [P₃]*

D0 : difference between results of previous and
present passes*

* values obtained only through programmed dump.





PROGRAM TO INTEGRATE DIFFERENTIAL RATE EQUATIONS

```
28 IS HIGHEST STATEMENT NUMBER
550 USED IN SUBROUTINES
DIMENSION C(5) D(0) J(6) N
X(4) Y(17) Z(39)
1 Y0=5,X0,1,2,4,Z0=3 READ
2 X3 = Y2
3 J1 = 1
4 J3 = 0
5 6, J5, 0, 1, 5,
6 CJ5 = YJ5
7 8, J2, 1, 1, J1,
8 RKSUB.(6, LY0, 28)
9 10, J0, 0, 1, 5,
10 Z(J0+6*J3+4) = YJ0
11 GO TO 18 IF J3 V 0
12 J3 = J3 + 1
13 J1 = 2PJ3
14 X2 = X2/2
15 16, J5, 0, 1, 5,
16 YJ5 = CJ5
17 GO TO 7
18 D0 = 0
19 20, J4, 6*J3+4, 1, 6*J3+9,
20 D0= A(ZJ4 - Z(J4-6)) + D0
21 GO TO 12 IF D0 V X4
22 TZ(6*J3+4)...Z(6*J3+9) TJ3
23 GO TO 1 IF X3/Z0V Y2
24 25, J6, 0, 1, 5,
25 YJ6 = Z(6*J3+J6+4)
X2 = X2 * J1
26 GO TO 3
27 TY0...Y5 TX2 TJ0...J6 N
TC0...C5 TZ4...Z(9+6*J3) TD0
HALT
28 Y6 = X2
Y7 = X2*Z1*Y1*Y2*X1P(-1.42 N
*Y1/X0)
Y8 = Y7+X2*(Z2*Y3+Z3*Y4)* N
(Y2*X1P(-2.4*Y1/X0))
Y9 = -Y7+X2*Z2*Y3*Y2*X1P N
(-2.40*Y1/X0)
Y10= -Y9-Y7+X2*Z3*Y4*Y2* N
X1P(-2.40*Y1/X0)
Y11= -Y10-Y9-Y7
GO TO 8
END
```

Program 2: Program to Reformulate Output from Program 1 for Use in Program 3

Purpose: The output from Program 1 is in the floating-point mode. The number $0.n_1n_2\dots n_8 \times 10^Y$ is stored in the IBM 650 as the ten-digit floating-point number $n_1n_2\dots n_8m$, where m is a two-digit integer equal to $50+y$. Program 2 reads in the output from Program 1, multiplies the values of $[B]_0$, k_2 , k_3 , t , and $[A]$ by sufficiently large powers of ten to allow their representation in the integral mode, and punches out these values for use in subsequent IBM 704 programs.

Logic: The values of the first three variables whose mode is to be changed are read from the data cards preceding the output for each run; the last two are read from the punchout itself. As Z0 is given as part of the data deck, it is used as a switch to allow the computer to discriminate between Program 1 data and Program 1 output, to insure the storage of the fixed-point variables in the proper elements of the I-field which comprises the Program 2 output.

Computer: IBM 650 with indexing

Language: GAT (Generalized Algebraic Translator)

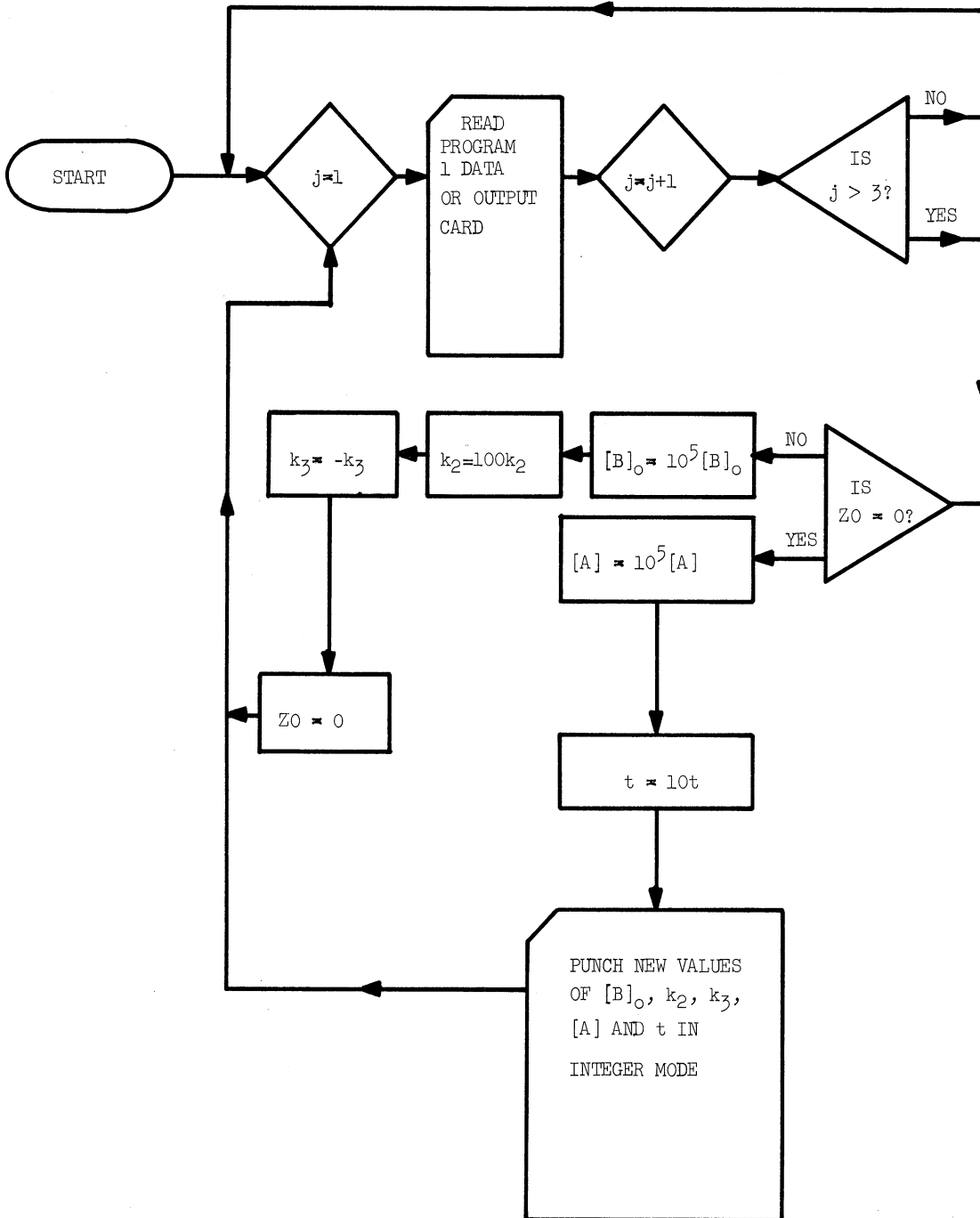
Subroutines needed: FIX (change from floating-point mode to fixed-point)
FLOAT (change from fixed-point mode to floating point)
READ (input)
PUNCH (output)

Storage requirements: 498 words

Correspondence of variables:

- Z0 : required fraction conversion of B, here used as a switch
- Y2 : $[B]_0$, floating-point
- Z2 : $-k_2$, floating-point
- Z3 : $-k_3$, floating-point
- Z(6*J3+5) : [A], floating-point
- Z(6*J3+4) : t, floating-point
- I0 : $[B]_0$, fixed-point
- I1 : [A], fixed-point
- I2 : t, fixed-point
- I3 : k_2 , fixed-point
- I4 : k_3 , fixed-point

FLWSHEET-PROGRAM 2



PROGRAM TO REFORMULATE OUTPUT FROM PROGRAM 1 FOR USE IN PROGRAM 3

11 IS HIGHEST STATEMENT NUMBER
300 USED IN SUBROUTINES

DIMENSION I(4) J(3) X(4) N
Y(5) Z(45)

1	2, J1, 1, 1, 3,
2	READ
3	GO TO 8 IF Z0 U 0
4	I0 = 10000*Y2
	I3 = -100*Z2
5	I4 = -Z3
6	Z0 = 0
7	GO TO 1
8	I1 = 10000*Z(6*J3+5)
9	I2 = 10*Z(6*J3+4)
10	T10...I4
11	GO TO 1

END

Program 3: Least Squares Determination of Parameter b for Explicit Solution

Purpose: The output from Program 2 is read in blocks, each block corresponding to a pair of values of K_2 and K_3 . The data within each block consist of the reformulated Program 1 output, for the particular pair of rate constant ratios. The best values of b are computed by fitting the data to Equation (3.40). The printout includes this value of the parameter as well as intermediate estimates of b and the minimized overall deviation and standard error.

Logic: The Theory of Least Squares is used to derive the non-linear equation

$$\frac{\partial D}{\partial b} = \sum_{\text{all data}} \left\{ \exp\left[\frac{2\beta_0}{b}(e^{-bt'}-1)\right] - \hat{y}_0 \exp\left[\frac{\beta_0}{b}(e^{-bt'}-1)\right] \right\} \left\{ -\frac{2t'\beta_0}{b} e^{-bt'} - \frac{2\beta_0 e^{-bt'}}{b^2} + \frac{2\beta_0}{b^2} \right\}, \quad (\text{A.1})$$

whose root is the best value of b; the equation is solved through the use of Newton's method. The derivative of $\frac{\partial D}{\partial b}$ is given by

$$\frac{\partial^2 D}{\partial b^2} = \sum_{\text{all data}} \left\{ \exp\left[\frac{2\beta_0}{b}(e^{-bt'}-1)\right] - \hat{y}_0 \exp\left[\frac{\beta_0}{b}(e^{-bt'}-1)\right] \right\} \left\{ \frac{2t'\beta_0}{b} e^{-bt'} \left(\frac{2}{b} + t'\right) + \frac{4\beta_0}{b^3} (e^{-bt'}-1) \right\} + \left(-\frac{2t'\beta_0}{b} e^{-bt'} - \frac{2\beta_0 e^{-bt'}}{b^2} + \frac{2\beta_0}{b^2} \right)^2 \left\{ \exp\left[\frac{2\beta_0}{b}(e^{-bt'}-1)\right] - \frac{\hat{y}_0}{2} \exp\left[\frac{\beta_0}{b}(e^{-bt'}-1)\right] \right\}. \quad (\text{A.2})$$

b is assumed to have been approximated with sufficient exactness when two successive estimates of the parameter differ by less than one-hundredth of one per cent.

Computer: IBM 704 with tapes

Language: FORTRAN

Library subroutines called: EXP (exponentiation)

SQRT (square root)

Storage requirements: 961_{10} words

Correspondence of variables:

N : number of pieces of data

GUESS : initial guess at b

BETA : β_0

YZERO : y_0

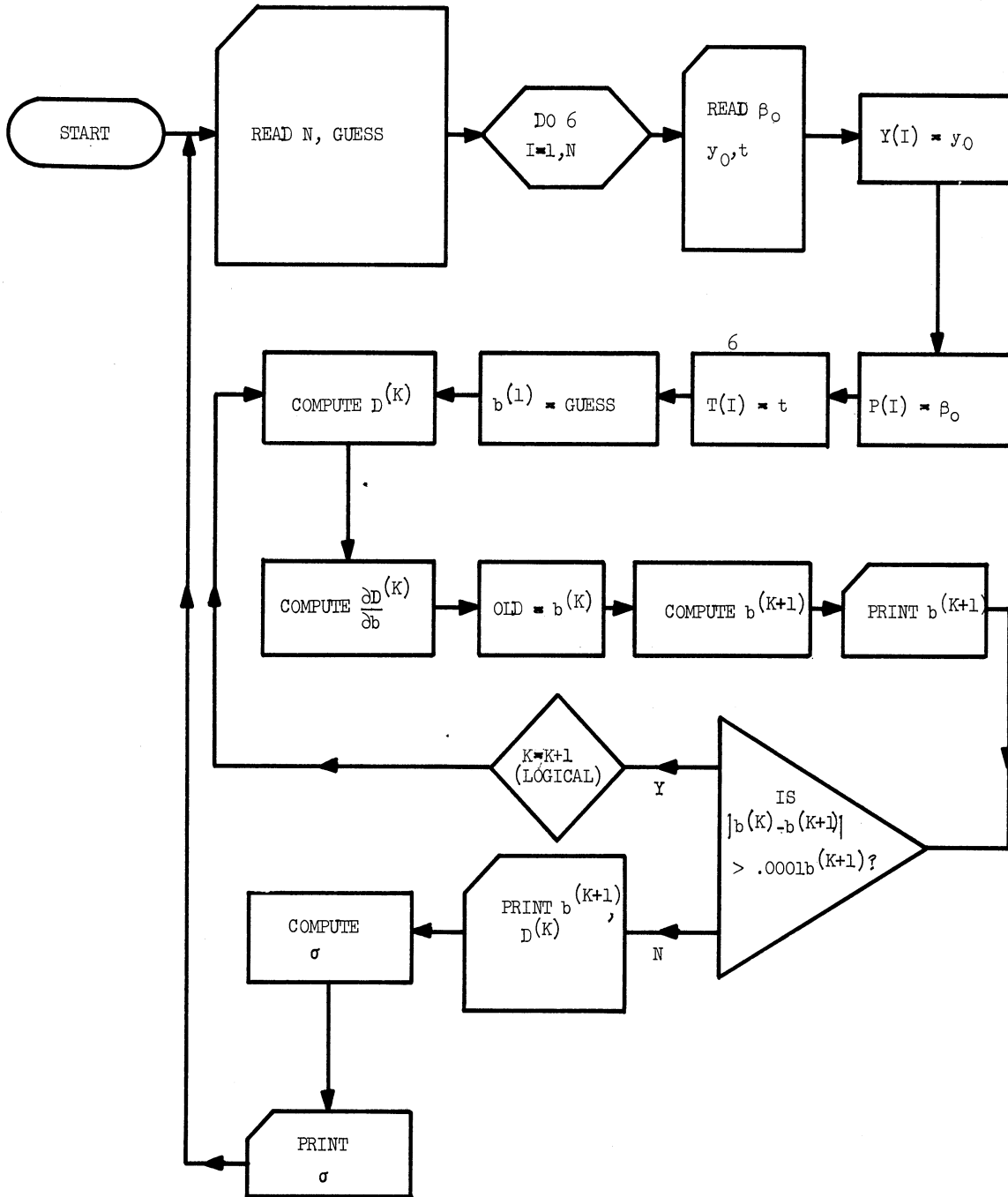
TIME : t'

B : b

SUM : overall deviation

SIGMA : standard error

FLWSHEET-PROGRAM 3



LEAST SQUARES DETERMINATION OF PARAMETER B FOR EXPLICIT SOLUTION

```
DIMENSION Y(200), T(200), P(200)
2 READ INPUT TAPE 7, 3, N, GUESS
3 FORMAT (I4, F6.3)
DO 6 I = 1, N
4 READ INPUT TAPE 7, 5, BETA, YZERO, TIME
5 FORMAT (F10.4, F10.4, F10.1)
  Y(I) = YZERO
  P(I) = BETA
6 T(I) = TIME
7 B = GUESS
8 SUM = 0.
9 DERIV = 0.
10 DO 20 I = 1, N
11 PART1 = EXP(2.*P(I)/B*(EXP(-B*T(I))-1.))
12 PART2 = EXP(P(I)/B*(EXP(-B*T(I))-1.))
13 PART6 = -2.*T(I)*P(I)/B*EXP(-B*T(I))
14 PART7 = -2.*P(I)*EXP(-B*T(I))/(B*B)+2.*P(I)/(B*B)
15 PART3 = PART6 + PART7
16 PART4 = (2.*T(I)*P(I)/B*EXP(-B*T(I)))*(2./B+T(I))
17 PART5 = (4.*P(I)/(B**3.))*EXP(-B*T(I))-1.
18 SUM = SUM+(PART1-Y(I)*PART2)*PART3
19 DERIV = DERIV+(PART1-Y(I)*PART2)*(PART4+PART5)
20 DERIV = DERIV+(PART3**2.)*(PART1-Y(I)/2.*PART2)
21 OLD = B
22 B = OLD-SUM/DERIV
23 WRITE OUTPUT TAPE 6, 24, B
24 FORMAT (11H TRIAL B = F7.4)
25 IF (ABS(OLD-B)-B/10000.) 26,26,8
26 WRITE OUTPUT TAPE 6, 27, B, SUM
27 FORMAT (11H FINAL B = F7.4, 8H SUM = E10.4)
28 ELEM = 0.
29 DO 31 I = 1, N
30 YPRED = EXP(P(I)/B*(EXP(-B*T(I))-1.))
31 ELEM = ELEM+(ABS(YPRED-Y(I)))**2.
  FLOATN = N
32 SIGMA = SQRT(ELEM/(FLOATN+1.))
33 WRITE OUTPUT TAPE 6, 34, SIGMA
34 FORMAT (9H SIGMA = E10.4)
35 GO TO 2
```

Program 4: Program Computing Standard Error of Prediction of Single-Reaction Model

Purpose: The output from Program 2 is read in as in Program 3. For each block of data, the printout consists of the standard deviation between the input values of y_0 and those obtained by assuming a single second-order reaction to have taken place.

Logic: The only decision made by the computer is whether β_0 is unity or not; accordingly, Equations (3.22a) or (3.22b) are used to find y_0 . No flowsheet is included for this program.

Computer: IBM 704 with tapes

Language: FORTRAN

Library subroutines called: EXP (exponentiation)

SQRT (square root)

Storage requirements: 750₁₀ words

Correspondence of variables:

N : number of pieces of data

BETA : β_0

YZERO : y_0

TIME : t'

SIGMA : standard error

PROGRAM COMPUTING STANDARD ERROR OF PREDICTION OF SINGLE REACTION MODEL

```

      DIMENSION Y(200), T(200), P(200)
2     READ INPUT TAPE 7, 3, N
3     F0RMAT (I4)
      DO 6 I = 1, N
4     READ INPUT TAPE 7, 5, BETA, YZER0, TIME
5     F0RMAT (F10.4, F10.4, F10.1)
      Y(I)   = YZER0
      P(I)   = BETA
6     T(I)   = TIME
7     ELEM   = 0
8     DO 14 I= 1, N
9     IF (P(I)-1.) 10, 13, 10
10    XPT    = EXPF(T(I)*(1.-P(I)))
11    YPRED  = ((P(I)-1.)*XPT)/(P(I)-XPT)
12    GO TO 14
13    YPRED  = 1./!(T(I)+1.)
14    ELEM   = ELEM+(Y(I)-YPRED)**2
15    FL0ATN = N
16    SIGMA  = SQRTF(ELEM/(FL0ATN+1.))
17    WRITE 0UTPUT TAPE 6, 18, SIGMA
18    F0RMAT (0H SIGMA = E10.4)
19    GO TO 2
```


Program 5: Program to Determine Relative Magnitudes of Rate Constants from Product Distribution Data

Purpose: For each reaction system, the product distributions corresponding to the experimental $\{y_0\}$ are read in. The values of K_2 which best fit the experimental data to the product distribution equations (3.20) are computed and printed. The standard error of prediction is also included in the output.

Logic: The Theory of Least Squares is used to derive the non-linear equations in the best values of the rate constant ratios:

For $j = 2$

$$\frac{\partial C}{\partial K_2} = \sum_{\text{all data}} (2y_{1P} - 2\hat{y}_1) \left[\frac{(K_2 - 1)(-y_0^{K_2}) \ln y_0 - y_0 - y_0^{K_2}}{(K_2 - 1)^2} \right] \quad (A.3)$$

For $j = 3$

$$\frac{\partial C}{\partial K_2} = \sum_{\text{all data}} (2y_{2P} - \hat{y}_1 - 2\hat{y}_2 + y_{1P}) \left[\frac{\begin{aligned} &+K_2^2 y_0 + K_2^2 y_0^{K_2} \ln y_0 - 2K_3 K_2 y_0 + K_3^2 y_0 - K_3^2 y_0^{K_2} \ln y_0 - K_3 K_2 y_0^{K_2} \ln y_0 \\ &+ K_3 y_0^{K_2} + K_3 K_2 y_0^{K_2} \ln y_0 + K_2^2 K_3 y_0^{K_2} - K_3 K_2 y_0^{K_2} \ln y_0 \\ &+ K_2^3 y_0^{K_2} \ln y_0 + K_3^2 K_2 y_0^{K_2} \ln y_0 - K_2^2 y_0^{K_2} \end{aligned}}{(1 - K_3)(1 - K_2)(K_2 - K_3)^2} \right] \quad (A.4)$$

and

$$+ \sum_{\text{all data}} (2y_{1P} - \hat{y}_2 - 2\hat{y}_1 + y_{2P}) \left[\frac{(K_2 - 1)(-y_0^{K_2}) \ln y_0 - y_0 + y_0^{K_2}}{(K_2 - 1)^2} \right]$$

$$\frac{\partial C}{\partial K_3} = \sum_{\text{all data}} \left\{ (2y_{2P} - \hat{y}_1 - 2\hat{y}_2 + y_{1P}) K_2 \right. \\ \left. \times \left[\frac{K_3^2 y_0 - K_3^2 y_0^{K_2} - 2K_3 K_2 y_0 + 2K_3^2 y_0^{K_2} - y_0^{K_2} + K_2^2 y_0}{(1 - K_3)^2 (1 - K_2)(K_2 - K_3)^2} + \frac{\begin{aligned} &-y_0^{K_3} (2K_3 - 1 - K_2) \\ &+ (K_3 - 1)(K_3 - K_2) y_0^{K_3} \ln y_0 \end{aligned}}{(K_3 - 1)^2 (K_3 - K_2)^2} \right] \right\} \quad (A.5)$$

These equations are solved by using Newton's method in $j-1$ variables; the second derivatives of the variable sum of squares are approximated by difference quotients. The best values of the rate constant ratios are assumed to have been found when two successive estimates of each agree to within 0.01 per cent. An iteration count is included to prevent time wastage if convergence is not attained in a reasonable amount of time.

Computer: Basic IBM 704 with tapes

Language: FORTRAN

Library subroutines called: FTRAP (floating trap)

ELOG (natural logarithm)

SQRT (square root)

Storage requirements: 1811_{10} words

Running time: .15 minutes x (number of reactions - 1) x number of runs.

This is an average value, taking into account bad guesses at the $\{K_i\}$, which will cause the iteration count to be exceeded, and bad data, which will require reruns. Average time per data set, regardless of outcome, is 1.4 minutes.

Correspondence of variables:

N : number of reactions

M : number of pieces of data

GK(I) : estimate of K_i

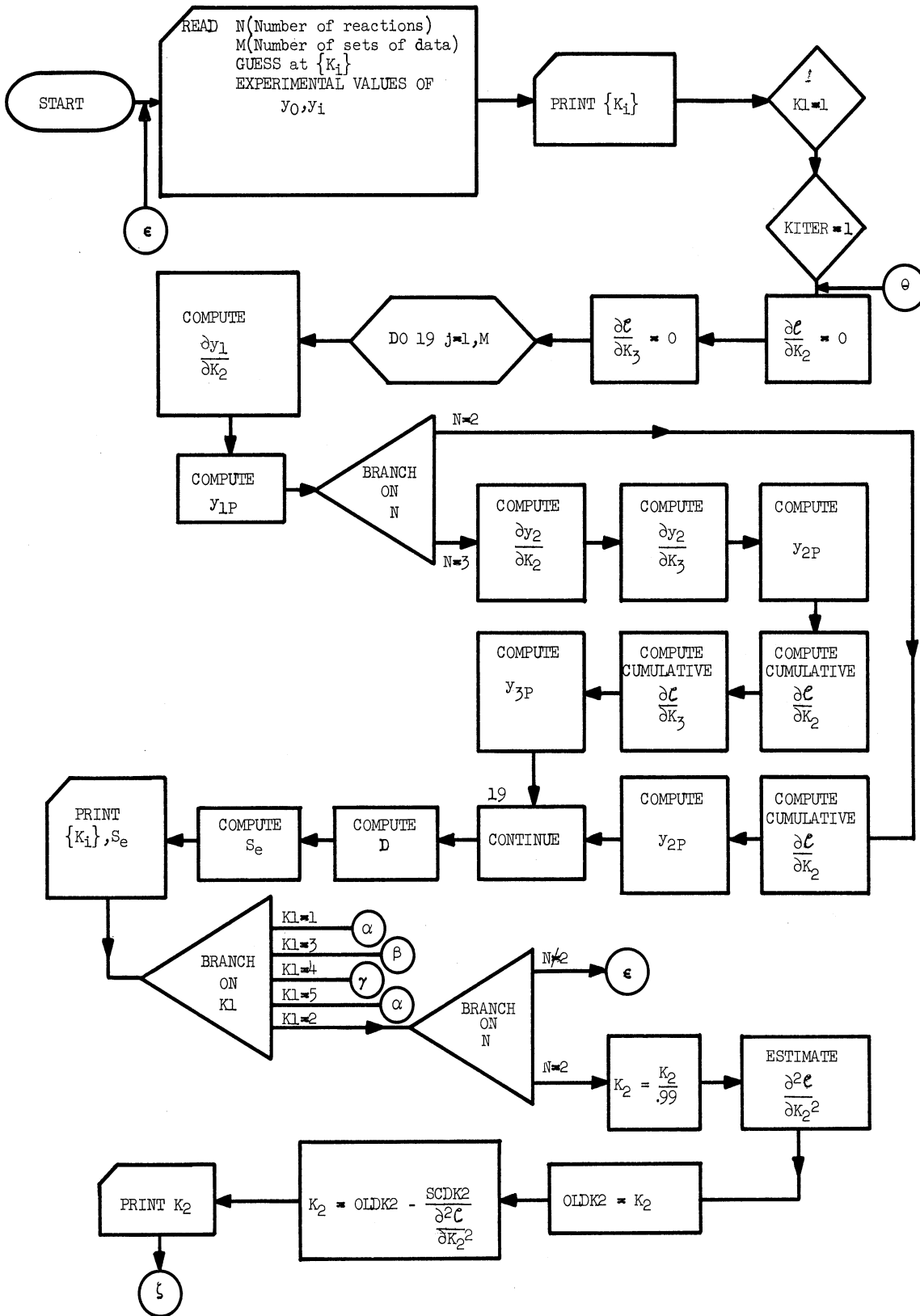
YO(I) : experimental y_0 for i -th run

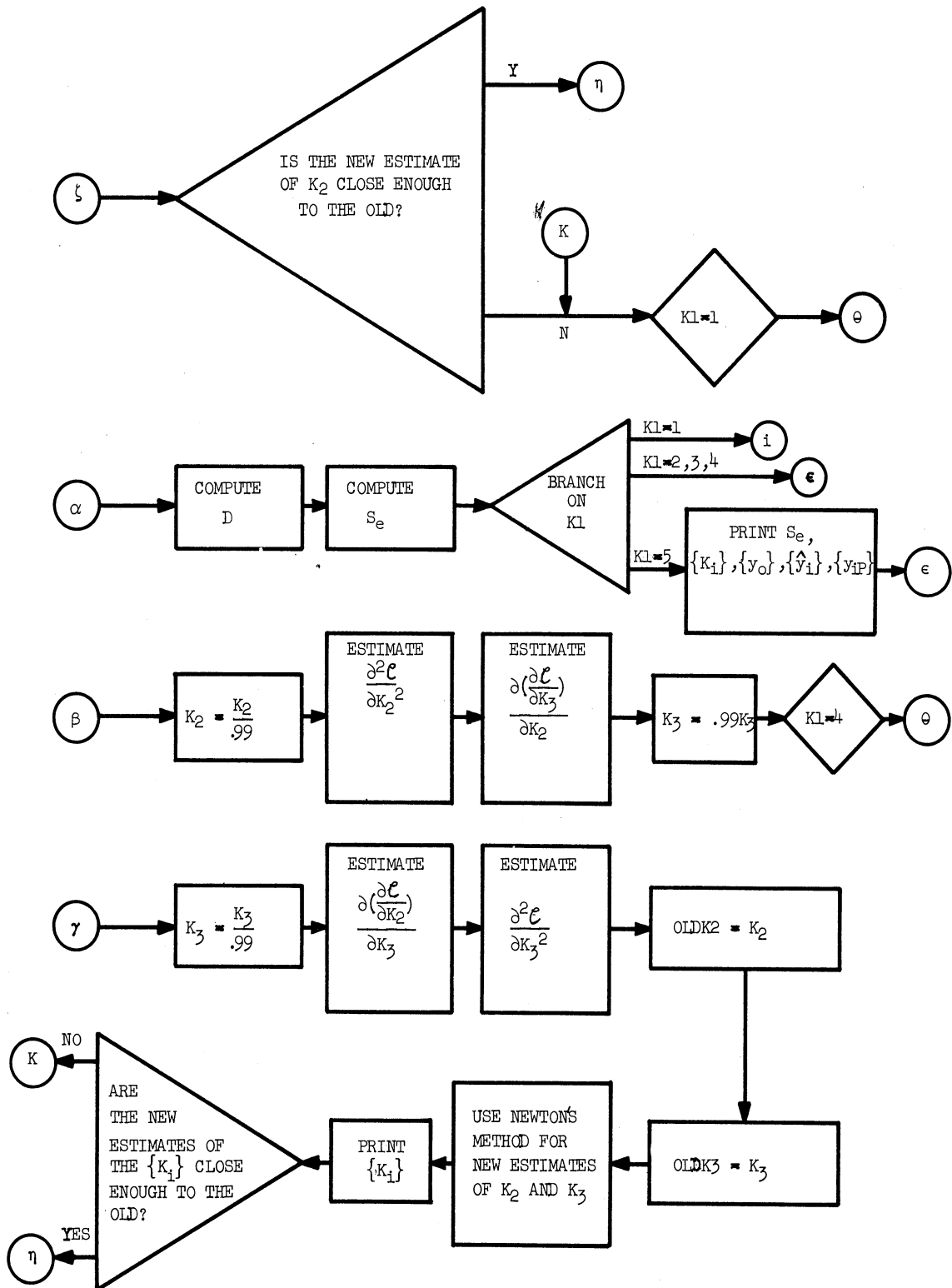
YE(J,I) : experimental y_j for i -th run

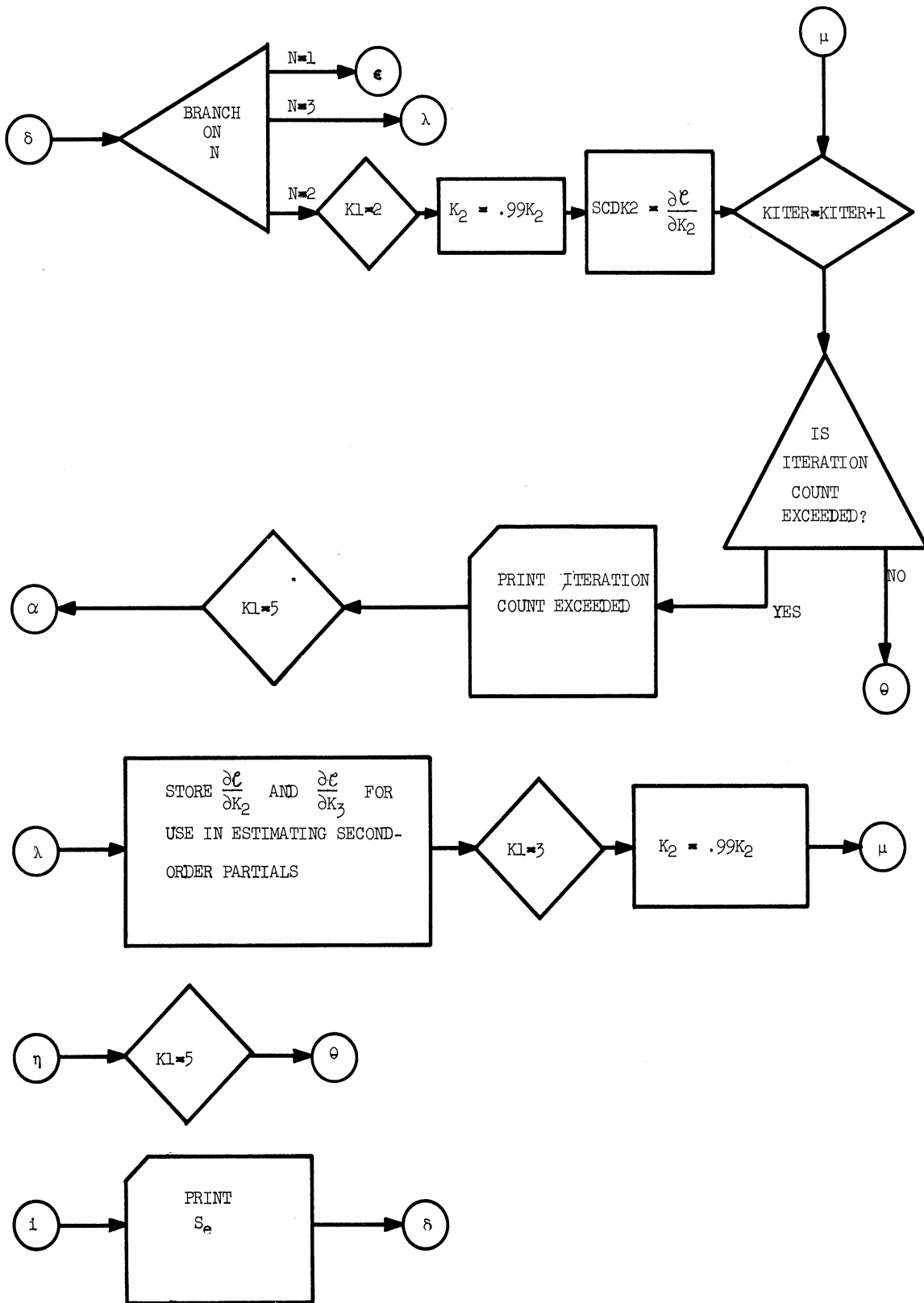
SIGMA : standard error

YP(I,J) : predicted y_i for j -th run

FLWSHEET-PROGRAM 5







PROGRAM TO DETERMINE RELATIVE MAGNITUDES OF RATE CONSTANTS FROM PRODUCT DISTRIBUTION DATA

```

DIMENSION GK(3), YO(100), YE(3,100), YP(3,100)
1 READ INPUT TAPE 7, 20, N, M, (GK(I), I=1,3), (YO(I), (YE(J,I)), J=1,
X3), I=1,M)
WRITE OUTPUT TAPE 6, 49, (GK(I), I=2,N)
K1 = 1
KITER = 1
2 DCDK2 = 0.
DCDK3 = 0.
3 DO 19 J=1,M
4 YOK2 = YO(J)**GK(2)
5 YOK2LN = YOK2*ELOG(YO(J))
6 DY1DK2 = ((GK(2)-1.)*(-YOK2LN)-YO(J)+YOK2)/((GK(2)-1.)*(GK(2)-1.))
10 YP(1,J) = (YO(J)-YOK2)/(GK(2)-1.)
7 GO TO (1, 15, 8), N
8 GNUM= (GK(2)*GK(2)*YO(J)-GK(2)*GK(2)*YOK2LN-2.*GK(3)*GK(2)*YO(J)
X+GK(3)*GK(3)*YO(J)-GK(3)*GK(3)*YOK2-GK(3)*GK(3)*GK(2)*YOK2LN+GK(3)
X*YOK2+GK(3)*GK(2)*YOK2LN+GK(2)*GK(2)*GK(3)*YOK2-GK(3)*GK(2)**3.
X*YOK2LN+GK(2)**3.*YOK2LN+GK(3)*GK(3)*GK(2)*GK(2)*YOK2LN-GK(2)
X*GK(2)*YOK2)
DEN = ((1.-GK(3))*(1.-GK(2))*(1.-GK(2))*(GK(2)-GK(3))*(GK(2)-GK(3)
X))
DY2DK2 =GNUM/DEN+GK(3)*YC(J)**GK(3)/((GK(3)-1.)*(GK(3)-GK(2))*(
XGK(3)-GK(2)))
9 DY2DK3 = GK(2)*((GK(3)*GK(3)*YO(J)-GK(3)*GK(3)*YOK2-2.*GK(3)*GK(2)
X*YO(J)+2.*GK(3)*YOK2-YOK2+GK(2)*GK(2)*YO(J))/((1.-GK(3))*(1.-GK(3)
X)*(1.-GK(2))*(GK(2)-GK(3))*(GK(2)-GK(3)))+(GK(3)-1.)*(GK(3)-GK(2)
X)*YO(J)**GK(3)*ELOG(YO(J))-YO(J)**GK(3)*(2.*GK(3)-1.-GK(2)))/((
XGK(3)-1.)*(GK(3)-1.)*(GK(3)-GK(2))*(GK(3)-GK(2)))
11 YP(2,J) = (GK(2)*GK(2)*YO(J)-GK(2)*GK(3)*YO(J)+GK(3)*GK(2)
X*YOK2-GK(2)*YOK2)/((1.-GK(3))*(1.-GK(2))*(GK(2)-GK(3))+GK(2)*YO(
XJ)**GK(3)/((GK(3)-1.)*(GK(3)-GK(2)))
12 DCDK2 = DCDK2+DY2DK2*(2.*YP(2,J)-YE(1,J)-2.*YE(2,J)+YP(1,J))+DY1D
XK2*(2.*YP(1,J)-YE(2,J)-2.*YE(1,J)+YP(2,J))
13 DCDK3 = DCDK3+DY2DK3*(2.*YP(2,J)-YE(1,J)-2.*YE(2,J)+YP(1,J))
14 GO TO 18
15 DCDK2 = DCDK2+DY1DK2*(2.*YP(1,J)-2.*YE(1,J))
16 YP(2,J) = 1.-YO(J)-YP(1,J)
17 GO TO 19
18 YP(3,J) = 1.-YO(J)-YP(1,J)-YP(2,J)
19 CONTINUE
20 FORMAT(I2, I4, 3E10.4/(4F6.3))
SUM = 0.
DO 21 J=1,M
DO 21 I=1,N
21 SUM = SUM+(YE(I,J)-YP(I,J))*(YE(I,J)-YP(I,J))
NUMTRM = M*N-N+1
SIGMA = SQRT(SUM/FLOATF(NUMTRM))
WRITE OUTPUT TAPE 6, 77, (GK(I), I=2,N)
WRITE OUTPUT TAPE 6, 75, SIGMA
GO TO (35, 27, 55, 61, 35), K1
22 GO TO (1, 23, 50), N
23 K1 = 2
24 GK(2) = .99*GK(2)
25 SCDK2 = DCDK2
26 GO TO 33

```

```
27 GO TO (1, 28, 1), N
28 GK(2) = GK(2)/.99
29 D2CDK2 = (SCDK2-DCDK2)/(.01*GK(2))
30 OLDK2 = GK(2)
31 GK(2) = OLDK2-SCDK2/D2CDK2
   WRITE OUTPUT TAPE 6, 49, GK(2)
32 IF (ABSF(OLDK2-GK(2))-GK(2)/10000.) 72, 72, 47
33 KITER = KITER+1
34 IF(KITER-100)2, 2, 44
35 SIJM = 0.
36 DO 38 J=1,M
37 DO 38 I=1,N
38 SIJM = SIJM+(YE(I,J)-YP(I,J))*(YE(I,J)-YP(I,J))
39 NUMTRM = M*N-N+1
40 SIGMA = SQRT(SIJM/FLOATF(NUMTRM))
   GO TO (74, 1, 1, 1, 41), K1
41 WRITE OUTPUT TAPE 6, 42, SIGMA, (GK(I), I=1,3)
42 FORMAT(49H ITERATION DONE - STANDARD ERROR OF PREDICTION = F8.5,
   X27H RATE CONSTANT RATIOS ARE 3E11.4/55H   YO   Y1E   Y1P
   X Y2E   Y2P   Y3E   Y3P)
   DO 425 J=1,M
425 WRITE OUTPUT TAPE 6, 71, YO(J), (YE(I,J), YP(I,J), I=1,N)
43 GO TO 1
44 WRITE OUTPUT TAPE 6, 45
45 FORMAT( 25H ITERATION COUNT EXCEEDED)
   K1 = 5
46 GO TO 35
47 K1 = 1
48 GO TO 2
49 FORMAT(57H INTERMEDIATE VALUE(S) OF RATE CONSTANT RATIOS IS (ARE)
   X 2E12.4)
50 F1 = DCDK2
51 F2 = DCDK3
52 K1 = 3
53 GK(2) = .99*GK(2)
54 GO TO 33
55 GK(2) = GK(2)/.99
56 D11 = (F1-DCDK2)/(.01*GK(2))
57 D21 = (F2-DCDK3)/(.01*GK(2))
58 GK(3) = .99*GK(3)
59 K1 = 4
60 GO TO 2
61 GK(3) = GK(3)/.99
62 D12 = (F1-DCDK2)/(.01*GK(3))
63 D22 = (F2-DCDK3)/(.01*GK(3))
64 OLDK2 = GK(2)
65 OLDK3 = GK(3)
66 GK(3) = (OLDK3*(D21*D12-D11*D22)-D21*F1+D11*F2)/(D21*D12-D11*D22)
67 GK(2) = (D11*OLDK2+D12*OLDK3-F1-D12*GK(3))/D11
68 WRITE OUTPUT TAPE 6, 49, GK(2), GK(3)
69 IF (ABSF(OLDK2-GK(2))-GK(2)/10000.)70, 70, 47
70 IF (ABSF(OLDK3-GK(3))-GK(3)/10000.)72, 72, 47
71 FORMAT (1H 7F8.4)
72 K1 = 5
73 GO TO 2
74 WRITE OUTPUT TAPE 6, 75, SIGMA
75 FORMAT(77H STANDARD ERROR OF PREDICTION FOR THE PRECEDING RATE CON
   XSTANT RATIO VECTOR = F8.5)
76 GO TO 22
77 FORMAT(77H RATE CONSTANT RATIO(S) PRECEDING ORDINARY PASS THROUGH
   XDIFFERENTIAL PORTION 2E12.4)
```

Program 6: Program to Determine Absolute Magnitudes of Rate Constants from Product Distributions with Time Given

Purpose: The program reads the initial conditions for each run, the composition of the reaction mixes, and the times at which these compositions obtained; in addition, the initial guesses at the rate constant for the first reaction and rate constant ratios for the subsequent reactions are read. The output is the best values of the first constant and rate constant ratios to characterize the system, using the applicable model. Also printed are the observed reaction mix compositions and those predicted using the computed best values and the appropriate model. The standard error of prediction using unit weighting is also computed.

Logic: The basic fitting method used is the creep method. OLDSIG is the standard error preceding each iteration; PRESIG is the minimized error within each iteration. An iteration count is included. The rate constants are originally changed by one per cent; when this becomes too coarse, factors of 0.1 per cent are used.

Computer: Basic IBM 704 with tapes

Language: IBM FORTRAN II (24)

Library subroutines called: EXP (exponentiation)

ELOG (natural logarithm)

SQRT (square root)

Storage requirements: 3810₁₀ words

Running time: .52 minutes x number of reactions x number of runs. This is an average value, taking into account bad guesses at GK, which will cause the iteration count to be exceeded, and bad data, which will require reruns. Average time per data set, regardless of outcome, is 2.1 minutes.

Correspondence of variables:

M : number of runs

N : number of reactions

MAXIT : maximum number of iterations

GK(1) : k_1 ; GK(I) : K_i , $i > 1$

CAO(J) : $[A]_0$ for the j-th run

T(J) : t for j-th run

BETAO(J) : β_0 for j-th run

YO(J) : observed y_0 for j-th run

BETA(J) : observed β for j-th run

Y(I,J) : observed y_i for j-th run

PRESIG : standard error of prediction available from main program

YOP(J) : predicted y_0 for j-th run

BETAP(J) : predicted β for j-th run

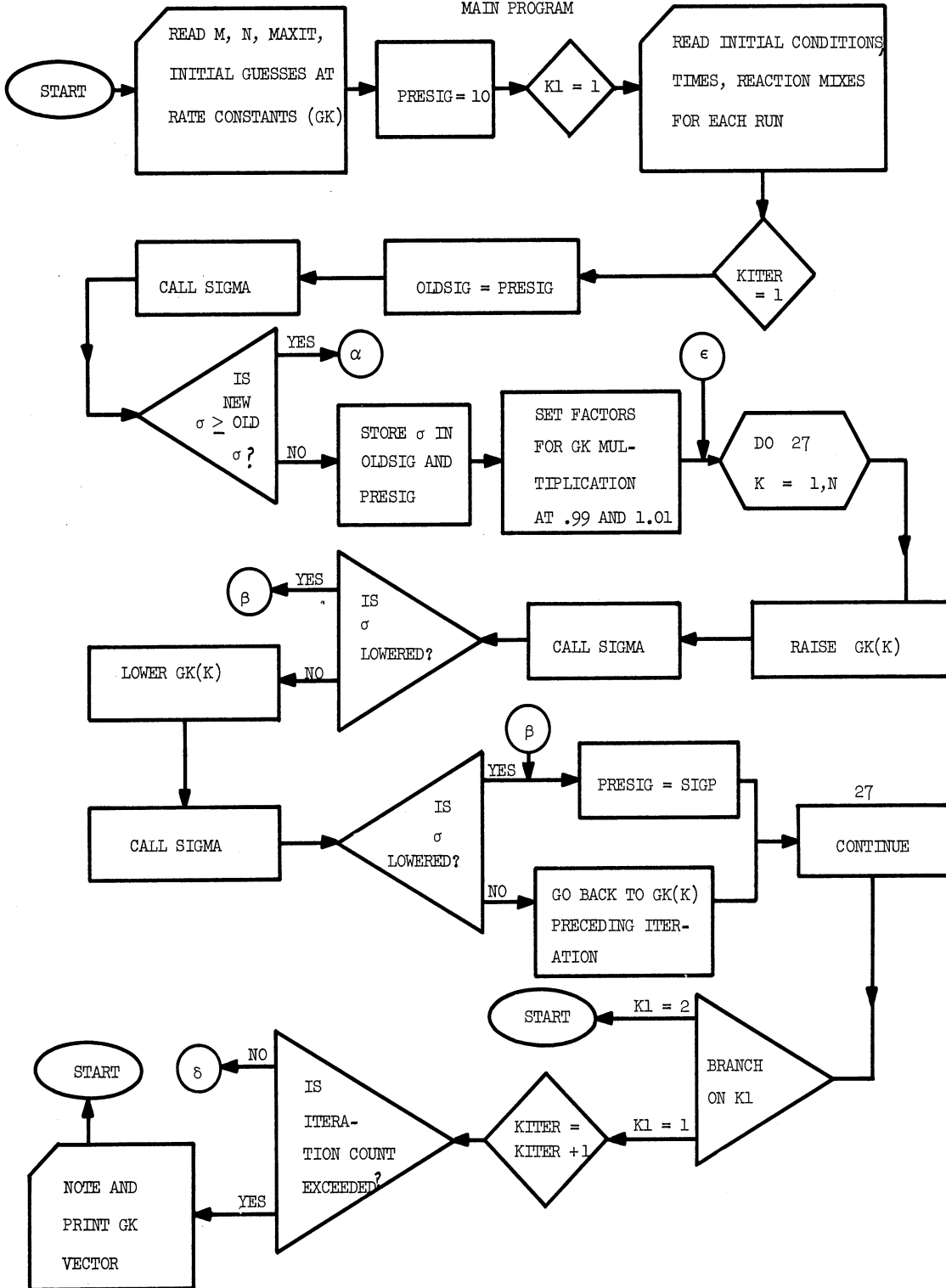
YP(I,J) : predicted y_i for j-th run

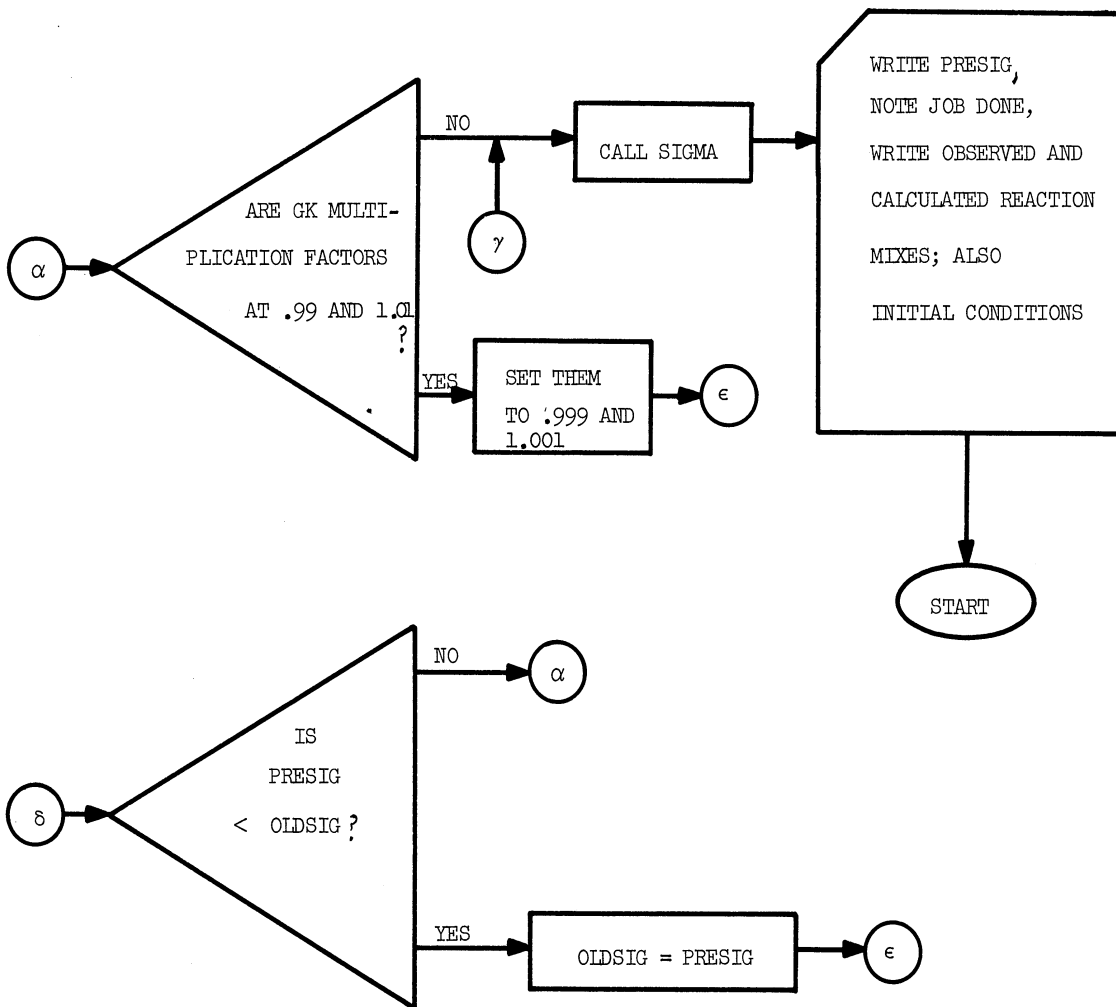
J : run number

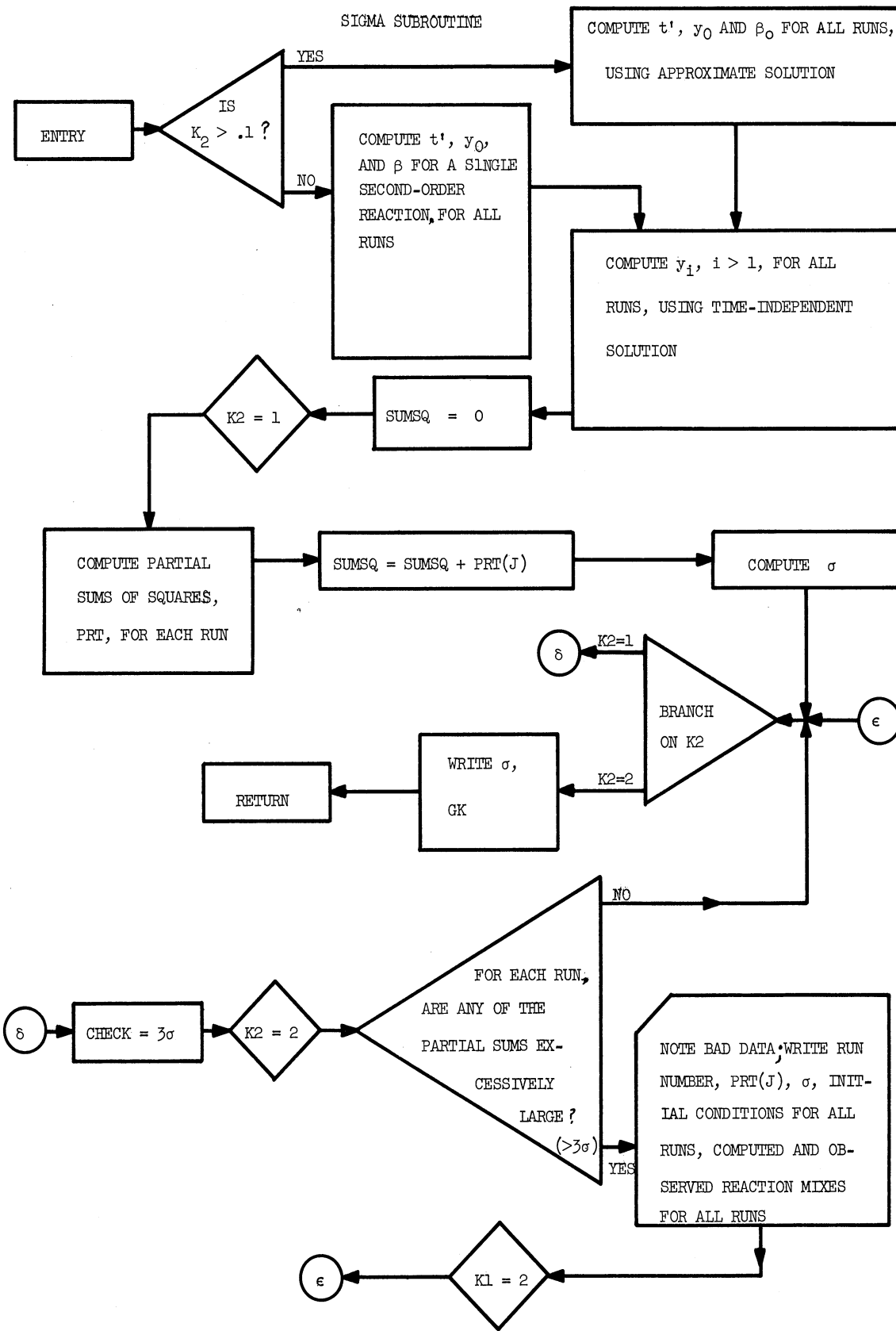
SIGP : standard error of prediction computed by SIGMA subroutine

PRT(J) : partial sum of squares for j-th run

FLWSHEET - PROGRAM 6
MAIN PROGRAM







PROGRAM TO COMPUTE ABSOLUTE VALUES OF RATE CONSTANTS FROM PRODUCT
DISTRIBUTION DATA WITH TIME GIVEN

```
DIMENSION GK(10), CAO(100), BETAO(100), T(100), YO(100), Y(10,100)
X, BETA(100), YOP(100), BETAP(100), YP(10,100), PRT(100)
COMMON SIGP, YOP, BETAP, YP, PRT, K1
1 READ INPUT TAPE 7, 3, M, N, MAXIT, (GK(I), I=1,N)
2 PRESIG = 10.
   K1 = 1
3 FORMAT(I4, I3, I4/(7E10.4))
4 DO 7 J=1,M
5 READ INPUT TAPE 7, 6, CAO(J), T(J), BETAO(J), YO(J), BETA(J),
  X(Y(I,J), I=1,N)
6 FORMAT (E10.4, E11.5, 2F6.3, F7.4/10F6.3)
7 CONTINUE
8 KITER = 1
   OLDSIG = PRESIG
9 CALL SIGMA(GK, M, T, CAO, BETAO, N, YO, Y, BETA)
10 IF (SIGP-OLDSIG) 18, 33, 33
11 WRITE OUTPUT TAPE 6, 12, PRESIG
12 FORMAT(54H ITERATION COMPLETED. STANDARD ERROR OF PREDICTION = E1
  X1.4/73H TIME (A)INIT BETAO YO YOP BETA BETA
  XP YI YOP)
13 DO 16 J=1,M
14 WRITE OUTPUT TAPE 6, 15, T(J), CAO(J), BETAO(J), YO(J), YOP(J),
  XBETA(J), BETAP(J), (*Y(I,J), YP(I,J), I=1,N)
15 FORMAT(1H E11.4, 2H E11.4, 7F7.3/(60H
  X 2F7.3))
16 CONTINUE
17 GO TO 1
18 PRESIG = SIGP
   FR1 = .99
   FR2 = 1.01
   OLDSIG = PRESIG
19 DO 27 K=1,N
20 GK(K) = FR1*GK(K)
21 CALL SIGMA(GK, M, T, CAO, BETAO, N, YO, Y, BETA)
22 IF (PRESIG-SIGP) 23, 23, 265
23 GK(K) = FR2*GK(K)/FR1
24 CALL SIGMA(GK, M, T, CAO, BETAO, N, YO, Y, BETA)
25 IF (PRESIG-SIGP) 26, 26, 265
26 GK(K) = GK(K)/FR2
   GO TO 27
265 PRESIG = SIGP
27 CONTINUE
   GO TO (28, 1), K1
28 KITER = KITER+1
29 IF(KITER-MAXIT) 37, 37, 30
30 WRITE OUTPUT TAPE 6, 31, (GK(K), K=1,N)
31 FORMAT(33H ITERATION COUNT EXCEEDED - K1 = E10.4/1H 9E10.4)
32 GO TO 1
33 IF (FR1-.99) 34, 34, 40
34 FR1 = .999
35 FR2 = 1.001
36 GO TO 19
37 IF (PRESIG-OLDSIG) 38, 33, 33
38 OLDSIG = PRESIG
39 GO TO 19
```

40 CALL SIGMA(GK, M, T, CAO, BETAO, N, YO, Y, BETA)
41 GO TO 11

SIGMA SUBROUTINE

```
SUBROUTINE SIGMA(GK, M, T, CAO, BETAO, N, YO, Y, BETA)
  DIMENSION GK(10), T(100), CAO(100), BETAO(100), YO(100), Y(10,100)
  X, BETA(100), YOP(100), BETAP(100), YP(10,100), PRT(100)
  COMMON SIGP, YOP, BETAP, YP, PRT, K1
  1 IF(GK(2)-0.1) 2, 2, 7
  2 DO 5 J=1,M
  3 TDIM = CAO(J)*GK(1)*T(J)
  4 YOP(J) = (BETAO(J)-1.)*EXP(TDIM*(1.-BETAO(J)))/(BETAO(J)-EXP(TDIM
  X*(1.-BETAO(J))))
  5 BETAP(J) = BETAO(J)-1.+YOP(J)
  6 GO TO 12
  7 DLGK2 = .4343*ELOG(GK(2))
  DLGK22 = DLGK2*DLGK2
  B = .897+.429*DLGK2+.053*DLGK22+(.0736+.0632*DLGK2+.0273*DLGK22
  X)*GK(3)+(-.0072-.00545*DLGK2-.00262*DLGK22)*GK(3)*GK(3)
  8 DO 11 J=1,M
  9 TDIM = CAO(J)*GK(1)*T(J)
  10 YOP(J) = EXP((BETAO(J)/B)*(EXP(-B*TDIM)-1.))
  11 BETAP(J) = BETAO(J)*EXP(-B*TDIM)
  12 DO 19 J=1,M
  YEX = YOP(J)**GK(2)
  13 YP(1,J) = (YOP(J)-YEX)/(GK(2)-1.)
  14 GO TO (19, 15, 17), N
  15 YP(2,J) = 1.-YOP(J)-YP(1,J)
  16 GO TO 19
  17 YP(2,J) = (GK(2)*GK(2)*YOP(J)-GK(2)*GK(3)*YOP(J)+GK(3)*GK(2)*YEX
  X-GK(2)*YEX)/((1.-GK(3))*(1.-GK(2))*(GK(2)-GK(3)))+GK(2)*YOP(J)
  X**GK(3)/((GK(3)-1.)*(GK(3)-GK(2)))
  18 YP(3,J) = 1.-YOP(J)-YP(1,J)-YP(2,J)
  19 CONTINUE
  20 SUMSQ = 0.
  21 K2 = 1
  22 DO 26 J=1,M
  23 PRT(J) = (YO(J)-YOP(J))*(YO(J)-YOP(J))+(BETA(J)-BETAP(J))*(BETA(J)
  X-BETAP(J))
  24 DO 25 I=1,N
  25 PRT(J) = PRT(J)+(Y(I,J)-YP(I,J))*(Y(I,J)-YP(I,J))
  26 SUMSQ = SUMSQ+PRT(J)
  27 NUMCOM = M*(2+N)
  28 SIGP = SQRT(SUMSQ/(FLOATF(NUMCOM)-1.))
  29 GO TO (33, 30), K2
  30 WRITE OUTPUT TAPE 6, 31, SIGP, (GK(I), I=1,N)
  31 FORMAT(33H STANDARD ERROR OF PREDICTION IS E11.4, 18H FOR THE K-VE
  XTOR 3E12.4)
  32 RETURN
  33 CHECK = 3.*SIGP
  34 K2 = 2
  35 DO 44 J=1,M
  36 IF (SQRT(PRT(J)/FLOATF(N+1))-CHECK) 44, 44, 37
  37 WRITE OUTPUT TAPE 6, 38, J, PRT(J), SIGP
  38 FORMAT(22H BAD DATA HALT ON RUN I3, 19H. SUM OF SQUARES = E11.4,
  X33H STANDARD ERROR OF PREDICTION = E11.4/73H TIME (A) IN
  XIT BETAO YO YOP BETA BETAP YI YOP)
  39 DO 42 K3=1,M
  40 WRITE OUTPUT TAPE 6, 41, T(K3), CAO(K3), BETAO(K3), YO(K3), YOP(K3
  X), BETA(K3), BETAP(K3), (Y(I,K3), YP(I,K3), I=1,N)
  41 FORMAT(1H E11.4, 2H E11.4, 7F7.3/(60H
  X 2F7.3))
  42 CONTINUE
  43 K1 = 2
  44 CONTINUE
  45 GO TO 29
```

Program 7: Program for Optimal Design of a Reactor to Carry Out a Single Second-Order Reaction

and

Program 8: Program for Optimal Design of a Reactor to Carry Out a Set of Consecutive Competitive Reactions

Purpose: These programs are identical in so many respects that they can be described concurrently without difficulty. Unless otherwise specified, the discussion to follow applies to both programs. The computer input consists of the physical properties of the reactants; the desired production rate; the rate constant for the first reaction, and the necessary rate constant ratios and b for Program 8; the reactor diameter; the required cost factors; the initial guesses at the values of the design and operating variables, including a guess at the reactor length for Program 8; and the maximum allowable number of iterations. From these data, the optimal reactor design is found; included in the output are the production rate; the physical properties of the feed; the rate constant for the first reaction, and rate constant ratios where applicable; the tube diameter; the cost factors and total cost; the optimizing values of the independent variables and reactor length; the composition of the reactor effluent; and the number of iterations required to find the best design.

Logic: The equations used to compute the reactor length and total production cost have been derived and adequately discussed in Chapter IV of the text. Separate subprograms are used to compute

the values of these dependent variables. A creep method, described in some detail in Appendix F, is used to find the best design. Multiplicative factors corresponding to ten per cent changes in the independent variables are first used; these are followed by one per cent, and finally, by one-tenth of one per cent, changes, as the optimum design is approached. The use of large initial modifications in these variables increases the chances of convergence in a limited number of iterations. However, it may result in combinations of the independent variables which are forbidden; that is, the desired production rate cannot be met, regardless of the reactor length. This eventuality is responded to in different ways by the two programs. In Program 7, as shown in Chapter IV, a design in the forbidden region occasions a negative argument of the logarithm in the expression for the reactor length. The sign of this argument is branched on in the reactor length subroutine of Program 7. If it is negative, the reactor length is assigned a value of 10^{20} ; the high production cost which results is regarded by the main program as a repudiation of the change in independent variable which occasioned the negative argument. A similar check insures that L' will be less than L . The reactor length is found in Program 8 by a Newton's method iteration. An iteration count is included and when the limit of one hundred cycles is exceeded, this is noted and the solution is continued.

The variables OLD T and PRE T , as values of the production cost, perform the same functions here as do OLDSIG and PRESIG,

respectively, as values of the standard error in Program 6. As indicated above, a count is kept of the number of iterations made in the creep ascent.

The subroutines DERIVS, in Program 7, and LAGMUL, in Program 8, and the switch, KEXIT, were not used by the programs as employed in this study, although the calls for these subroutines are included in the flowsheet. Briefly, the function of these subprograms was to compute the partial derivatives of the production cost with respect to the independent variables. As the total cost subroutine prints out, every time it is entered, the current values of these variables and the production cost, the derivative subprograms are not needed.

Both total cost subroutines are straightforward and will not be included in the flowsheet.

Computer: Basic IBM 704 with tapes

Language: IBM FORTRAN II

Library subroutines called	<u>Program 7</u>	<u>Program 8</u>
	EXP (exponentiation)	EXP
	LOG (natural logarithm)	ELOG
Storage requirements, words ₁₀	965	1691
Running time, min/design	1.09	2.0

Correspondence of Variables

VA : v_A

VB : v_B

Z : Z

RC : k₁

D : D

R : R

CM : M

VI : V_i

VF : V_f

XAO : x_{A0}

FRACT : fraction to be used of the change in independent variable indicated by Newton's method. This is no longer used.

MAXIT : maximum allowable number of iterations

PTINJ : L'

RCTRL : L

KCOUNT : iteration counter

CAF : $[A]_f$

CBF : $[B]_f$

TOTCST : τ

ARGLN : argument of the logarithm in computation of reactor length in Program 7

RCR2 : K_2

RCR3 : K_3

B : b

COSTR : R

COSTM : M

COSTA : A

COSTW : W

COSTB : B

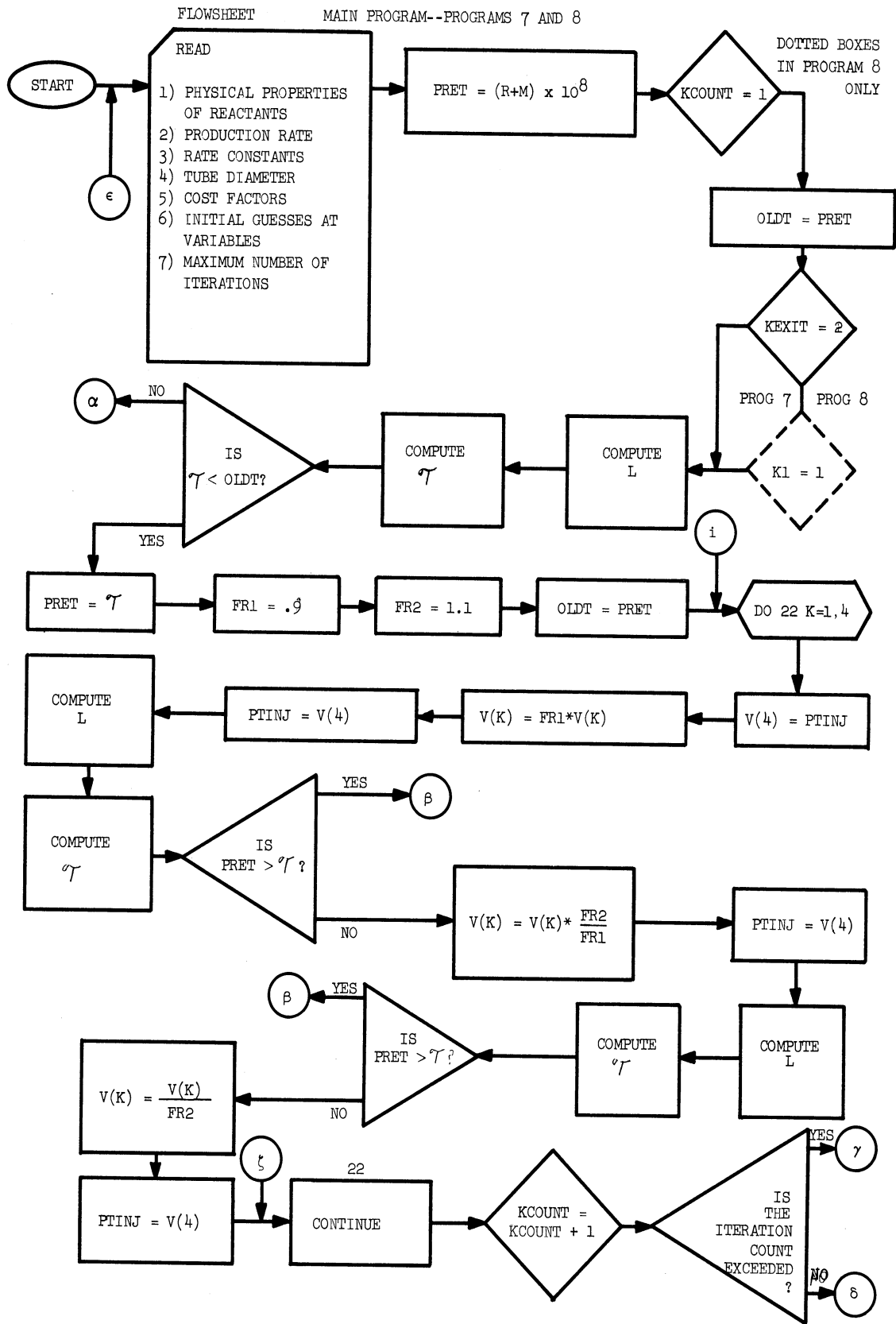
UNDET : undetermined multiplier, used in LAGMUL, but not applicable here

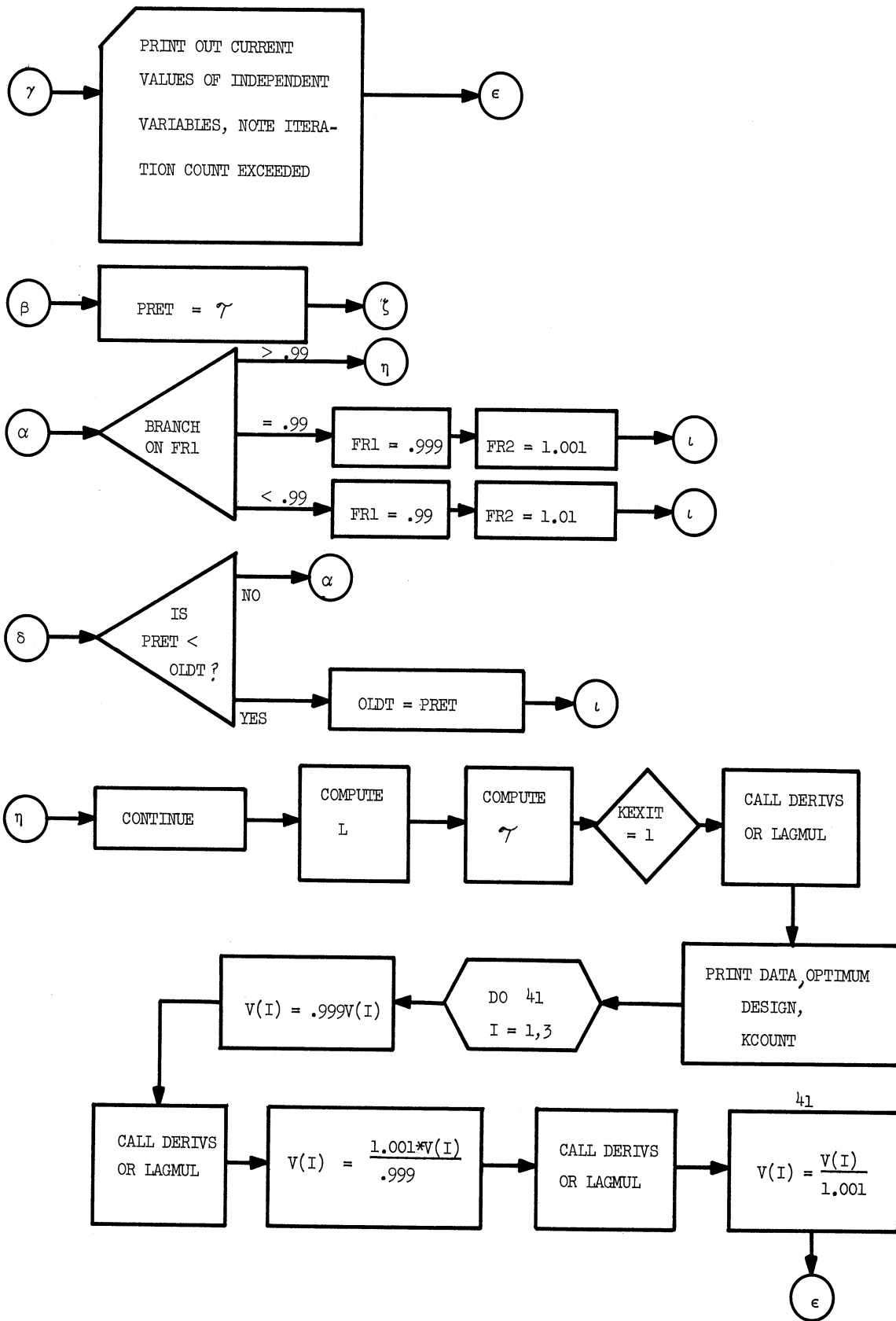
PRODRT : production rate of P_1 (should equal Z)

BYPRT : b'

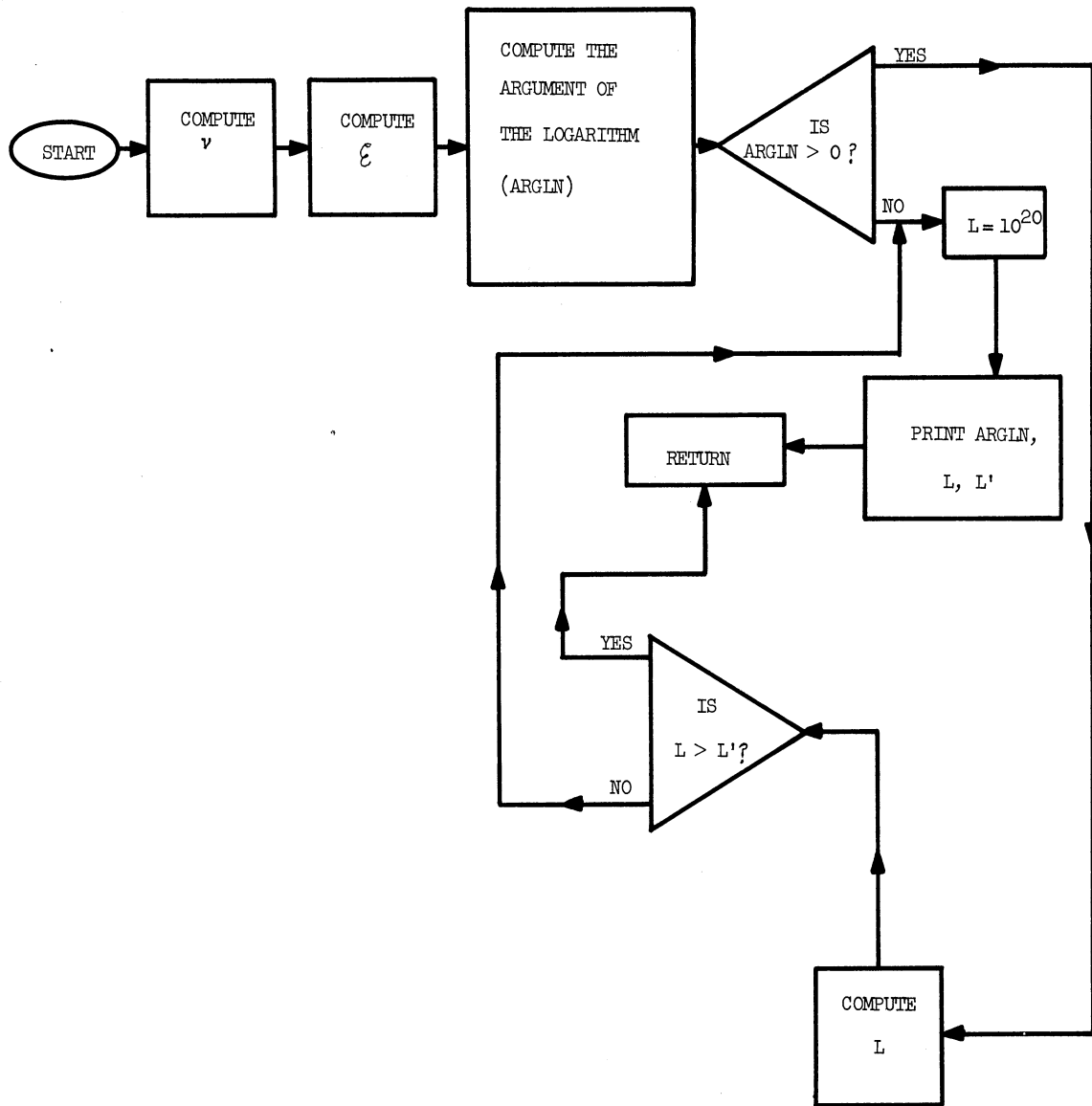
WASTRT : molar flow rate of A combined in products higher than P_2

WBSTRT : same as WASTRT, for B

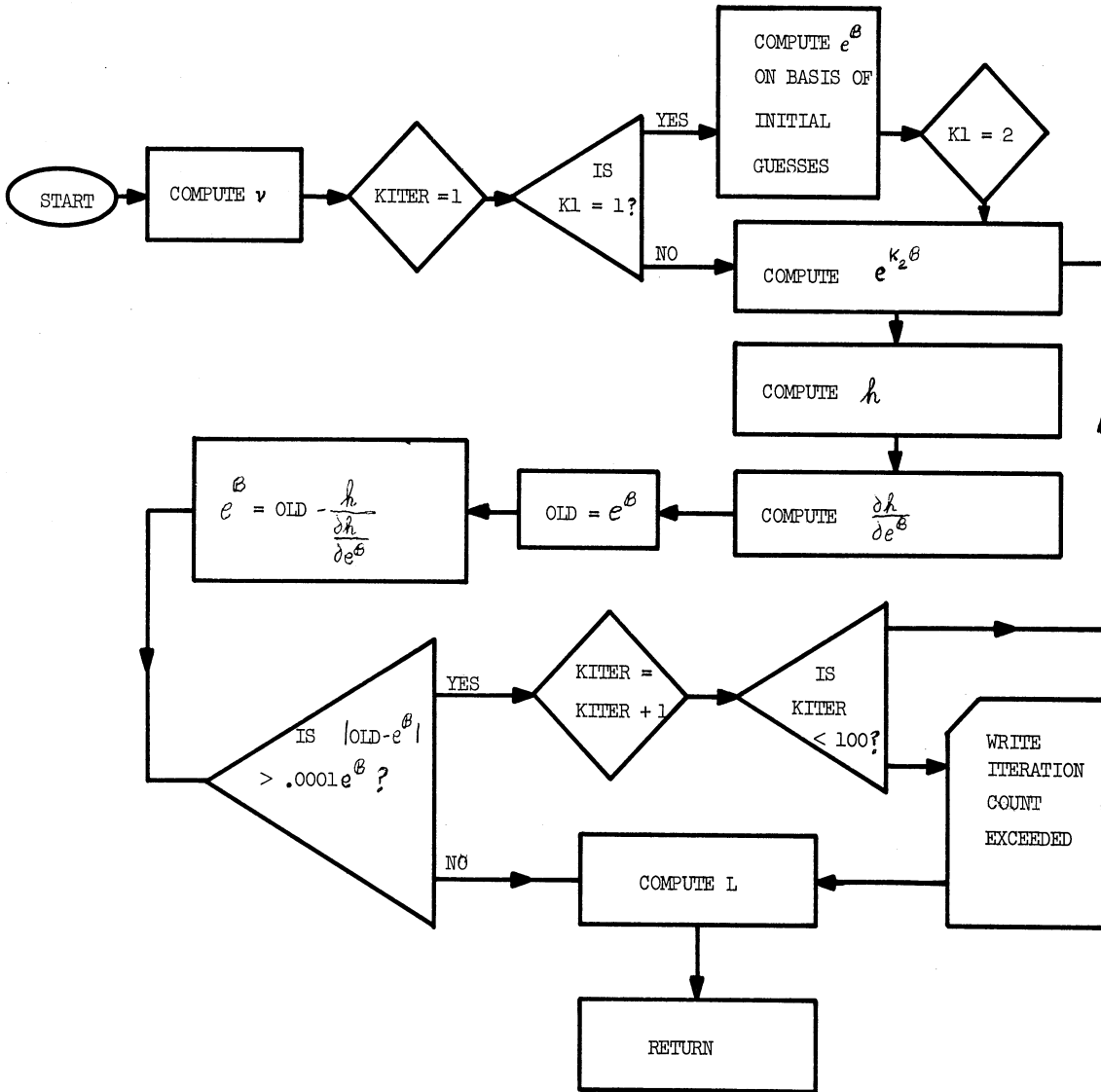




REACTOR LENGTH SUBROUTINE
PROGRAM 7



REACTOR LENGTH SUBROUTINE
PROGRAM 8



PROGRAM FOR OPTIMAL DESIGN OF A REACTOR TO CARRY OUT A SINGLE SECOND-ORDER REACTION

```
DIMENSION V(4)
COMMON DTDXAO, DTDVI, DTDVF, PTINJ, RCTRL
EQUIVALENCE (VI, V(1)), (VF, V(2)), (XAO, V(3))
1 READ INPUT TAPE 7, 3, VA, VB, Z, RC, D, R, CM, VI, VF, XAO, FRACT,
  XMAXIT, PTINJ
2 PRET = (R+CM)*10.**8.
3 FORMAT(7E10.4/2E10.4, 2F6.3, I4, E10.4)
  KCOUNT = 1
4 OLDT = PRET
5 KEXIT = 2
  CALL RL(VB, PTINJ, VI, VF, XAO, Z, RC, D, VA)
  T = TOTCST(CM, RCTRL, R, XAO, VI, VF, VA, VB, Z, PTINJ)
6 IF (T-OLDT) 7, 24, 24
65 KEXIT = 1
47 CALL DERIVS(VB, CM, VI, VF, XAO, Z, RC, D, VA, R, KEXIT)
43 WRITE OUTPUT TAPE 6, 49, Z, VA, VB, RC, D, R, CM, VF, VI, XAO,
  XPTINJ, RCTRL
4) FORMAT(78H OPTIMUM SINGLE-INJECTION REACTOR TO PRODUCE THE FOLLOWI
  XNG AMOUNT OF PRODUCT E10.4/21H MOLAR VOLUME OF A = E10.4, 22H MO
  XLAR VOLUME OF B = E10.4, 7H K1 = E10.4, 18H TUBE DIAMETER = E10.
  X4/48H COST FACTORS- REACTANT REMOVAL COST PER MOL = $F11.5, 34H UN
  XIT OPERATING COST PER FOOT = $F8.5/15H FEED VOLUME = E10.4, 21H I
  XNJECTION VOLUME = E10.4, 30H INITIAL MOL FRACTION OF A = F6.3/
  X19H INJECTION POINT = E10.4, 19H REACTOR LENGTH = E10.4)
43 WRITE OUTPUT TAPE 6, 44, KCOUNT
4+ FORMAT(54H NUMBER OF ITERATIONS NECESSARY TO REACH A SOLUTION = I4
  X////////)
  GO TO 36
7 PRET = T
3 FR1 = .9
9 FR2 = 1.1
1) OLDT = PRET
14 DO 22 K=1,4
  V(4) = PTINJ
15 V(K) = FR1*V(K)
  PTINJ = V(4)
  CALL RL(VB, PTINJ, VI, VF, XAO, Z, RC, D, VA)
  T = TOTCST(CM, RCTRL, R, XAO, VI, VF, VA, VB, Z, PTINJ)
16 IF (PRET-T) 17, 17, 21
17 V(K) = FR2*V(K)/FR1
  PTINJ = V(4)
  CALL RL(VB, PTINJ, VI, VF, XAO, Z, RC, D, VA)
  T = TOTCST(CM, RCTRL, R, XAO, VI, VF, VA, VB, Z, PTINJ)
18 IF (PRET-T) 19, 19, 21
19 V(K) = V(K)/FR2
  PTINJ = V(4)
20 GO TO 22
21 PRET = T
22 CONTINUE
4) KCOUNT = KCOUNT+1
23 IF (KCOUNT-MAXIT) 32, 32, 50
5) WRITE OUTPUT TAPE 6, 51, VF, VI, XAO
51 FORMAT(32H ITERATION COUNT EXCEEDED VF = E11.4, 7H VI = E11.4,
  -X8H XAO = F6.3)
52 GO TO 1
```


24 IF (FR1-.99) 26, 29, 345

25 FR1 = .99

27 FR2 = 1.01

28 GO TO 14

29 FR1 = .999

30 FR2 = 1.001

31 GO TO 14

32 IF (PRET-OLDT) 33, 24, 24

33 OLDT = PRET

34 GO TO 14

345 CONTINUE

CALL RL(VB, PTINJ, VI, VF, XAO, Z, RC, D, VA)

T = TOTCST(CM, RCTRL, R, XAO, VI, VF, VA, VB, Z, PTINJ)

35 GO TO 65

36 DO 41 I=1,3

37 V(I) = .999*V(I)

38 CALL DERIVS(VB, CM, VI, VF, XAO, Z, RC, D, VA, R, KEXIT)

39 V(I) = 1.001*V(I)/.999

CALL DERIVS(VB, CM, VI, VF, XAO, Z, RC, D, VA, R, KEXIT)

41 V(I) = V(I)/1.001

42 GO TO 1

TOTAL COST SUBROUTINE

FUNCTION TOTCST(CM, RCTRL, R, XAO, VI, VF, VA, VB, Z, PTINJ)

1 GNU = 1./(VA*XAO+VB-VB*XAO)

2 CAF = (VF*XAO*GNU-Z)/(VI+VF)

3 CBF = (VF*(1.-XAO)*GNU*VB+VI-Z*VB)/(VB*(VI+VF))

4 TOTCST = CM*RCTRL+R*(VI+VF)*(CAF+CBF)

5 WRITE OUTPUT TAPE 6, 6, XAO, VI, VF, PTINJ, CAF, CBF, RCTRL, TOTCS
XT

6 FORMAT(33HINDEPENDENT VARIABLES ARE XAO = F6.3, 7H VI = E11.4,
X7H VF = E11.4, 10H PTINJ = E11.4/8H (A)F = E11.4, 9H (B)F = E11
X.4, 19H REACTOR LENGTH = E11.4, 16H TOTAL COST = \$F11.2)

7 RETURN

REACTOR LENGTH SUBROUTINE

SUBROUTINE RL(VB, PTINJ, VI, VF, XAO, Z, RC, D, VA)

COMMON DTXAO, DTDVI, DTDVF, PTINJ, RCTRL

2 GNU = 1./(VA*XAO+VB-VB*XAO)

3 FN1 = VF*(1.-2.*XAO)*GNU*VB+VI

4 FN2 = VF-(1.-2.*XAO)*GNU*(VI+2.*VF)*VB

5 FN3 = VF*(1.-XAO)*GNU*VB+VI-Z*VB

6 FN4 = RC*3.14159*D*D

7 EPS = FN4*PTINJ*(2.*XAO-1.)*GNU/(4.*VF)

8 EXPEPS = EXP(EPS)

9 ARGLN = ((VF*GNU*VB*(2.*XAO-3.+1./XAO)+VI*((1.-XAO)/XAO-EXPEPS))

X*(VF*XAO*GNU-Z))/(VF*(1.-2.*XAO)*GNU*EXPEPS*FN3)

10 IF (ARGLN) 11, 11, 15

11 RCTRL = 10.**20.

12 WRITE OUTPUT TAPE 6, 13, ARGLN, RCTRL, PTINJ

13 FORMAT(9H ARGLN = E12.4, 10H RCTRL = E12.4, 10H PTINJ = E12.4)

14 GO TO 17

15 RCTRL = PTINJ-4.*(VI+VF)*(VI+VF)*VB*LOGF(ARGLN)/(FN1*FN4)

16 IF (RCTRL-PTINJ) 11, 11, 17

17 RETURN

PROGRAM FOR OPTIMAL DESIGN OF A REACTOR TO CARRY OUT A SET OF CONSECUTIVE
COMPETITIVE REACTIONS

```
DIMENSION V(4)
COMMON DEDVI, DEDVF, DEDXAO, DEDL, DEDLP, H
EQUIVALENCE (VI, V(1)), (VF, V(2)), (XAO, V(3))
1 READ INPUT TAPE 7, 3, VA, VB, Z, RC, RCR2, RCR3, D, B, COSTR, COST
XM, COSTA, COSTW, COSTB, VF, VI, RCTRL, PTINJ, UNDET, XAO, FRACT,
XMAXIT
2 PRET = (COSTR+COSTM)*10.**8.
3 FORMAT(7E10.4/F6.3, 5E10.4/5E10.4, 2F6.3, I4)
KCOUNT = 1
4 OLDT = PRET
46 KEXIT = 2
K1 = 1
RCTRL = RL(VB, PTINJ, VI, VF, XAO, Z, RC, RCR2, RCR3, B, D, VA, RCTRL, K1)
T = TOTCST(COSTR, COSTM, COSTA, COSTW, COSTB, RCTRL, XAO, VI, VF,
XVA, VB, Z, PTINJ, B, RC, D, RCR2, RCR3)
6 IF (T-OLDT) 7, 24, 24
65 KEXIT = 1
47 CALL LAGMUL(B, VF, XAO, RC, D, RCTRL, PTINJ, VI, VA, VB, RCR2,
XR3, COSTR, COSTA, COSTW, COSTB, COSTM, UNDET, Z)
81 WRITE OUTPUT TAPE 6, 82, Z, VA, VB, RC, RCR2, RCR3, B, D, COSTR,
XCOSTW, COSTA, COSTB, COSTM, UNDET, VF, VI, XAO, PTINJ, RCTRL
82 FORMAT(78H OPTIMUM SINGLE-INJECTION REACTOR TO PRODUCE THE FOLLOWI
XNG AMOUNT OF PRODUCT E10.4/21H MOLAR VOLUME OF A = E10.4, 22H MO
XLAR VOLUME OF B = E10.4, 7H K1 = E10.4, 10H K2/K1 = E10.4/9H K3/
XK1 = E10.4, 6H B = F6.3, 18H TUBE DIAMETER = E10.4//13H COST FAC
XTORS/46H MOLAR REACTANT AND BYPRODUCT REMOVAL COST = $F8.5, 30H B
XYPRODUCT CREDIT PER MOL = $F8.5/20H MOLAR COST OF A = $F8.5, 21H
XMOLAR COST OF B = $F8.5, 29H OPERATING COST PER FOOT = $F8.5//20H
X SOLUTION--LAMBDA = E10.4/15H FEED VOLUME = E10.4, 21H INJECTION
XVOLUME = E10.4, 30H INITIAL MOL FRACTION OF A = F6.3/19H INJECTIO
XN POINT = E10.4, 19H REACTOR LENGTH = E10.4)
43 WRITE OUTPUT TAPE 6, 44, KCOUNT
44 FORMAT(54H NUMBER OF ITERATIONS NECESSARY TO REACH A SOLUTION = I4
X////////)
GO TO 36
7 PRET = T
8 FR1 = .9
9 FR2 = 1.1
10 OLDT = PRET
14 DO 22 K=1,4
V(4) = PTINJ
15 V(K) = FR1*V(K)
PTINJ = V(4)
RCTRL = RL(VB, PTINJ, VI, VF, XAO, Z, RC, RCR2, RCR3, B, D, VA, RCTRL, K1)
T = TOTCST(COSTR, COSTM, COSTA, COSTW, COSTB, RCTRL, XAO, VI, VF,
XVA, VB, Z, PTINJ, B, RC, D, RCR2, RCR3)
16 IF (PRET-T) 17, 17, 21
17 V(K) = FR2*V(K)/FR1
PTINJ = V(4)
RCTRL = RL(VB, PTINJ, VI, VF, XAO, Z, RC, RCR2, RCR3, B, D, VA, RCTRL, K1)
T = TOTCST(COSTR, COSTM, COSTA, COSTW, COSTB, RCTRL, XAO, VI, VF,
XVA, VB, Z, PTINJ, B, RC, D, RCR2, RCR3)
18 IF (PRET-T) 19, 19, 21
19 V(K) = V(K)/FR2
PTINJ = V(4)
```

```
20 GO TO 22
21 PRET = T
22 CONTINUE
40 KCOUNT = KCOUNT+1
23 IF (KCOUNT-MAXIT) 32, 32, 50
50 WRITE OUTPUT TAPE 6, 51, VF, VI, XAO
51 FORMAT(32H ITERATION COUNT EXCEEDED VF = E11.4, 7H VI = E11.4,
X8H XAO = F6.3)
52 GO TO 1
24 IF (FR1-.99) 26, 29, 345
26 FR1 = .99
27 FR2 = 1.01
28 GO TO 14
29 FR1 = .999
30 FR2 = 1.001
31 GO TO 14
32 IF (PRET-OLDT) 33, 24, 24
33 OLDT = PRET
34 GO TO 14
345 CONTINUE
RCTRL = RL(VB,PTINJ,VI,VF,XAO,Z,RC,RCR2,RCR3,B,D,VA,RCTRL,K1)
T = TOTCST(COSTR, COSTM, COSTA, COSTW, COSTB, RCTRL, XAO, VI, VF,
XVA, VB, Z, PTINJ, B, RC, D, RCR2, RCR3)
35 GO TO 65
36 DO 41 I=1,3
37 V(I) = .999*V(I)
38 CALL LAGMUL(B, VF, XAO, RC, D, RCTRL, PTINJ, VI, VA, VB, RCR2,
XRCCR3, COSTR, COSTA, COSTW, COSTB, COSTM, UNDET, Z)
39 V(I) = 1.001*V(I)/.999
CALL LAGMUL(B, VF, XAO, RC, D, RCTRL, PTINJ, VI, VA, VB, RCR2,
XRCCR3, COSTR, COSTA, COSTW, COSTB, COSTM, UNDET, Z)
41 V(I) = V(I)/1.001
42 GO TO 1
```

TOTAL COST SUBROUTINE

```
FUNCTION TOTCST(COSTR, COSTM, COSTA, COSTW, COSTB, RCTRL, XAO,
XVI, VF, VA, VB, Z, PTINJ, B, RC, D, RCR2, RCR3)
1 GNU = 1./((VA*XAO+VB-VB*XAO)
2 SA = -B*VF*XAO*RC*GNU*3.14159*D*D*(RCTRL-PTINJ)/(4.*(VF+VI)**2.)
3 SF = -B*3.14159*D*D*PTINJ*RC*XAO*GNU/(4.*VF)
5 ESF = EXPF(SF)
12 FN1 = EXPF((1.-XAO)*(ESF-1.)/(B*XAO))
13 FN2 = EXPF(SA*FN1)
4 ESA = EXPF(SA)
6 SB = (ESA*(VI+VF*VB*GNU*(1.-XAO)*ESF)-(VI+VF*VB*GNU*(1.-XAO)))/
X(B*GNU*VF*XAO*VB)
14 SC = (VF*GNU*(1.-XAO)*ESF+VI/VB)*FN2
26 ESB = EXPF(SB)
20 C1 = RCR2/((1.-RCR3)*(1.-RCR2))
27 EK2B = EXPF(RCR2*SB)
21 C2 = -RCR2/((1.-RCR2)*(RCR2-RCR3))
22 C3 = RCR2/((RCR3-1.)*(RCR3-RCR2))
28 EK3B = EXPF(RCR3*SB)
7 TOTCST = COSTM*RCTRL+VF*GNU*(COSTA*XAO+COSTB*(1.-XAO))+COSTB*VI
X/VB+(COSTR-COSTB)*SC+VF*XAO*GNU*(ESB*(COSTR-COSTA+C1*(COSTR-COSTW
X))+EK2B*(C2*(COSTR-COSTW))+C3*(COSTR-COSTW)*EK3B)
```

```
8 CAF = VF*XAO*GNU*ESB/(VI+VF)
9 PRODRT = VF*XAO*GNU*(ESB-EK2B)/(RCR2-1.)
10 BYPRT = (VI+VF)*CAF*(C1+C2*EK2B/ESB+C3*EK3B/ESB)
11 WASTRT = VF*XAO*GNU-(VI+VF)*CAF-PRODRT-BYPRT
15 CBF = SC/(VI+VF)
16 WBSTRT = VF*(1.-XAO)*GNU+VI/VB-(VI+VF)*CBF-PRODRT-2.*BYPRT
17 WRITE OUTPUT TAPE 6, 18, XAO, VI, VF, PTINJ, RCTRL, CAF, CBF,
XPRODRT, BYPRT, WASTRT, WBSTRT, TOTCST
18 FORMAT(33H0INDEPENDENT VARIABLES ARE XAO = F6.3, 7H VI = E11.4,
X7H VF = E11.4, 10H PTINJ = E11.4/18H REACTOR LENGTH = E11.4,
X9H (A)F = E11.4, 9H (B)F = E11.4/16H PRODUCT RATE = E11.4, 19H
XBYPRODUCT RATE = E11.4, 30H WASTAGE RATES OF A AND B ARE 2E12.4/
X15H TOTAL COST = $F11.2)
19 RETURN
```

REACTOR LENGTH SUBROUTINE

```
FUNCTION RL(VB, PTINJ, VI, VF, XAO, Z, RC, RCR2, RCR3, B, D, VA,
XRCTRL, K1)
1 GNU = 1./(VA*XAO+VB-VB*XAO)
2 KITER = 1
GO TO (3, 9), K1
3 SA = -B*VF*XAO*RC*GNU*3.14159*D*D*(RCTRL-PTINJ)/(4.*(VF+VI)**2.)
4 SF = -B*3.14159*D*D*PTINJ*RC*XAO*GNU/(4.*VF)
5 ESF = EXPF(SF)
6 ESA = EXPF(SA)
7 SB = (ESA*(VI+VF*VB*GNU*(1.-XAO)*ESF)-(VI+VF*VB*GNU*(1.-XAO)))/
X(B*GNU*VF*XAO*VB)
8 ESB = EXPF(SB)
K1 = 2
9 EK2B = ESB**RCR2
10 H = (ESB-EK2B)/(RCR2-1.)-Z/(VF*XAO*GNU)
11 DHDESB = (1.-RCR2*EK2B/ESB)/(RCR2-1.)
12 OLD = ESB
13 ESB = OLD-H/DHDESB
14 IF (ABS(OLD-ESB)-ESB/10000.) 19, 19, 15
15 KITER = KITER+1
16 IF (KITER-100) 9, 9, 17
17 WRITE OUTPUT TAPE 6, 18
18 FORMAT (55H ITERATION COUNT EXCEEDED IN REACTOR LENGTH COMPUTATION
X)
19 ESF = EXPF(-B*3.14159*D*D*PTINJ*RC*XAO*GNU/(4.*VF))
20 ESA = (VI+VF*VB*GNU*(1.-XAO)+B*GNU*VF*XAO*VB*ELOG(ESB))/(VI+VF*VB
X*GNU*(1.-XAO)*ESF)
21 RL = PTINJ-4.*(VF+VI)*(VF+VI)*ELOG(ESA)/(B*VF*XAO*RC*GNU*3.14159
X*D*D)
22 RETURN
```

Program 9: Chemical Reactor Simulation Program

Purpose: The computer reads the data required to specify completely the mode of operation of the reactor, and computes the concentration profiles along its length by integrating the differential rate equations which govern the course of the reactions. Ten or fewer consecutive competitive reactions can be treated and an exponential dependence of the rate constants on composition can be inserted if this is of interest. Two types of discontinuity in the concentration profiles may be introduced: injection and recycle; up to ten of each of these may be included in the design. The output consists of the flow rate, concentration profiles and the values of several of the counters employed by the program.

Logic: The most important switch in the program is KODE, the value of which indicates whether injection, recycle, both or neither is used in the reactor being simulated. Another switch, LAY, indicates whether or not the rate constants are composition-dependent.

There are two subprograms included in the overall program; Program 9 was written in basic FORTRAN, so these subroutines are not called, but simply transferred to. The first of these is GRES, which carries out the actual integration of the rate equations. The logic used by GRES is very similar to that in Program 1 and will not be elaborated on. There are, however, checks in GRES which were not used in Program 1, both on the number of reactions and on the need for too many halvings of the length interval in the computation of the true solution. The second is FLOP; this program orders and codes the several injection and

recycle points, for treatment by the main program. The logic of FLOP demands that the recycles be read into the computer in order of increasing distance of the drawoff point from the reactor inlet. FLOP has a single exit, while GRES has four, coded by KEY; the one to be used depends on whether the integration has been carried to an injection point, a recycle feed or sidestream point, or the end of the reactor.

When recycle is employed, it is first assumed that the concentrations of all the components in the recycle streams are zero; in the next iteration, those values found on the basis of the prior assumption are used. The iterative solution is continued until sufficient convergence is obtained. As the entire composition profile in the reactor is computed in each iteration, any combination of recycle points, including the reactor inlet, can be assumed, and forward and backward recycle systems are permitted.

Statements 185-214 are to be used for describing the format of the printout of the concentration profiles; as only three consecutive competitive reactions were considered in this study, the output formats and write tape statements are not given for any greater number of reactions.

NOTE: Some Greek letters are used in the flowsheets for one or both subprograms as well as the main program. If the subprograms are treated as separate from the main program, no ambiguity is introduced.

Computer: Basic IBM 704 with tapes

Language: FORTRAN

Library subroutines called: XLOC (location operator)
XCNTL (control on XDEQ operation)
XRKG (Runge-Kutta-Gill subroutine)
XDEQ (differential equation)
EXP (exponentiation)

Storage requirements: 2886_{10} words

Running time: 0.0029 min x number of reactions x number of length intervals.

As a rule of thumb, use an interval size given by

$$\Delta L = \frac{200 V_f \epsilon_{max}}{k_1 [B]_0 A} \quad (A.6)$$

where ϵ_{max} = maximum allowable error per length interval, concentration units

and the other variables are in engineering units.

Correspondence of variables:

LAY : switch on composition dependence of rate constants

KODE : switch on type of reactor

N : number of reactions

A : cross-sectional area of reactor

EMAX : ϵ_{max}

DF : reactor length

DELTAD : length interval, ΔL

EMAXT : maximum allowable error in recycle iteration

DENSA : molar density of A

DENSB : molar density of B

DENSP(I) : molar density of P_i

RATCON(I) : k_i when no composition dependence;
 \underline{k}_i when composition dependence included

CONCA : $[A]_0$

CONCB : $[B]_0$

CONCP(I) : $[P_i]_0$

V : volumetric feed rate; volumetric flow rate

NUMBI : number of injections

PTSINJ(I) : distance of the i-th injection point from the reactor inlet

VINJ(I,J) : volumetric injection rate of the j-th component at the i-th injection point. Here, $j = 1$ for A, $j = 2$ for B, $j = k+2$ for P_k .

NUMBR : number of recycles

PTSOUT(I) : distance of the i-th drawoff point, counted as required by the logic of FLOP, from the reactor inlet

PTSIN(I) : distance from reactor inlet of point at which recycle stream taken at i-th drawoff point is reintroduced

VREC(I) : volumetric recycle rate of the stream taken off at the i-th drawoff point

X(1) : reactor length

Y(J) : concentrations of the several components, indexed in the same way as J in VINJ(I,J)

L : number of halvings required, identical to J3 in Program 1

KOUNTU : number of recycle and injection points

KOUNTR : number of iterations required when recycle is used

CONR(I,J) : concentrations of the several components in the i-th recycle stream, indexed by J as in VINJ(I,J)

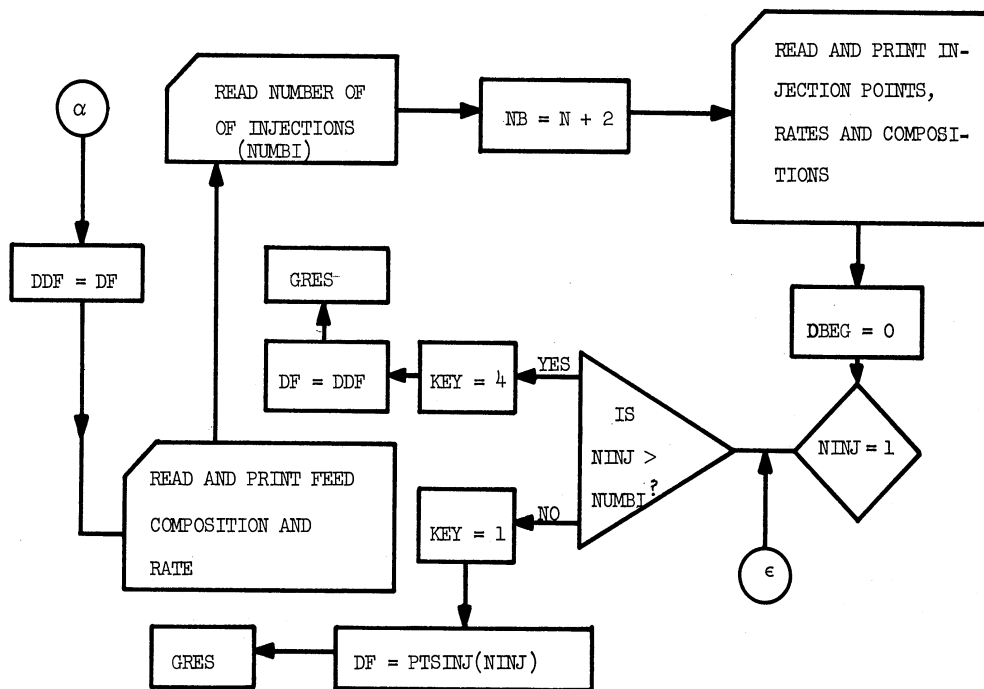
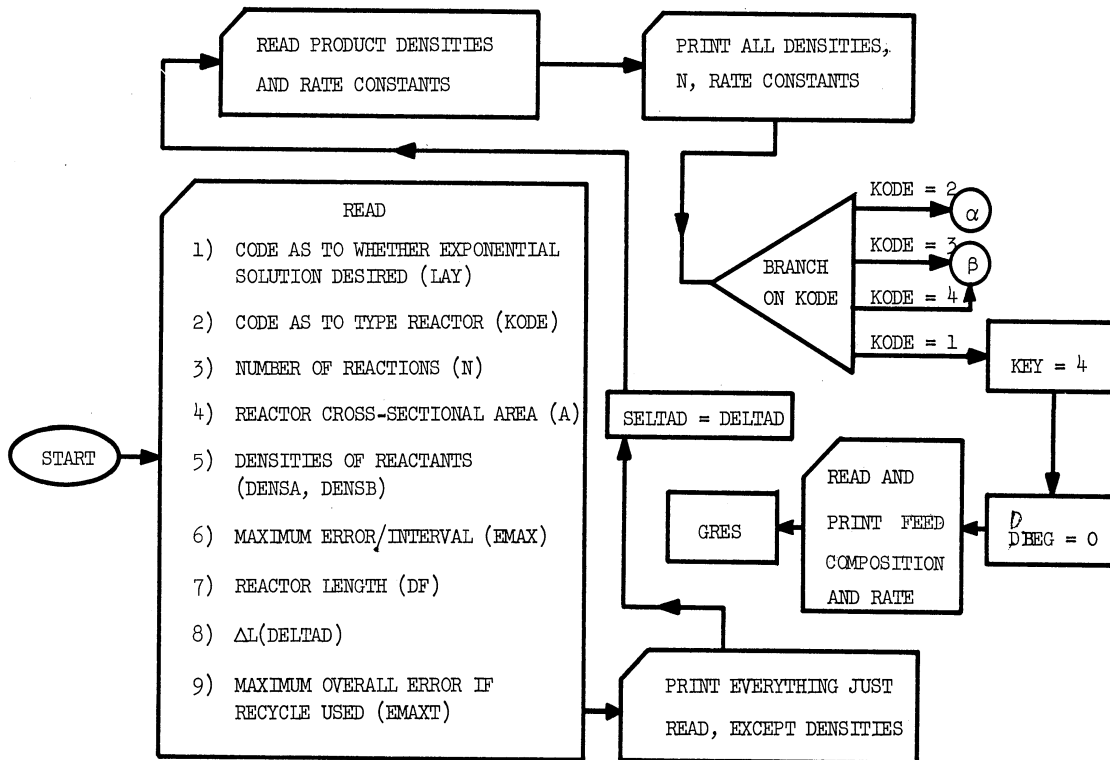
ZED(I) : intermediate values of the recycle compositions

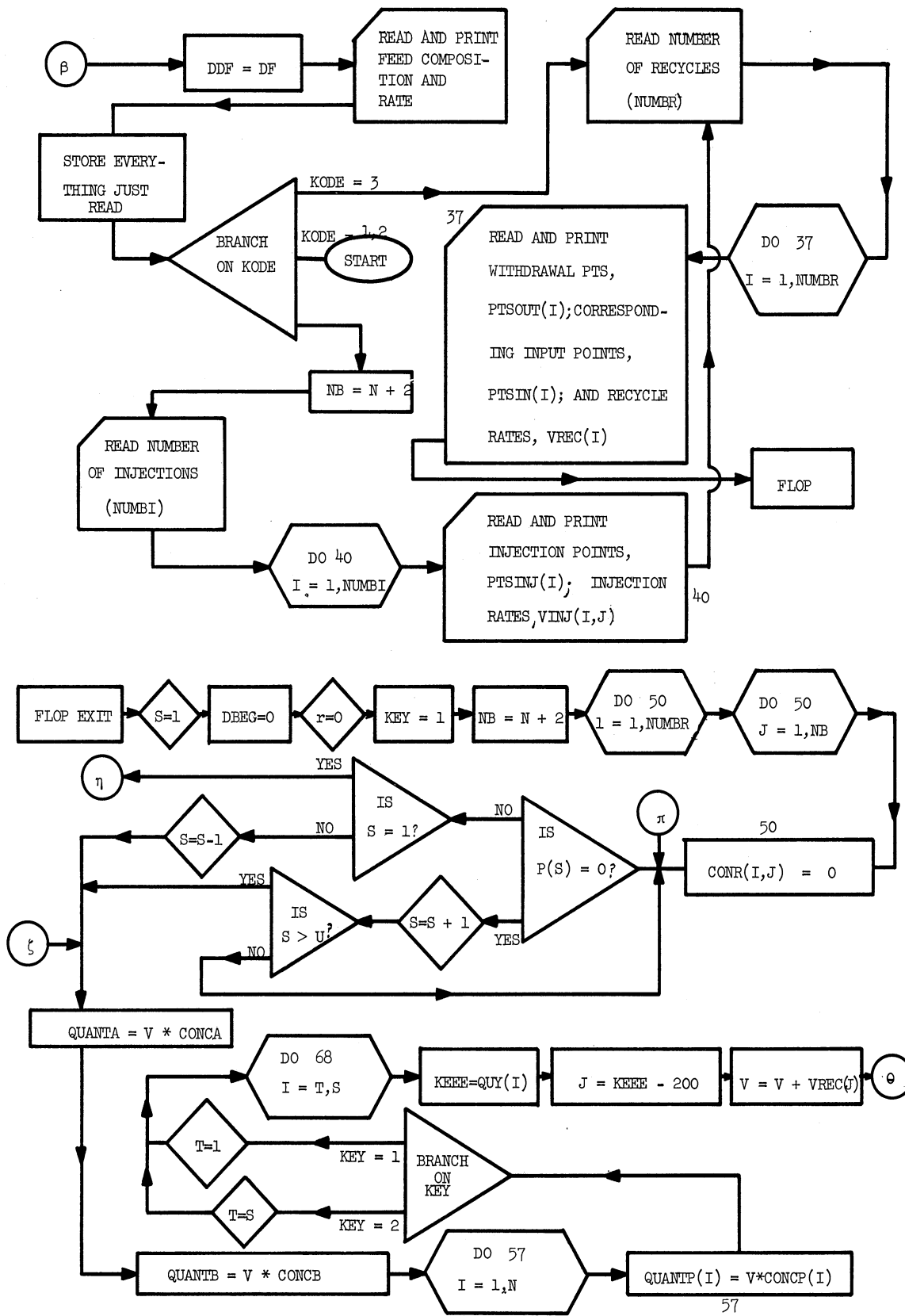
DEVN : final difference between reaction mix compositions from the last two recycle iterations

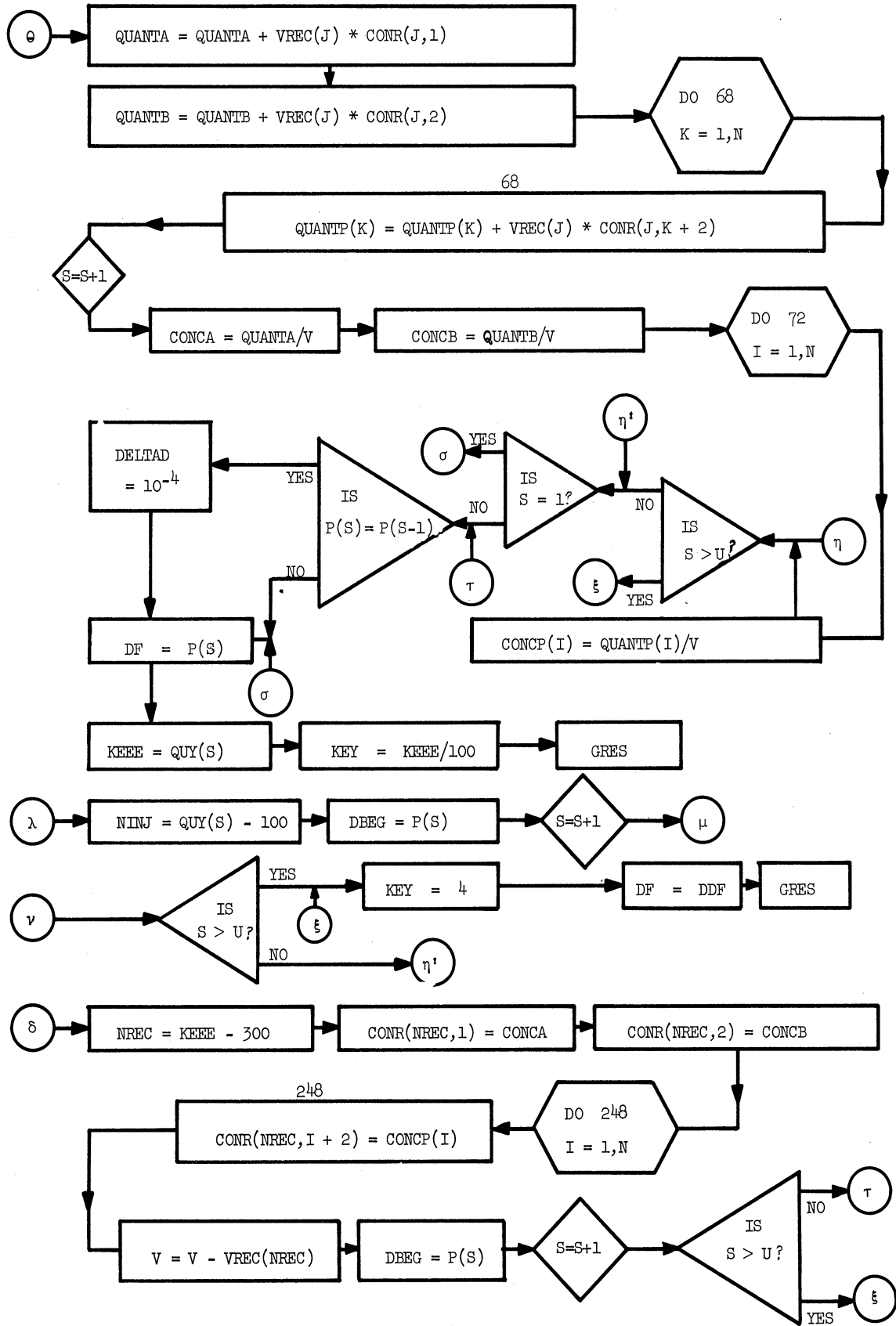
P(I) : counting from the reactor inlet, the distance of the i-th injection, recycle in or recycle out point from the inlet

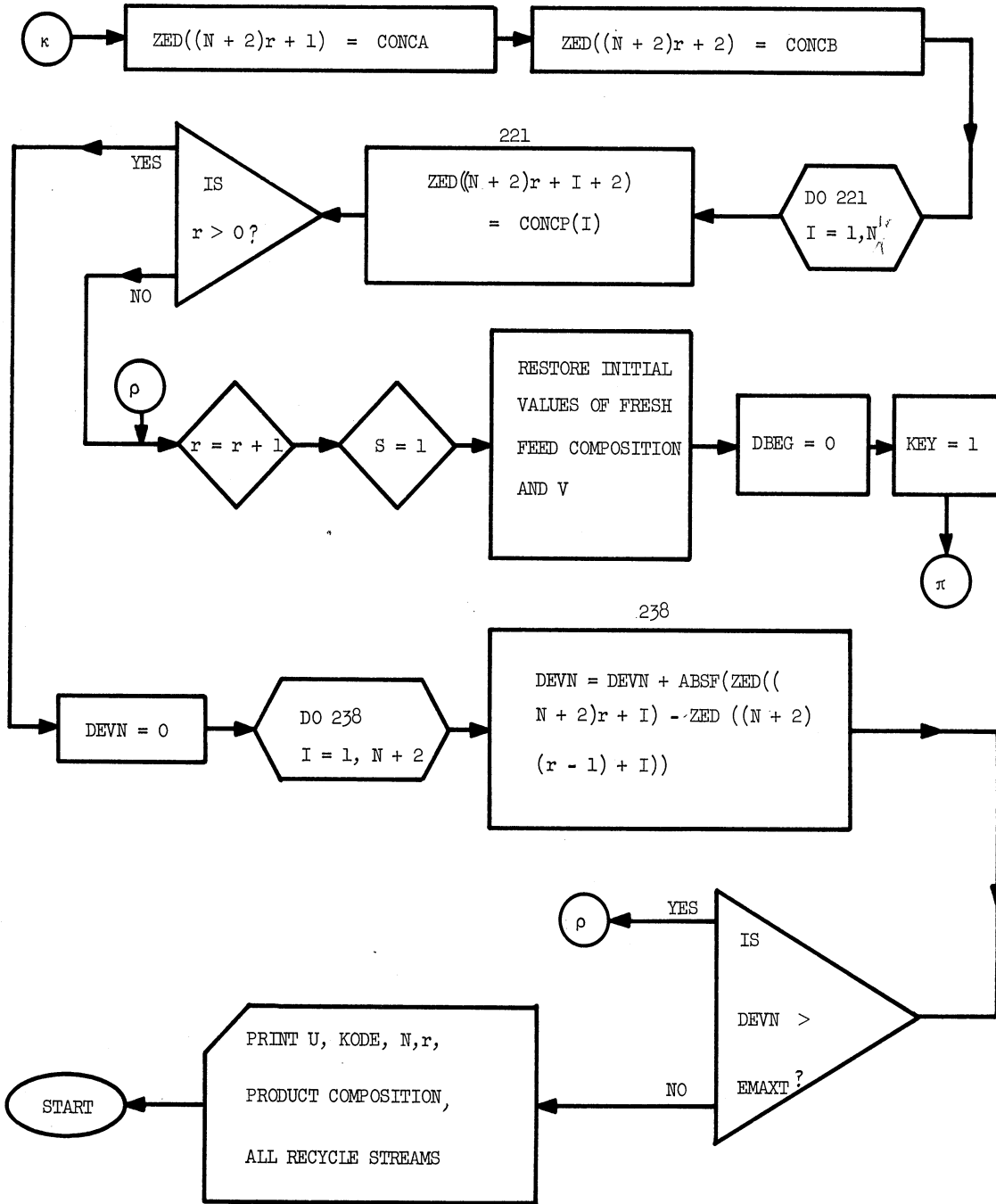
QUY(I) : code associated with P(I)

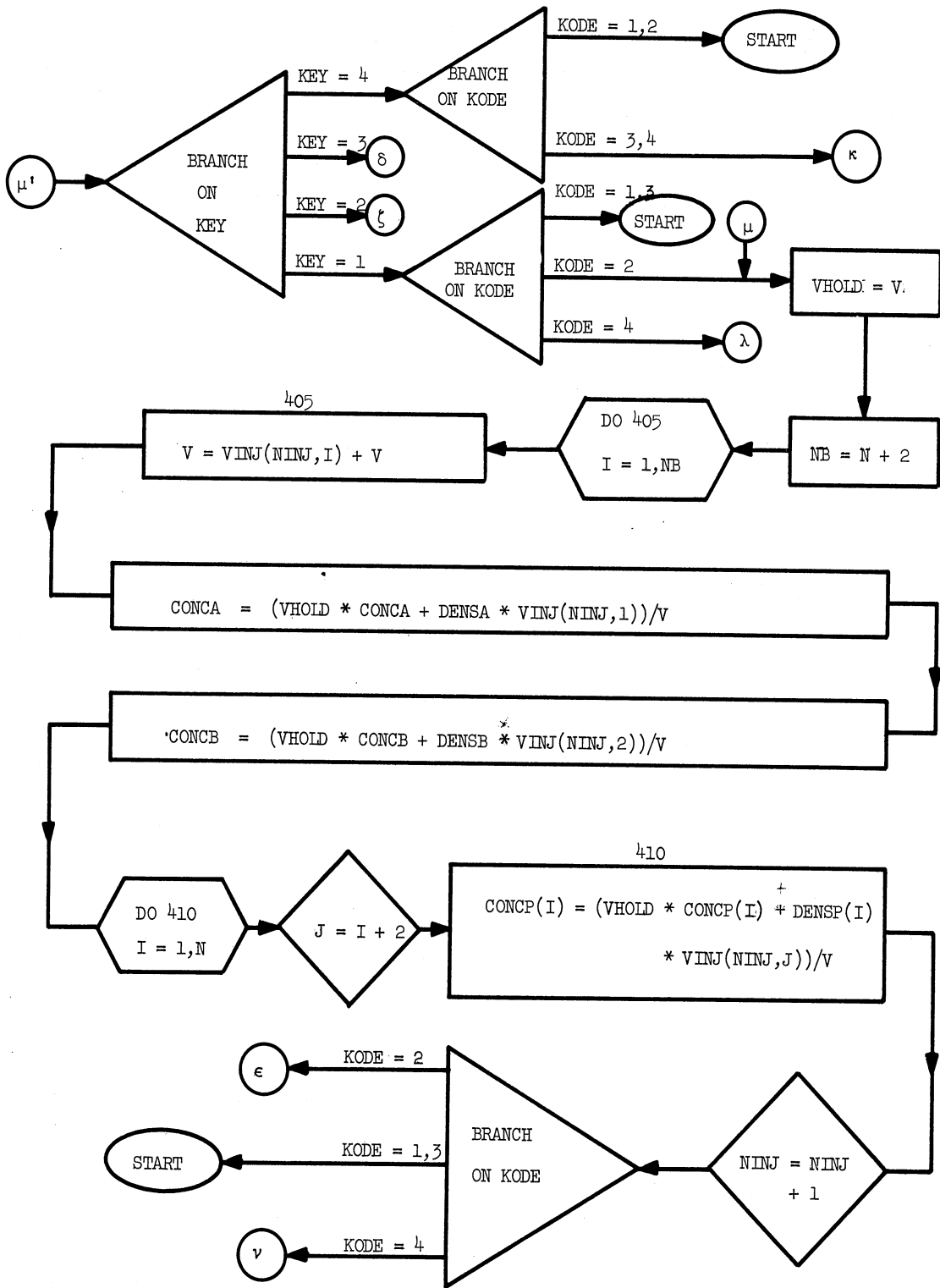
FLWSHEET - PROGRAM 9

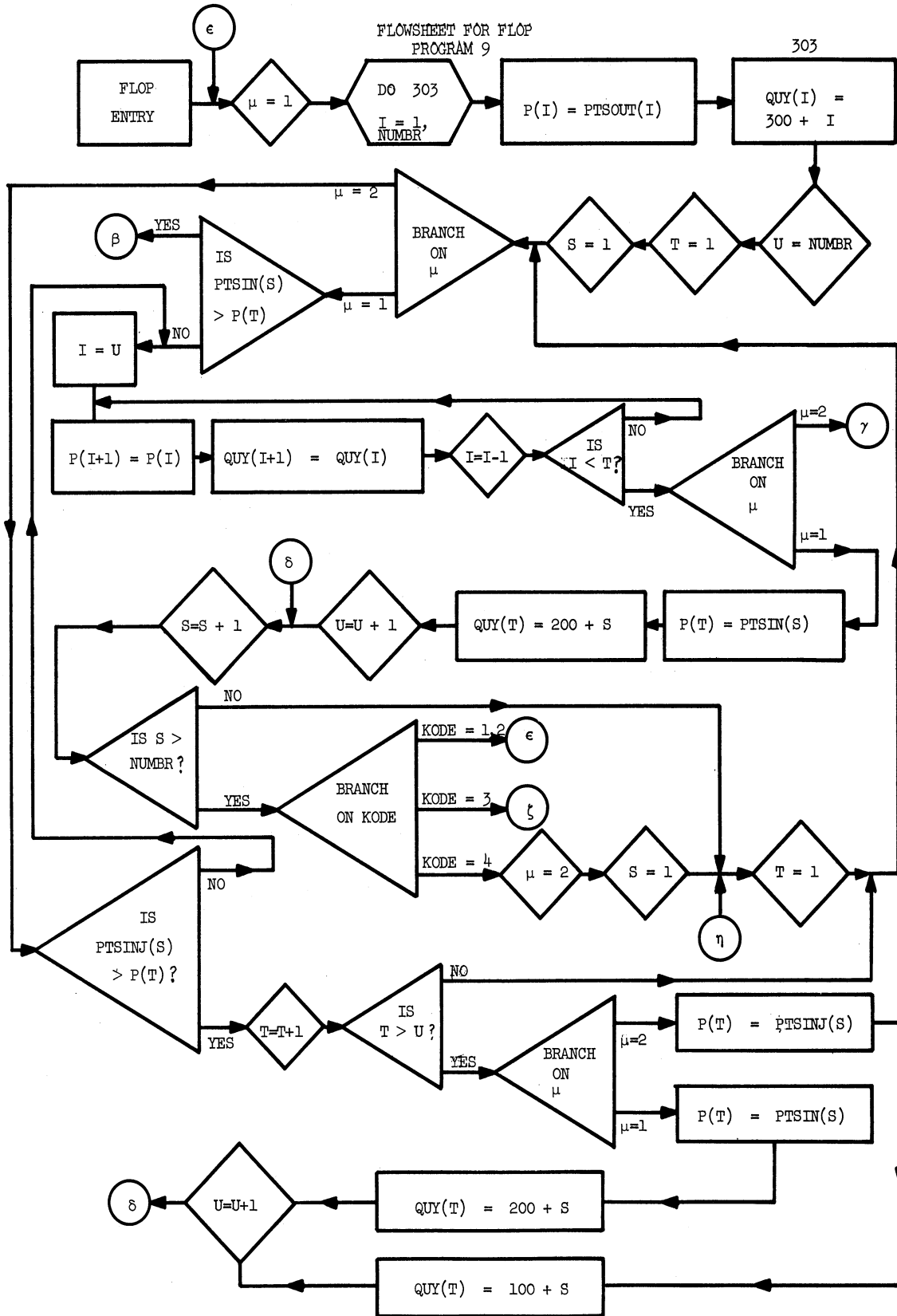


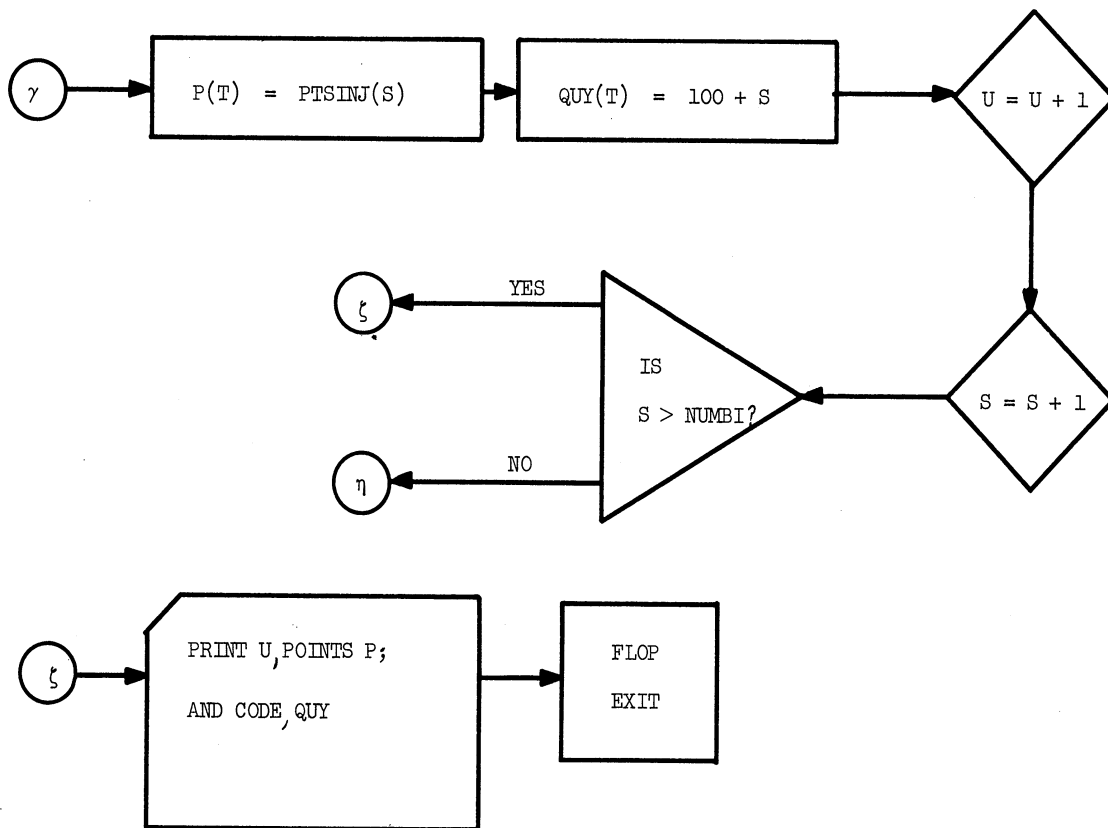




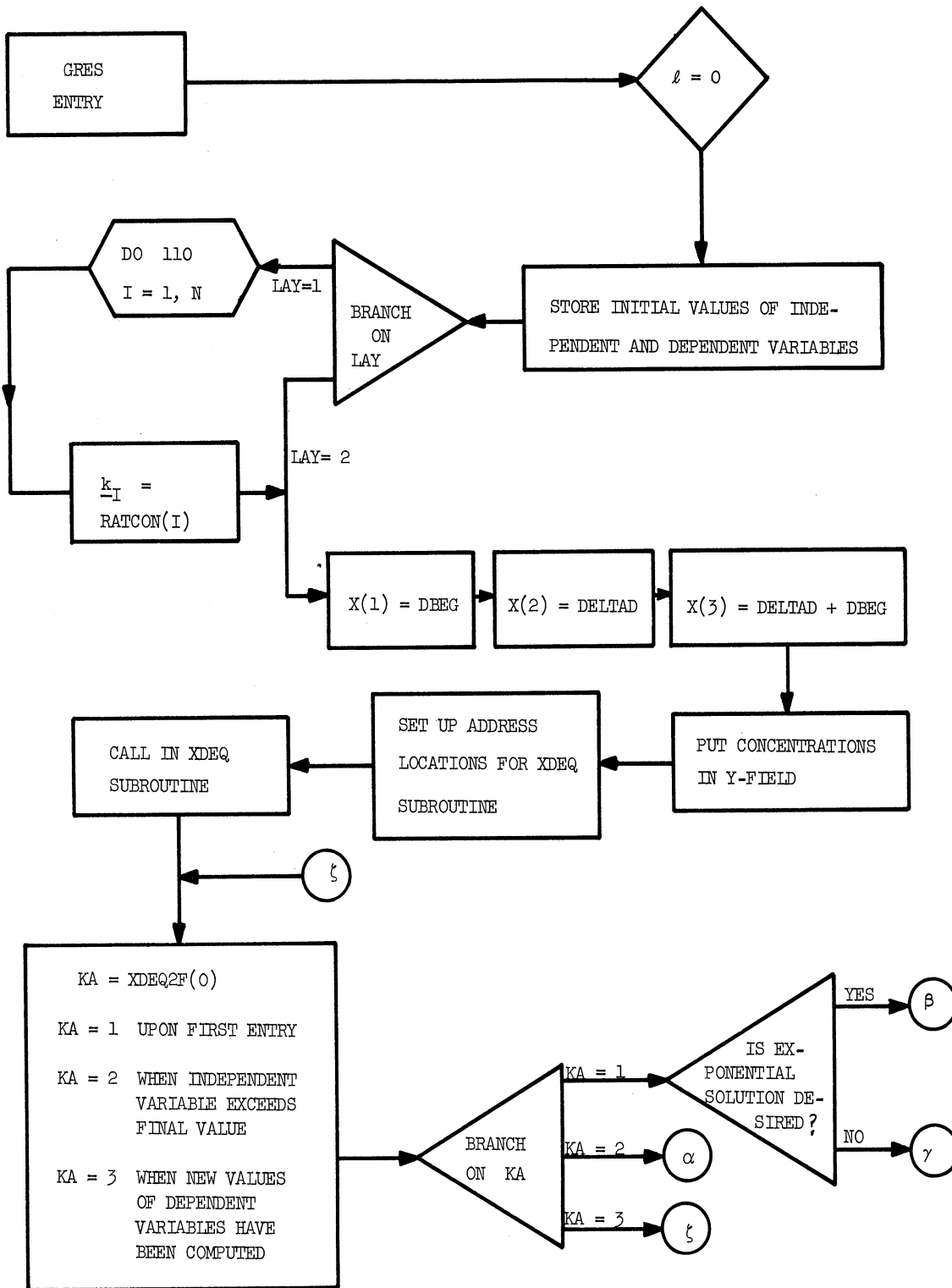


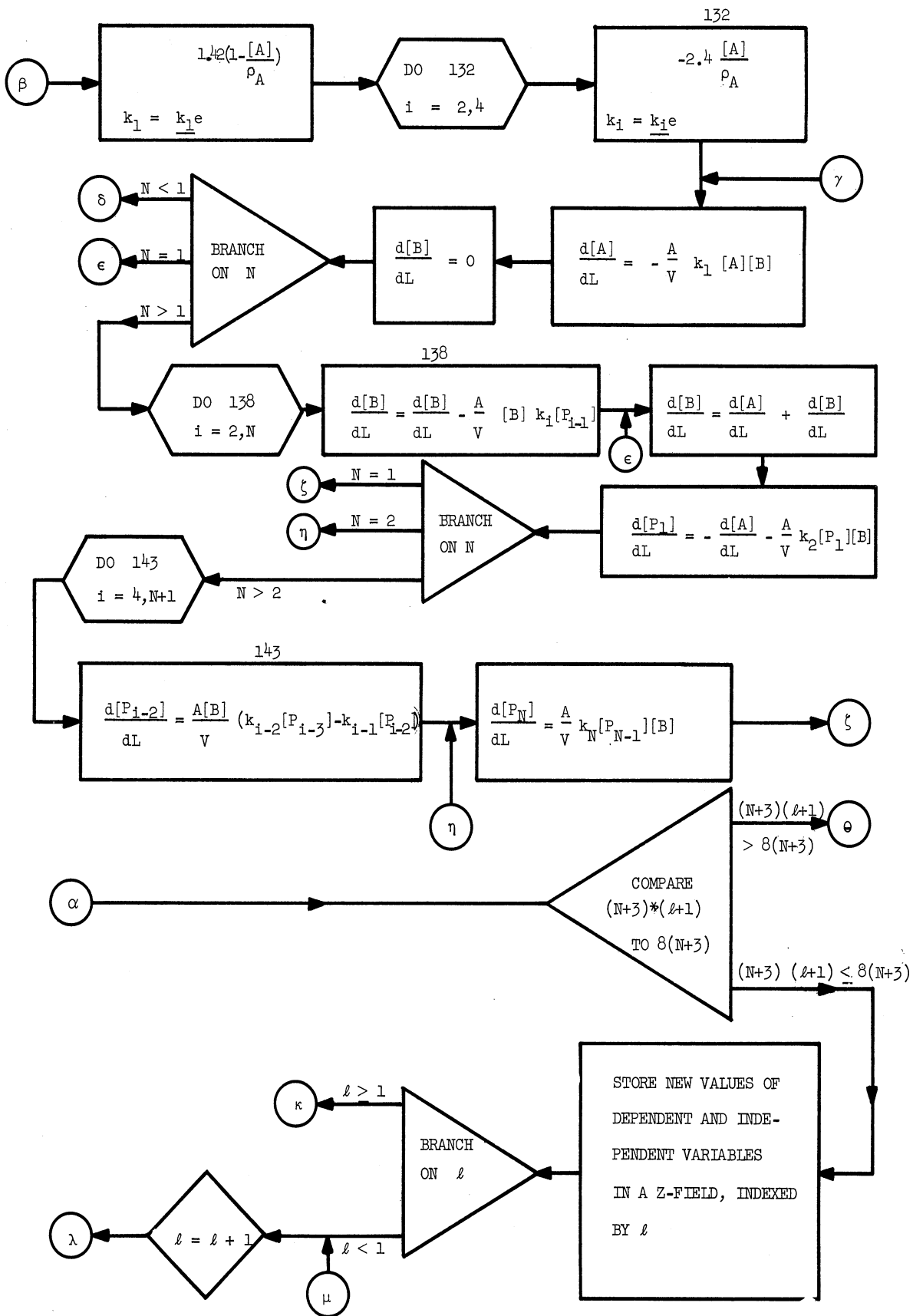


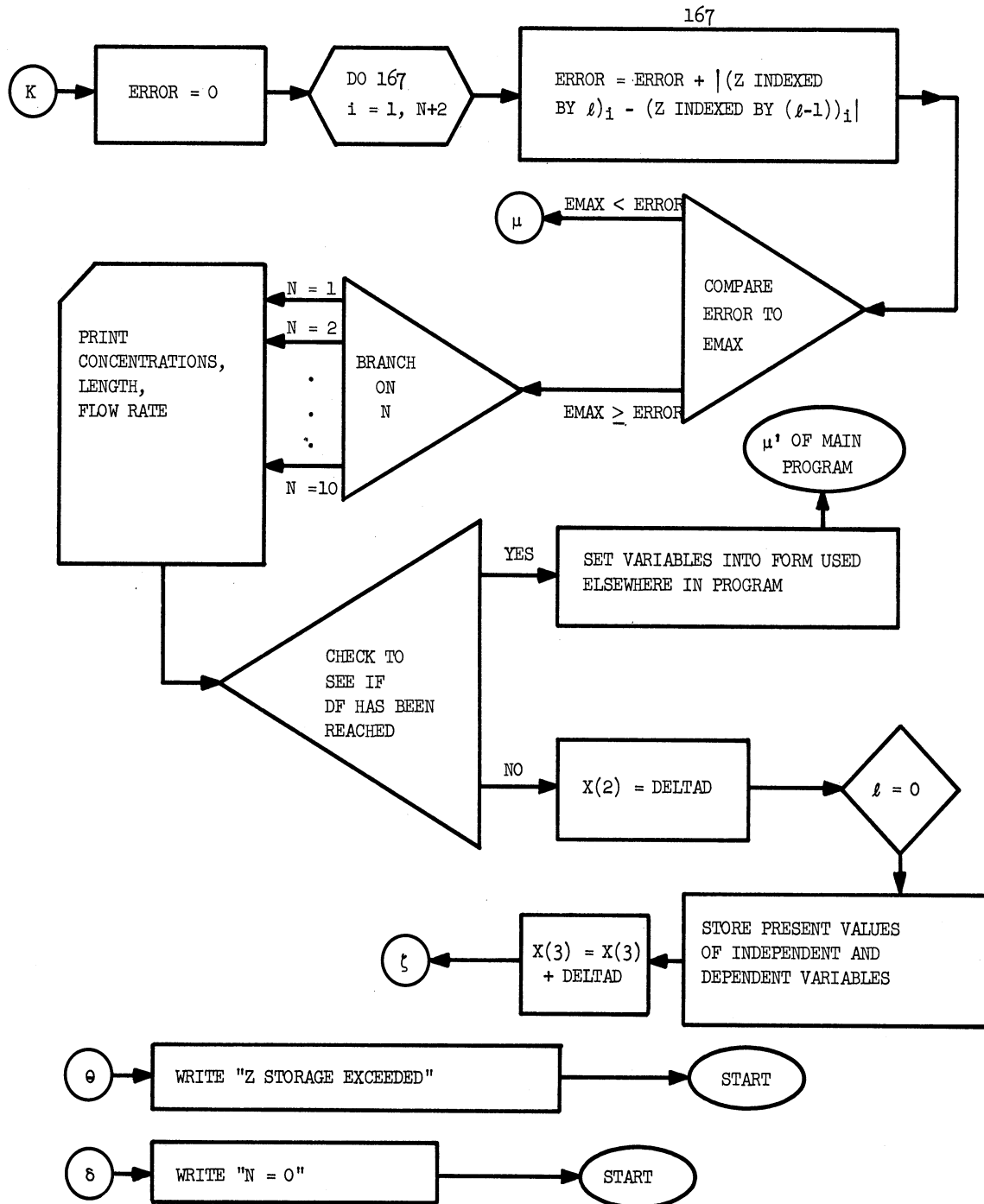
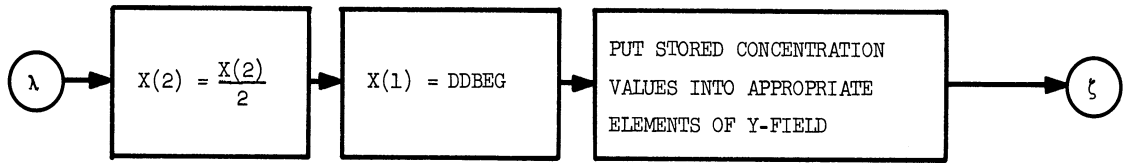




FLWSHEET FOR GRES
PROGRAM 9







CHEMICAL REACTOR SIMULATION PROGRAM

C IDENTIFICATION OF INPUT VARIABLES

C LAY = 1 IF EXPONENTIAL SOLUTION IS DESIRED, OR 2 IF NOT

C KJDE = (1 IF THERE IS NO INJECTION OR RECYCLE), (2 IF INJECTION ONLY)

C (3 IF RECYCLE ONLY),(4 IF BOTH)

C N = NUMBER OF REACTIONS

C BEGINNING OF OVERALL PROGRAM

DIMENSION DENSP(10), RATCON(10), CONCP(10), PTSINJ(10),

CVINJ(10,12), SCONCP(10), PTSOUT(10), PTSIN(10), VREC(10),

CCONR(10,12), P(30), QUANTP(10), QUY(30), ZED(120), DCONCP(10),

CX(3), Y(12), LOP(10), F(12), Q(12), Z(100), SATCON(10)

1 READ INPUT TAPE 7, 3, LAY, KODE, N, A, EMAX, DF, DELTAD, EMAXT,

CDENSA, DENSB

3 FORMAT(2I2, I3, 6E10.4/E10.4)

WRITE OUTPUT TAPE 6, 256, LAY, KODE, N, A, EMAX, DF, DELTAD, EMAXT

SFLTAD = DELTAD

4 READ INPUT TAPE 7, 5, (DENSP(I), RATCON(I), I=1,N)

5 FORMAT(7E10.4)

WRITE OUTPUT TAPE 6, 257, DENSA, DENSB, N, (DENSP(I), I=1,N)

WRITE OUTPUT TAPE 6, 258, N, (RATCON(I), I=1,N)

GO TO (6, 11, 28, 28), KODE

6 KEY = 4

7 DBEG = 0.

8 READ INPUT TAPE 7, 9, V, CONCA, CONCB, (CONCP(I), I=1,N)

9 FORMAT(7E10.4)

WRITE OUTPUT TAPE 6, 259, V, CONCA, CONCB, N, (CONCP(I), I=1,N)

10 GO TO 100

11 DDF = DF

12 READ INPUT TAPE 7, 13, V, CONCA, CONCB, (CONCP(I), I=1,N)

13 FORMAT(7E10.4)

WRITE OUTPUT TAPE 6, 259, V, CONCA, CONCB, N, (CONCP(I), I=1,N)

14 READ INPUT TAPE 7, 15, NUMBI

15 FORMAT(I3)

16 NB = N+2

17 READ INPUT TAPE 7, 18, (PTSINJ(I), I=1,NUMBI),

X((VINJ(I,J),I=1,NUMBI),J=1,NB)

18 FORMAT(7E10.4)

WRITE OUTPUT TAPE 6, 260, NUMBI, (PTSINJ(I),I=1,NUMBI),

C((VINJ(I,J), I=1,NUMBI), J=1,NB)

19 DBEG = 0.

20 NINJ = 1

21 IF(NINJ-NUMBI) 22, 22, 25

22 KEY = 1

23 DF = PTSINJ(NINJ)

24 GO TO 100

25 KEY = 4

26 DF=DDF

27 GO TO 100

28 DDF = DF

29 READ INPUT TAPE 7, 30, V, CONCA, CONCB, (CONCP(I),I=1,N)

30 FORMAT(7E10.4)

WRITE OUTPUT TAPE 6, 259, V, CONCA, CONCB, N, (CONCP(I), I=1,N)

31 SCONCA = CONCA

32 SCONCB = CONCB

33 DO 34 I=1,N

34 SCONCP(I) = CONCP(I)

SV = V

```
33 GO TO (1, 1, 36, 39), KODE
33 READ INPUT TAPE 7, 37, NUMBR,
  X(PTSOUT(I), PTSIN(I), VREC(I), I=1,NUMBR)
37 FORMAT(I3, 6E10.4/(7E10.4))
  WRITE OUTPUT TAPE 6, 261, NUMBR, (PTSOUT(I), PTSIN(I), VREC(I),
  CI=1,NUMBR)
33 GO TO 300
39 NB = N+2
4) READ INPUT TAPE 7, 41, NUMBI, (PTSINJ(I), I=1,NUMBI),
  X((VINJ(I,J),I=1,NUMBI), J=1,NB)
4) FORMAT(I3, 6E10.4/(7E10.4))
  WRITE OUTPUT TAPE 6, 260, NUMBI, (PTSINJ(I),I=1,NUMBI),
  C((VINJ(I,J), I=1,NUMBI), J=1,NB)
4) GO TO 36
4) KOUNTS = 1
4) DREG = 0.
4) KOUNTR = 0
45 KEY = 1
47 NB = N+2
43 DO 50 I=1,NUMBR
49 DO 50 J=1,NB
50 CONR(I,J) = 0.
51 IF(P(KOUNTS)) 1, 52, 84
52 KOUNTS = KOUNTS+1
53 IF(KOUNTS-KOUNTU) 51, 51, 54
54 QUANTA = V*CONCA
55 QUANTB = V*CONCB
56 DO 57 I=1,N
57 QUANTP(I) = V*CONCP(I)
58 GO TO (59, 81), KEY
59 KOUNTT = 1
61 DO 68 I=KOUNTT,KOUNTS
62 KEEE = QUY(I)
63 J = KEEE-200
64 V = V+VREC(J)
65 QUANTA = QUANTA+VREC(J)*CONR(J,1)
66 QUANTB = QUANTB+VREC(J)*CONR(J,2)
67 DO 68 K=1,N
68 QUANTP(K) = QUANTP(K)+VREC(J)*CONR(J,K+2)
69 KOUNTS = KOUNTS+1
70 CONCA = QUANTA/V
71 CONCB = QUANTB/V
  DO 72 I = 1,N
72 CONCP(I) = QUANTP(I)/V
72 IF(KOUNTS-KOUNTU) 255, 255, 91
7) IF (P(KOUNTS)-P(KOUNTS-1)) 1, 76, 77
76 DELTAD = 0.0001
77 DF = P(KOUNTS)
73 KEEE = QUY(KOUNTS)
77 KEY = KEEE/100
80 GO TO 100
81 KOUNTT = KOUNTS
8) GO TO 61
8) IF(KOUNTS-1) 1, 73, 253
83 KEEF = QUY(KOUNTS)
85 NINJ = KEEE-100
87 DREG = P(KOUNTS)
83 KOUNTS = KOUNTS+1
```

```
89 GO TO 401
90 IF(KOUNTS-KOUNTU) 255, 255, 91
91 KFY = 4
92 DF = DDF
93 GO TO 100
94 NMOD6 = (N+2)*KOUNTR
95 ZFD(NMOD6+1) = CONCA
96 ZFD(NMOD6+2) = CONCB
97 GO TO 219
C END OF FIRST SECTION OF OVERALL PROGRAM. CONTINUES WITH STATEMENT 219
C BEGINNING OF DIFFERENTIAL EQUATION SUBPROGRAM
100 L = 0
103 DCONCA = CONCA
104 DCONCB = CONCB
105 DDBEG = DBEG
106 DO 107 I = 1,N
107 DCONCP(I) = CONCP(I)
108 GO TO (109,111), LAY
109 DO 110 I = 1, N
110 SATCON(I) = RATCON(I)
111 X(1) = DBEG
    X(2) = DELTAD
    X(3) = DELTAD+ DBEG
112 Y(1) = CONCA
113 Y(2) = CONCB
114 DO 115 I=1,N
115 Y(I+2) = CONCP(I)
116 LOP(1) = XLOCF(LOP(1))
117 LOP(2) = XLOCF(Y(1))
118 LOP(3) = XLOCF(F(1))
119 LOP(4) = XLOCF(Q(1))
120 LOP(5) = XLOCF(X(1))
121 LOP(6) = N+2
122 LOP(7) = XCNTRLF(0)
123 LOP(8) = 1
124 LOP(9) = XRKGF(0)
125 LOP(10) = 0
126 K = XDEQ1F(LOP(1))
127 KA = XDEQ2F(0)
128 GO TO (129,148,127), KA
129 GO TO (130,133), LAY
130 RATCON(1) = SATCON(1)*EXPF(1.42*(1.-Y(1)/DENSA))
131 DO 132 I=2,4
132 RATCON(I) = SATCON(I)*EXPF(-2.40*Y(1)/DENSA)
133 F(1) = -(A/V)*RATCON(1)*Y(1)*Y(2)
134 FPART = 0
135 FLOATN = N
136 IF (FLOATN-1.) 217, 139, 137
137 DO 138 I=2,N
138 FPART = FPART-(A/V)*Y(2)*RATCON(I)*Y(I+1)
139 F(2) = F(1)+FPART
140 F(3) = -F(1)-(A/V)*RATCON(2)*Y(3)*Y(2)
141 IF (FLOATN-2.) 127,144, 142
142 NA = N+1
    DO 143 I = 4,NA
143 F(I) = (A*Y(2)/V)*(RATCON(I-2)*Y(I-1)-RATCON(I-1)*Y(I))
144 F(N+2) = (A/V)*RATCON(N)*Y(N+1)*Y(2)
145 GO TO 127
```

```
143 NMOD = N+3
MAXZ = NMOD*(L+1)
MAXZA = 8*NMOD
IF (MAXZ-MAXZA) 149,149,215
14) NB = N+2
15) DO 151 I=1,NB
NMOD2 = NMOD*L+I
151 Z(NMOD2) = Y(I)
NMOD3 = NMOD*L+NMOD
152 Z(NMOD3) = X(1)
153 IF (L-1) 154, 164, 164
154 L = L+1
156 X(2) = X(2)/2.
158 X(1) = DDBEG
159 Y(1) = DCONCA
160 Y(2) = DCONCB
161 DO 162 I = 1,N
162 Y(I+2) = DCONCP(I)
163 GO TO 127
164 ERROR = 0
165 LMO = L-1
166 DO 167 I = 1,NB
NMOD4 = NMOD*L+I
NMOD5 = NMOD*LMO+I
167 ERROR = ERROR+ABS(Z(NMOD4)-Z(NMOD5))
163 IF (ERROR-EMAX) 169, 169, 154
16) GO TO (185,188,191,194,197,200,203,206,209,212),N
171 XMIN = X(1)+0.0001
IF(DF-XMIN) 172,172,176
172 CONCA = Y(1)
CONCB = Y(2)
DREG = X(1)
DO 173 I = 1,N
173 CONCP(I) = Y(I+2)
DELTAD = SELTAD
GO TO (400, 54, 244, 413) , KEY
17) X(2) = DELTAD
17) L = 0
17) DCONCA = Y(1)
18) DCONCB = Y(2)
DDBEG = X(1)
181 DO 182 I=1,N
182 DCONCP(I) = Y(I+2)
183 X(3) = X(3)+DELTAD
184 GO TO 127
185 WRITE OUTPUT TAPE 6, 186, X(1), (Y(I), I= 1,3), L, V
185 FORMAT(5HOL = E10.4, 8H (A) = E10.4, 8H (B) = E10.4,
C8H (P1) = E10.4, 13H HALVINGS = I3, 6H V = E10.4)
187 GO TO 171
188 WRITE OUTPUT TAPE 6, 189, X(1), (Y(I), I = 1,4), L, V
189 FORMAT(5HOL = E10.4, 8H (A) = E10.4, 8H (B) = E10.4,
C8H (P1) = E10.4, 9H (P2) = E10.4, 13H HALVINGS = I3/5H V = E10.4
C)
190 GO TO 171
191 WRITE OUTPUT TAPE 6, 192, X(1), (Y(I), I=1,5), L, V
192 FORMAT(5HOL = E10.4, 8H (A) = E10.4, 8H (B) = E10.4/
C8H (P1) = E10.4, 9H (P2) = E10.4, 9H (P3) = E10.4,
C12H HALVINGS = I3, 6H V = E10.4)
```

```
193 GO TO 171
194 CONTINUE
197 CONTINUE
200 CONTINUE
203 CONTINUE
205 CONTINUE
207 CONTINUE
210 CONTINUE
213 WRITE OUTPUT TAPE 6, 216, L
215 FORMAT(25H Z STORAGE EXCEEDED L = I2)
    GO TO 1
217 WRITE OUTPUT TAPE 6, 218, N
219 FORMAT(9H N = 0      I2)
    GO TO 1
C END OF GRES. BEGINNING OF SECOND SECTION OF OVERALL PROGRAM
210 DO 221 I=1,N
220 NMOD7 = (N+2)*KOUNTR+I+2
221 ZFD(NMOD7) = CONCP(I)
222 IF(KOUNTR) 1, 223, 233
223 KOUNTR = KOUNTR+1
224 KOUNTS = 1
225 CONCA = SCONCA
226 CONCB = SCONCB
227 DO 228 I=1,N
228 CONCP(I) = SCONCP(I)
229 V=SV
230 DREG = 0.
231 KFY = 1
232 GO TO 51
233 DEVN = 0.
234 NB = N+2
235 DO 238 I=1,NB
236 NMOD8 = (N+2)*KOUNTR+I
237 NMOD9 = (N+2)*(KOUNTR-1)+I
238 DEVN = DEVN+ABSF(ZED(NMOD8)-ZED(NMOD9))
239 IF (DEVN=EMAXT) 240, 240, 223
240 WRITE OUTPUT TAPE 6, 241, KOUNTU, KODE, N, KOUNTR,
    X((CONR(I,J),I=1,NUMBR),J=1,NB),(ZED(I),I=1,NMOD7),DEVN
241 FORMAT(64H THE PREVIOUS CONCENTRATION PROFILE IS TRUE AT THE REACT
    COR EXIT./10H KOUNTU = I3, 9H KODE = I2, 24H NUMBER OF REACTIONS
    C= I3/71H KOUNTR, FOLLOWED BY THE RECYCLE-CONCENTRATION VECTOR, ZED
    CS, AND DEVN I3/(1H 9E12.4))
242 GO TO 1
244 NREC = KEEE-300
245 CONR(NREC,1) = CONCA
246 CONR(NREC,2) = CONCB
247 DO 248 I=1,N
248 CONR(NREC,I+2) = CONCP(I)
249 V = V-VREC(NREC)
250 DREG = P(KOUNTS)
251 KOUNTS = KOUNTS+1
252 IF (KOUNTS-KOUNTU) 74, 74, 91
253 KOUNTS = KOUNTS-1
254 GO TO 54
255 IF(KOUNTS-1) 1, 77, 74
256 FORMAT(7H1LAY = I2, 9H KODE = I2, 6H N = I3, 9H AREA = E10.4
    C, 18H EMAX PER STEP = E10.4, 19H REACTOR LENGTH = E10.4/
    C20H LENGTH INTERVAL = E10.4, 19H EMAX PER CYCLE = E10.4)
```

```
257 FORMAT(9H DENSEA = E10.4, 10H DENSEB = E10.4,  
C51H PRODUCT DENSITIES IN ORDER AFTER N, WHICH EQUALS I3/(1H 9E12.  
C4))  
258 FORMAT(47H RATE CONSTANTS IN ORDER AFTER N, WHICH EQUALS I3/(1H 9E  
C12.4))  
259 FORMAT(15H FEED VOLUME = E10.4, 16H INITIAL (A) = E10.4,  
C16H INITIAL (B) = E10.4/  
C47H INITIAL (P(I)) IN ORDER AFTER N, WHICH EQUALS I3/(1H 9E12.4))  
260 FORMAT(91H INJECTION POINTS AND THE INJECTION VOLUME VECTOR AFTER  
C THE NUMBER OF INJECTIONS, WHICH IS I3/(1H 9E12.4))  
261 FORMAT(85H RECYCLE OUT, RECYCLE IN, AND RECYCLE VOLUMES AFTER THE  
C NUMBER OF RECYCLES, WHICH IS I3/(1H 9E12.4))  
C END OF OVERALL PROGRAM. BEGINNING OF ORDERING PROGRAM  
300 MU = 1  
301 DO 303 I=1,NUMBR  
302 P(I) = PTSOUT(I)  
303 QUY(I) = 300+I  
304 KOUNTU = NUMBR  
305 KOUNTT = 1  
306 KOUNTS = 1  
307 GO TO (308, 321), MU  
308 IF (PTSIN(KOUNTS)-P(KOUNTT)) 309, 309, 322  
309 I = KOUNTU  
310 P(I+1) = P(I)  
311 QUY(I+1) = QUY(I)  
I = I-1  
IF (I-KOUNTT) 312, 310, 310  
312 GO TO (313, 328), MU  
313 P(KOUNTT) = PTSIN(KOUNTS)  
314 QUY(KOUNTT) = 200 + KOUNTS  
315 KOUNTU = KOUNTU+1  
316 KOUNTS = KOUNTS+1  
317 IF (NUMBR-KOUNTS) 318, 334, 334  
318 GO TO (300, 300, 350, 319), KODE  
319 MU = 2  
KOUNTS = 1  
320 GO TO 334  
321 IF (PTSINJ(KOUNTS)-P(KOUNTT)) 309, 309, 322  
322 KOUNTT = KOUNTT+1  
323 IF (KOUNTT-KOUNTU) 307, 307, 324  
324 GO TO (325,332), MU  
325 P(KOUNTT) = PTSIN(KOUNTS)  
QUY(KOUNTT) = 200+KOUNTS  
326 KOUNTU = KOUNTU+1  
327 GO TO 316  
328 P(KOUNTT) = PTSINJ(KOUNTS)  
329 QUY(KOUNTT) = 100+KOUNTS  
KOUNTU = KOUNTU+1  
330 KOUNTS = KOUNTS+1  
331 IF (NUMBI-KOUNTS) 350, 334, 334  
332 P(KOUNTT) = PTSINJ(KOUNTS)  
QUY(KOUNTT) = 100+KOUNTS  
333 GO TO 326  
334 KOUNTT = 1  
335 GO TO 307  
350 WRITE OUTPUT TAPE 6, 351, KOUNTU  
351 FORMAT(5H U = I3)  
352 WRITE OUTPUT TAPE 6, 354, (P(I), QUY(I), I=1, KOUNTU)  
353 FORMAT(2F8.1)  
354 GO TO 43  
C END OF ORDERING PROGRAM. BEGIN GRES EXITS  
400 GO TO (1, 401, 1, 85), KODE  
401 VHOLD = V  
402 NR = N+2  
403 DO 405 I=1,NB  
404 V = VINJ(NINJ,I)+V  
405 CONCA = (VHOLD*CONCA+DENSEA*VINJ(NINJ,1))/V  
406 CONCB = (VHOLD*CONCB+DENSEB*VINJ(NINJ,2))/V  
407 DO 410 I=1,N  
408 J = I+2  
409 CONCP(I) = (VHOLD*CONCP(I)+DENSEP(I)*VINJ(NINJ,J))/V  
410 NINJ = NINJ + 1  
411 GO TO (1, 21, 1, 90), KODE  
412 GO TO (1, 1, 94, 94), KODE
```


Program 10: Auxiliary Program in Reactor Optimization by Steepest Ascent

Purpose: The Method of Steepest Descent is described in detail in Appendix F and the discussion of the use of this method to design a flow reactor to produce monoethanolamine is included in Chapter IV. Program 10 is used to compute the coordinates of the $k+1$ st point in the descent from the cost response and its derivatives at, and the angle between the normalized directions of descent to and from, the k -th point. The computer then punches out the data cards to be used by Program 9 for the determination of the costs in the neighborhood of the $k+1$ st point.

As the simulation program prints the concentration profiles only at ten-foot intervals along the length of the reactor, interpolation is required to find the true length corresponding to the desired production rate. For this reason, the computer input consists of ten reactor lengths and associated compositions, a pair for each of the five simulations carried out in the neighborhood of each point in the descent. The input also includes the initial and operating conditions for each of the five runs; the normalized derivatives and step size, as discussed in Appendix F; and the cost response at the previous point in the descent. In addition to the data cards for Program 9, the punchout includes the initial and operating conditions for the next set of simulations, the normalized derivatives and step size, and the current production cost, to be used as input for the determination of the $k+2$ nd point. The coordinates of the $k+1$ st point and the pertinent data regarding their determination are printed.

Logic: The program follows exactly the procedure described in Appendix F for applying the Method of Steepest Descent. The only decision made by the program is whether the k-th point is "better" than the k-1st; that is, whether the cost has been reduced by the latest step. If it has not, this is noted and the next set of data, if any, is read. The program as written is not at all general, because the cost factors are compiled as fixed point numbers, rather than as variables to be read in with the data. This is easily remedied if it is desired to study other systems.

The derivatives of the cost function with respect to the independent variables are approximated by difference quotients; one per cent changes are made in the flow rates and the mol fraction of A in the feed; the modified injection point is taken to be ten feet less than the unmodified values.

As the program is quite straightforward, no flowsheet is included.

Computer: Basic IBM 704 with tapes

Language: FORTRAN

Library subroutines called: FTRAP (floating trap)

SQRT (square root)

Storage requirements: 935₁₀ words

Running time: Maximum of 1.0 min/point found

Correspondence of variables:

RCTRL(I,J): L. I = 1 for lower interpolation point; I = 2 for higher interpolation point. J = 1 for unmodified run; J = 2 when V_1 is modified; J = 3 when L' is modified; J = 4 when x_{A0} is modified; J = 5 when V_f is modified. I and J have the same meaning as subscripts of the four concentrations to follow. J is also a run counter.

CAF(I,J): $[A]_F$ for i-th interpolation point, j-th run
CBF(I,J): $[B]_F$ for i-th interpolation point, j-th run
CAB(I,J): $[P_1]_F$ for i-th interpolation point, j-th run
CAB2(I,J): $[P_2]_F$ for i-th interpolation point, j-th run
VF(I): V_F for i-th run
VI(I): V_i for i-th run
CAO(I): $[A]_O$ for i-th run
CBO(I): $[B]_O$ for i-th run
XAO(I): x_{A0} for i-th run
PTINJ(I): L' for i-th run
DVI: normalized $\partial T / \partial V_i$ at k-1st point
DLP: normalized $\partial T / \partial L'$ at k-1st point
DVF: normalized $\partial T / \partial V_F$ at k-1st point
DXAO: normalized $\partial T / \partial x_{A0}$ at k-1st point
ALPHA: α
COSTM: M
TOLD: cost response at k-1st point
RC: k_1
CPFOLD: $[P_1]_F$ at k-th point
T(1): cost response at k-th point
DDVI: normalized $\partial T / \partial V_i$ at k-th point
DDL P: normalized $\partial T / \partial L'$ at k-th point
DDXAO: normalized $\partial T / \partial x_{A0}$ at k-th point
DDVF: normalized $\partial T / \partial V_F$ at k-th point
COS: $\cos \theta$

J: J = 6 for unmodified values at k+1st point;
J = 7 for modified values at k+1st point

EMAX: maximum allowable error per length interval in simulation
runs at k+1st point

DF: reactor length for simulation runs at k+1st point

RC2: k_2

RC3: k_3

ZERO: 0

AUXILIARY PROGRAM IN STEEPEST ASCENT DESIGN OF MONOETHANOLAMINE REACTOR

```

DIMENSION RCTRL(3,5), CAF(3,5), CBF(3,5), CAB(3,5), CAB2(3,5),
XVF(7), VI(7), CAO(7), CBO(7), XAO(7), PTINJ(7), V(5), F(5), T(5),
XGNU(7)
1 READ INPUT TAPE 7, 3, ((RCTRL(I,J), CAF(I,J), CBF(I,J), CAB(I,J),
XCAB2(I,J), I=1,2), J=1,5)
2 READ INPUT TAPE 7, 56, (VF(I), VI(I), CAQ(I), CBO(I), XAO(I),
XPTINJ(I), I=1,5), DVI, DLP, DVF, DXAO, ALPHA, COSTM, TOLD, RC
3 FORMAT(5E10.4)
4 FORMAT(6E10.4)
5 DO 11 I=1,5
V(I) = VF(I)+VI(I)
6 F(I) = (34.2/V(I)-CAB(1,I))/(CAB(2,I)-CAB(1,I))
7 RCTRL(3,I) = RCTRL(1,I)+F(I)*(RCTRL(2,I)-RCTRL(1,I))
8 CAF(3,I) = CAF(1,I)+F(I)*(CAF(2,I)-CAF(1,I))
9 CBF(3,I) = CBF(1,I)+F(I)*(CBF(2,I)-CBF(1,I))
10 CAB2(3,I) = CAB2(1,I)+F(I)*(CAB2(2,I)-CAB2(1,I))
11 T(I) = 229.87*V(I)*CAF(3,I)+225.69*V(I)*CBF(3,I)+206.80*V(I)*CAB2
X(3,I)+COSTM*RCTRL(3,I)+2.63*VF(I)*CAO(I)+VF(I)*CBO(I)*6.81+8.566
X*VI(I)
12 IF (T(1)-TOLD) 16, 13, 13
13 WRITE OUTPUT TAPE 6, 14, T(1), TOLD, ALPHA
14 FORMAT(12H NEW COST, $F11.2, 30H, IS NOT LESS THAN OLD COST, $F11.
X2, 29H, SO QUARTER ALPHA, WHICH IS E12.4)
15 GO TO 1
16 DTDVI = (T(2)-T(1))/(VI(2)-VI(1))
17 DTDLP = (T(3)-T(1))/(PTINJ(3)-PTINJ(1))
18 DTDXAO = (T(4)-T(1))/(XAO(4)-XAO(1))
19 DTDVF = (T(5)-T(1))/(VF(5)-VF(1))
20 DFN = SQRT(((1.+VI(1)*VI(1))*DTDVI)**2.+((1.+PTINJ(1))*PTINJ(1))
X*DTDLP)**2.+((1.+XAO(1)*XAO(1))*DTDXAO)**2.+((1.+VF(1))*VF(1))
X*DTDVF)**2.)
21 DDVI = -((1.+VI(1)*VI(1))*DTDVI)/DEN
22 DDLP = -((1.+PTINJ(1))*PTINJ(1))*DTDLP)/DEN
23 DDXAO = -((1.+XAO(1)*XAO(1))*DTDXAO)/DEN
24 DDVF = -((1.+VF(1))*VF(1))*DTDVF)/DEN
25 COS = DVI*DDVI+DLP*DDL+DVF*DDVF+DXAO*DDXAO
26 ALPHA = ALPHA*(1.+5*COS*COS)
27 VF(6) = VF(1)+ALPHA*DDVF
28 VF(7) = .99*VF(6)
29 VI(6) = VI(1)+ALPHA*DDVI
30 VI(7) = .99*VI(6)
31 XAO(6) = XAO(1)+ALPHA*DDXAO
32 XAO(7) = .99*XAO(6)
33 DO 36 I=6,7
34 GNU(I) = 1./(1.019*XAO(I)+(1.-XAO(I))*0.795)
35 CAO(I) = XAO(I)*GNU(I)
36 CRO(I) = (1.-XAO(I))*GNU(I)
37 CPFNEW = 34.2/(VF(6)+VI(6))
38 CPFMVF = 34.2/(VF(7)+VI(6))
39 CPFMVI = 34.2/(VF(6)+VI(7))
40 CPFOLD = 34.2/V(1)
41 EMAX = INTF(10.*CBO(6))/10.**6.
42 DF = 1.5*RCTRL(3,1)
44 PTINJ(6) = INTF((PTINJ(1)+ALPHA*DDL)/10.)*10.
45 PTINJ(7) = PTINJ(6)-10.
46 WRITE OUTPUT TAPE 6, 47, VF(1), VI(1), XAO(1), PTINJ(1), RCTRL(3,

```

```
X1), CAF(3,1), CBF(3,1), CPFOLD, CAB2(3,1), T(1), DDVI, DDLP,  
XDDXAO, DDVF, COS, ALPHA, VF(6), VI(6), XAO(6), CAO(6), CBO(6),  
XPTINJ(6)  
4' FORMAT(28H COEFFICIENTS OF THIS POINT- /9H VF = E10.4/9H VI =  
X E10.4/9H XAO = F7.4/9H PTINJ = E10.4/32H COMPUTED VALUES FOR TH  
XIS POINT- /10H RCTRL = E10.4/10H (A)F = E10.4/10H (B)F = E10.4  
X/10H (AB)F = E10.4/10H (AB2)F = E10.4//16H TOTAL COST = $ F11.2  
X//24H NORMALIZED DIRECTIONS - /8H DVI = E11.4/8H DLP = E11.4/  
X8H DXAO = E11.4/8H DVF = E11.4/16H COSINE THETA = E11.4/9H ALPHA  
X= E11.4/27H COEFFICIENTS OF NEW POINT- /9H VF = E10.4/9H VI =  
X E10.4/9H XAO = F7.4,9H (CAO = E11.4, 11H AND CBO = E11.4, 1H)  
X/9H PTINJ = E10.4)  
RC2 = RC*6.048  
RC3 = RC*4.529  
ZERO = 0.  
48 DO 49 I =1,5  
49 PUNCH 50, EMAX, DF, RC, RC2, RC3  
50 FORMAT (17H+2+2+03+.3340E-012E10.4, 30H+.1000E+02+.1000E-04+.9810E  
X+00/10H+.1258E+01/10H+.5510E+00E10.4, 10H+.3830E+00E10.4, 10H+.293  
X0F+00E10.4/3H+01)  
51 DO 52 I=1,3  
52 PUNCH 4, VF(6), CAO(6), CBO(6), ZERO, ZERO, ZERO, PTINJ(6), ZERO,  
XVI(6), ZERO, ZERO, ZERO  
53 PUNCH 4, VF(7), CAO(6), CBO(6), ZERO, ZERO, ZERO, VF(6), CAO(7),  
XCBO(7), ZERO, ZERO, ZERO, PTINJ(7), ZERO, VI(6), ZERO, ZERO, ZERO,  
XPTINJ(6), ZERO, VI(7), ZERO, ZERO, ZERO  
54 PUNCH 56, VF(6), VI(6), CAO(6), CBO(6), XAO(6), PTINJ(6), VF(6), VI(  
X7), CAO(6), CBO(6), XAO(6), PTINJ(6), VF(6), VI(6), CAO(6), CBO(6)  
X, XAO(6), PTINJ(7), VF(6), VI(6), CAO(7), CBO(7), XAO(7), PTINJ(6),  
XVF(7), VI(6), CAO(6), CBO(6), XAO(6), PTINJ(6), DDVI, DDLP, DDVF,  
XDDXAO, ALPHA, COSTM, T(1), RC  
53 GO TO 1  
53 FORMAT(6E10.4/6E10.4/6E10.4/6E10.4/6E10.4/6E10.4/F11.2, E10.4)
```

Program 11: Program to Solve Analytical Design Equations for a Reactor to Carry Out a Second-Order Reaction

Purpose: The roots of Equations (4.80) and (4.81) are the design values of the feed rate and composition for a simple flow reactor in which a single second-order reaction is to be carried out. These roots are found by Program 11. The input to the computer is essentially the same as that for Program 7. The printout consists of the current values of the mol fraction of A in the feed, and the feed and injection rates --in the present study, the last of these is identically zero--as well as the partial derivatives of the production cost with respect to the two independent variables. When the optimal design has been found, the reactor length, production rate, physical properties of the reactants, rate constant, tube diameter and cost factors are printed, as well as the roots of the equations.

Logic: The independent variables are changed by multiplicative factors, which decrease from ten per cent to one-tenth of one per cent as the solution is approached. In each iteration, the partial derivatives given by the equations listed above are found and the independent variable, x_i , is increased or decreased according as $\partial T / \partial x_i$ is negative or positive. Whenever the sign of $\partial T / \partial x_i$ has been changed by the latest modifications in the independent variables, the change in x_i is reduced by an order of magnitude; if, at this point, both multiplicative factors are 0.999 and 1.001 and the sign of both derivatives has been changed by the last iteration, the roots of the equations are

assumed to have been approached with sufficient accuracy to permit interpolation between the results of the last two iterations to find the required design values.

An iteration count is included to save computer time if the solution diverges, as is sometimes the case if the initial guesses at the values of the design parameters are particularly errant. The value of x_{A0} is checked after each iteration to make sure that it remains between zero and one.

The partial derivatives of the production cost with respect to the design variables are computed by the DERIVS subroutine. As this program is designed for no-injection optimization, L' and $\partial r/\partial V_1$ are set to zero whenever DERIVS is entered.

Computer: Basic IBM 704 with tapes

Language: IBM FORTRAN II

Library subroutines called: ELOG (natural logarithm)

Storage requirements: 963_{10} words

Running time: 0.40 min/design

Correspondence of variables:

VA: v_A

VB: v_B

Z: Z

RC: k_1

D: D

R: R

CM: M

VI: V_i

VF: V_f

XAO: x_{A0}

FRACT: fraction to be used of the change in independent variable indicated by Newton's method. This is no longer used

MAXIT: maximum allowable number of iterations

PTINJ: L'

SVF: temporarily stored value of V_f . This is no longer used.

SVI: temporarily stored value of V_i . This is no longer used.

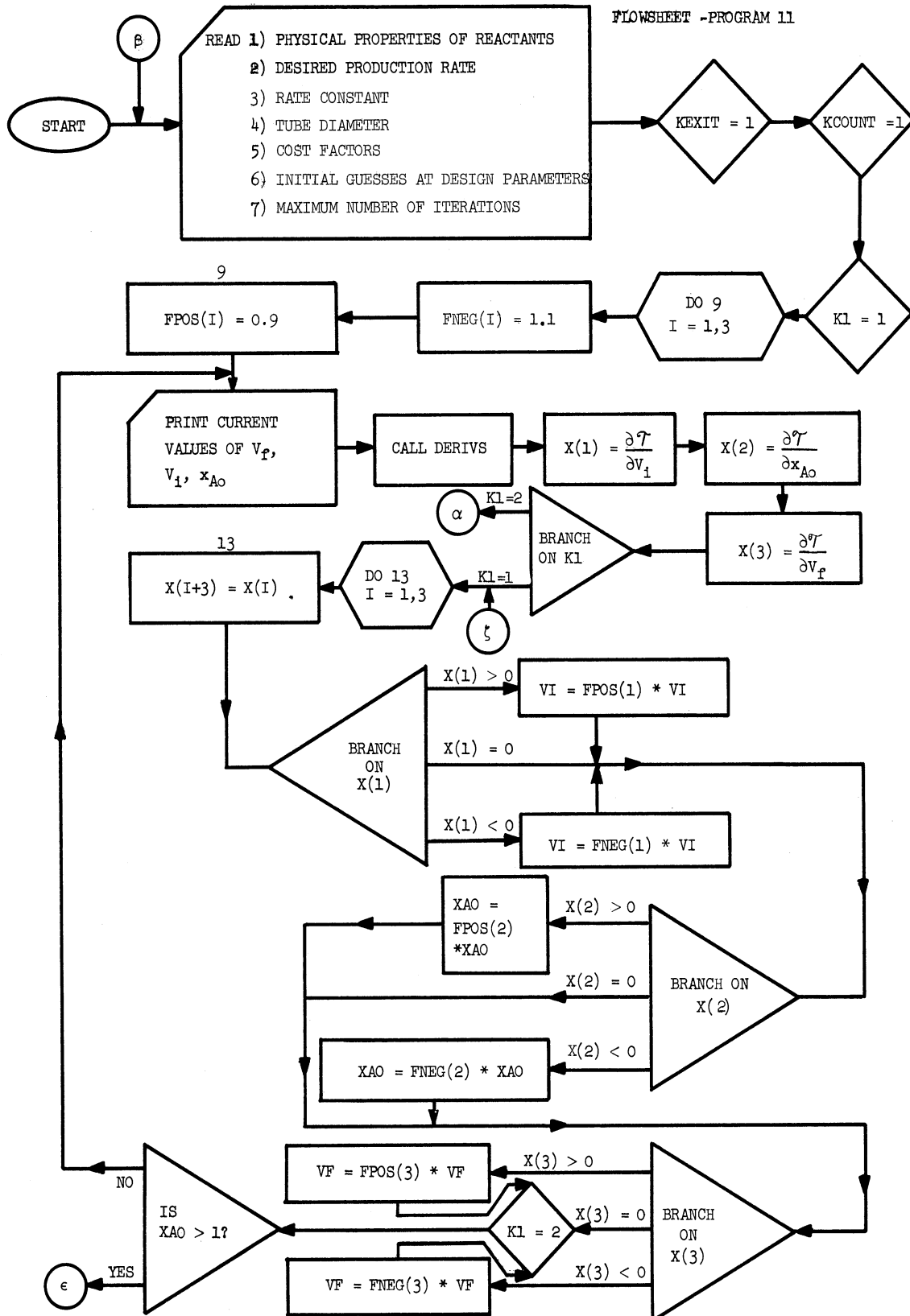
SXAO: temporarily stored value of x_{A0} . This is no longer used.

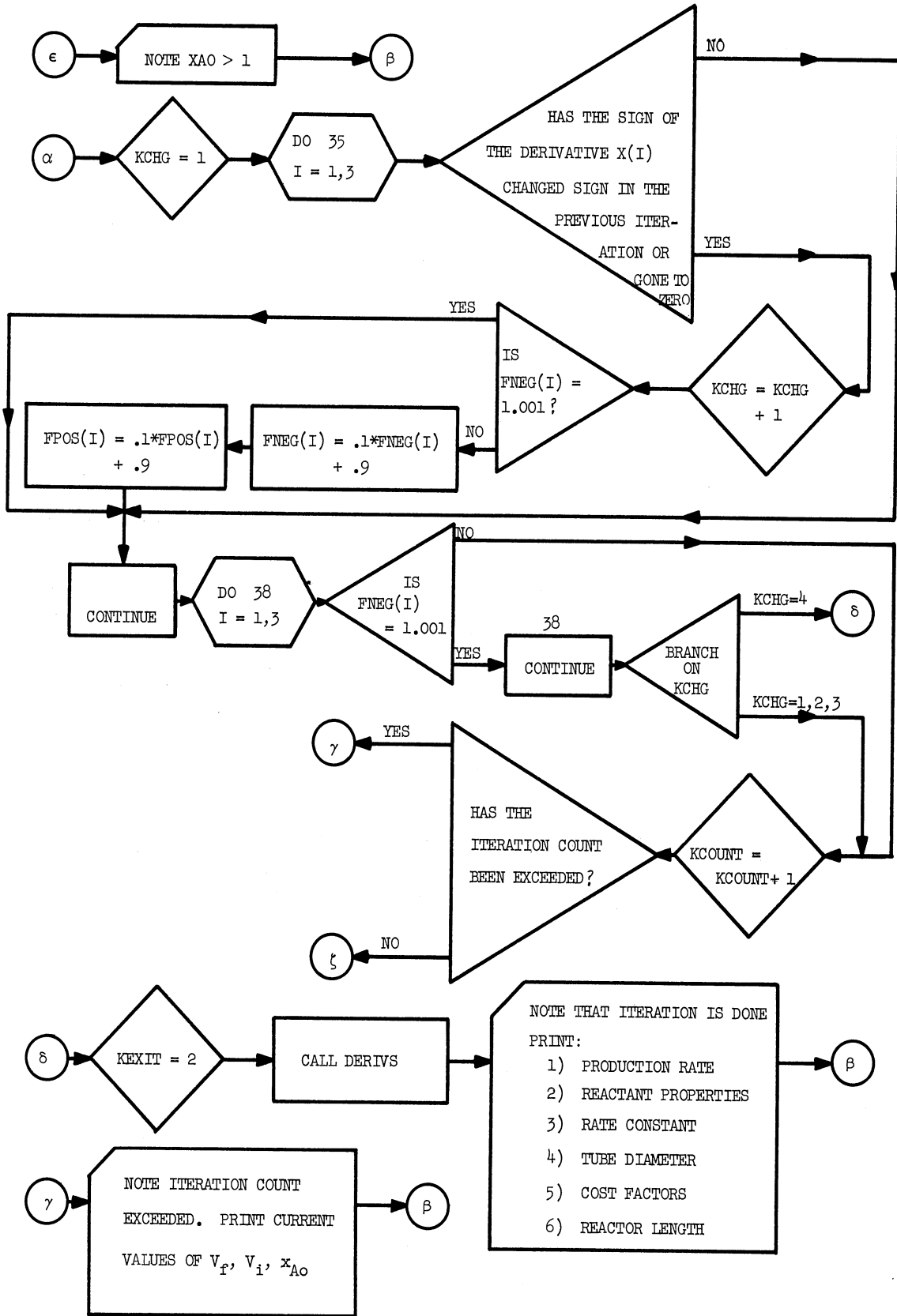
RCTRL: L

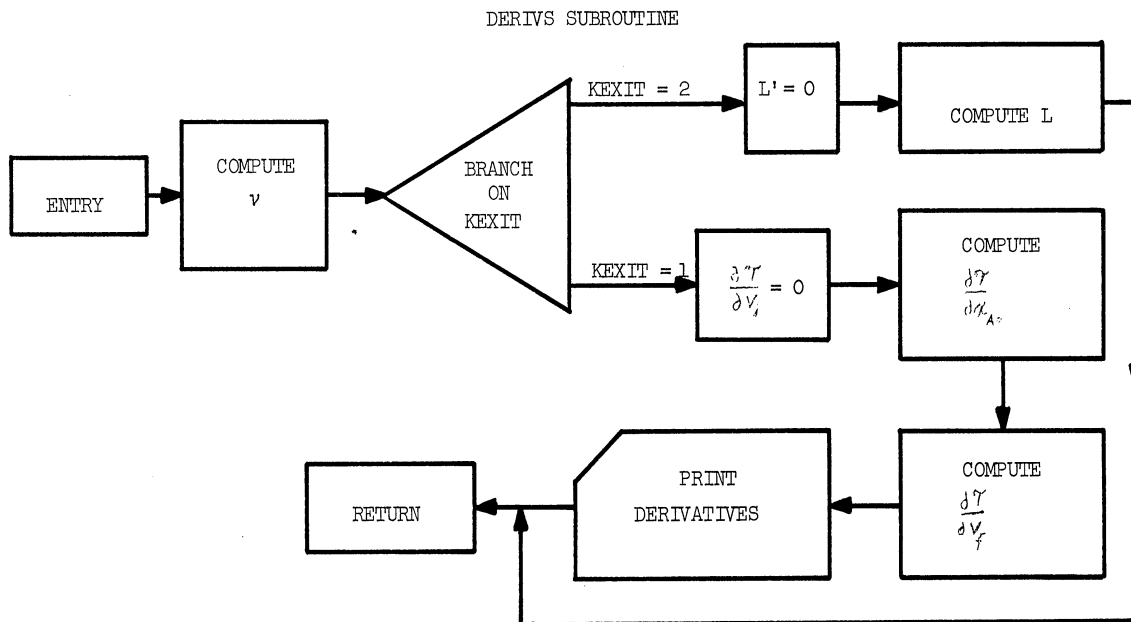
FN1, FN2, FN3: functions used in the computation of the partial derivatives

DTDXAO: $\partial T / \partial x_{A0}$

DTDVF: $\partial T / \partial V_f$







PROGRAM TO SOLVE ANALYTICAL DESIGN EQUATIONS FOR A REACTOR TO CARRY OUT A
SECOND-ORDER REACTION

```
DIMENSION X(12), A(10,10), B(10), C(10), SC(10), FNEG(3), FPOS(3)
COMMON DTDXAO, DTDVI, DTDVF, PTINJ, RCTRL
1 READ INPUT TAPE 7, 3, VA, VB, Z, RC, D, R, CM, VI, VF, XAO, FRACT,
  XMAXIT
  KEXIT = 1
  KCOUNT = 1
  K1 = 1
  GO TO 8
3 FORMAT (7E10.4/2E10.4, 2F6.3, I4)
4 WRITE OUTPUT TAPE 6, 10, VF, VI, XAO
  CALL DERIVS(VB, CM, VI, VF, XAO, Z, RC, D, VA, R, KEXIT)
5 X(1) = DTDVI
6 X(2) = DTDXAO
7 X(3) = DTDVF
  GO TO (12,30), K1
8 DO 9 I=1,3
  FNEG(I) = 1.1
  FPOS(I) = 0.9
10 FORMAT(15HOFEEED VOLUME = E11.4, 21H INJECTION VOLUME = E11.4, 30H
  X INITIAL MOL FRACTION OF A = F6.3)
11 GO TO 4
12 DO 13 I=1,3
13 X(I+3) = X(I)
14 IF (X(1)) 15, 18, 17
15 VI = FNEG(1)*VI
15 GO TO 18
17 VI = FPOS(1)*VI
13 IF (X(2)) 19, 22, 21
19 XAO = FNEG(2)*XAO
20 GO TO 22
21 XAO = FPOS(2)*XAO
22 IF (X(3)) 23, 26, 25
23 VF = FNEG(3)*VF
24 GO TO 26
25 VF = FPOS(3)*VF
26 K1 = 2
  IF (XAO-1.) 4, 4, 27
27 WRITE OUTPUT TAPE 6, 28, XAO
23 FORMAT(26H VARIABLE OVERSHOOT XAO = F6.3)
27 GO TO 1
30 KCHG = 1
  DO 35 I=1,3
31 IF (ABS(F(X(I+3)-X(I))-ABS(F(X(I+3)+X(I)))) 35, 32, 32
32 KCHG = KCHG+1
  IF (FNEG(I)-1.001) 35, 35, 33
33 FNEG(I) = .1*FNEG(I)+.9
34 FPOS(I) = .1*FPOS(I)+.9
35 CONTINUE
36 DO 38 I=1,3
37 IF (FNEG(I)-1.001) 38, 38, 40
38 CONTINUE
39 GO TO (40, 40, 40, 46), KCHG
40 KCOUNT = KCOUNT+1
41 IF (KCOUNT-MAXIT) 12, 12, 50
46 KEXIT = 2
```

```
47 CALL DERIVS(VB, CM, VI, VF, XAO, Z, RC, D, VA, R, KEXIT)
48 WRITE OUTPUT TAPE 6, 49, Z, VA, VB, RC, D, R, CM, SVF, SVI, SXAO,
   PTINJ, RCTRL
   GO TO 1
49 FORMAT(78H OPTIMUM SINGLE-INJECTION REACTOR TO PRODUCE THE FOLLOWI
   XNG AMOUNT OF PRODUCT E10.4/21H MOLAR VOLUME OF A = E10.4, 22H MO
   XLAR VOLUME OF B = E10.4, 7H K1 = E10.4, 18H TUBE DIAMETER = E10.
   X4/48H COST FACTORS- REACTANT REMOVAL COST PER MOL = $F11.5,34H UN
   XIT OPERATING COST PER FOOT = $F8.5/15H FEED VOLUME = E10.4, 21H I
   XNJECTION VOLUME = E10.4, 30H INITIAL MOL FRACTION OF A = F6.3/
   X19H INJECTION POINT = E10.4, 19H REACTOR LENGTH = E10.4)
50 WRITE OUTPUT TAPE 6, 51, VF, VI, XAO
51 FORMAT(32H ITERATION COUNT EXCEEDED VF = E11.4, 7H VI = E11.4,
   X8H XAO = F6.3)
52 GO TO 1
```

DERIVATIVE SUBROUTINE

```
   SUBROUTINE DERIVS (VB, CM, VI, VF, XAO, Z, RC, D, VA, R, KEXIT)
   COMMON DTDXAO, DTDVI, DTDVF, PTINJ, RCTRL
1 GNU = 1./((VA*XAO+VB-VB*XAO)
2 FN1 = ELOG(((1.-XAO)*Z-VF*GNU*XAO*(1.-XAO))/(Z*XAO-VF*GNU*XAO*
   X(1.-XAO)))
3 FN2 = RC*3.14159*D*D
4 FN3 = FN2*(2.*XAO-1.)
5 GO TO (6,12), KEXIT
6 DTDVI = 0.
7 DTDXAO = -CM*4.*VF*(VA+VB)*FN1/(FN3*(2.*XAO-1.))+4.*CM*VF*Z*(-Z
   X+VF*GNU*GNU*(VA*XAO*XAO+VB*(1.-XAO)**2.))/(GNU*FN3*XAO*(1.-XAO)*
   X(Z*Z-VF*GNU*Z+VF*VF*GNU*GNU*XAO*(1.-XAO)))+R*VF*(VB-VA)*GNU*GNU
8 DTDVF = 4.*CM*FN1/(GNU*FN3)-4.*CM*VF*Z/(FN2*(Z*Z-Z*VF*GNU+VF*VF*
   XGNU*GNU*XAO*(1.-XAO)))+R*GNU
9 WRITE OUTPUT TAPE 6, 10, FN1, FN2, FN3, DTDXAO, DTDVF
10 FORMAT(13H FUNCTIONS = 3E12.4, 12H DT/DXAO = E11.4, 11H DT/DVF =
   X E11.4)
11 RETURN
12 PTINJ = 0.
13 RCTRL = 4.*VF*FN1/(GNU*FN3)
14 GO TO 11
```

APPENDIX B

INTEGRATED SOLUTION OF RATE EQUATIONS FOR EQUIMOLAR INITIAL
CONCENTRATIONS OF REACTANTS AND SEVERAL SETS OF RATE CONSTANT RATIOS

APPENDIX B

INTEGRATED SOLUTION OF RATE EQUATIONS FOR EQUIMOLAR INITIAL
CONCENTRATIONS OF REACTANTS AND SEVERAL SETS OF RATE CONSTANT RATIOS

Part 1 - $K_3 = 0$

$K_2 = 0.01$

t'	y_0	β	y_1	y_2
0	1.000	1.000	0.000	0.000
3	0.252	0.254	0.742	0.006
6	0.146	0.136	0.843	0.011
9	0.105	0.091	0.882	0.013
12	0.083	0.067	0.901	0.016
15	0.069	0.052	0.913	0.017
18	0.060	0.042	0.921	0.018
21	0.054	0.034	0.927	0.020
24	0.049	0.029	0.931	0.020
27	0.045	0.024	0.934	0.021
30	0.042	0.021	0.936	0.022
33	0.040	0.018	0.938	0.022
36	0.038	0.015	0.939	0.023
39	0.036	0.013	0.940	0.023
42	0.035	0.012	0.941	0.024
48	0.033	0.009	0.943	0.024

$K_2 = 0.1$

0	1.000	1.000	0.000	0.000
1	0.503	0.485	0.478	0.019
2	0.343	0.303	0.617	0.040
3	0.267	0.210	0.677	0.056
4	0.223	0.154	0.709	0.069
5	0.195	0.116	0.727	0.078
6	0.176	0.090	0.739	0.086
7	0.162	0.071	0.746	0.092
8	0.152	0.056	0.751	0.096
9	0.145	0.045	0.755	0.100
10	0.139	0.036	0.758	0.103
11	0.135	0.029	0.760	0.106

12	0.131	0.024	0.761	0.108
13	0.128	0.019	0.762	0.109
14	0.126	0.016	0.763	0.111
15	0.125	0.013	0.764	0.112
17	0.122	0.009	0.765	0.113

K₂ = 1

0	1.000	1.000	0.000	0.000
0.3	0.772	0.743	0.200	0.028
0.6	0.636	0.559	0.288	0.076
0.9	0.549	0.427	0.329	0.121
1.2	0.490	0.330	0.349	0.160
1.5	0.449	0.258	0.360	0.191
1.8	0.419	0.203	0.364	0.216
2.1	0.397	0.161	0.367	0.236
2.4	0.380	0.128	0.368	0.252
2.7	0.367	0.103	0.368	0.265
3.0	0.357	0.083	0.368	0.275
3.3	0.350	0.067	0.367	0.283
3.6	0.343	0.054	0.367	0.290
3.9	0.338	0.043	0.367	0.295
4.2	0.334	0.035	0.366	0.299
4.5	0.331	0.029	0.366	0.303
4.8	0.329	0.023	0.366	0.306
5.1	0.327	0.019	0.365	0.308
5.4	0.325	0.015	0.365	0.310
5.7	0.324	0.012	0.365	0.311
6.0	0.323	0.010	0.365	0.312
6.3	0.322	0.008	0.365	0.313

K₂ = 10

0	1.000	1.000	0.000	0.000
0.1	0.910	0.878	0.058	0.032
0.2	0.839	0.752	0.074	0.087
0.3	0.783	0.643	0.077	0.140
0.4	0.737	0.551	0.077	0.186
0.5	0.701	0.476	0.075	0.225
0.6	0.670	0.413	0.072	0.257
0.7	0.645	0.360	0.070	0.285
0.8	0.623	0.315	0.068	0.308
0.9	0.605	0.277	0.067	0.328

1.0	0.590	0.244	0.065	0.345
1.1	0.576	0.216	0.064	0.360
1.2	0.565	0.192	0.062	0.373
1.3	0.555	0.170	0.061	0.384
1.4	0.546	0.152	0.060	0.394
1.5	0.538	0.135	0.060	0.403
1.6	0.531	0.121	0.059	0.410
1.7	0.525	0.108	0.058	0.417
1.8	0.520	0.097	0.058	0.423
1.9	0.515	0.087	0.057	0.428
2.0	0.511	0.078	0.057	0.433
2.1	0.507	0.070	0.056	0.437
2.2	0.504	0.063	0.056	0.441
2.3	0.501	0.057	0.056	0.444
2.4	0.498	0.051	0.055	0.447
2.5	0.495	0.046	0.055	0.450
2.6	0.493	0.041	0.055	0.452
2.7	0.491	0.037	0.055	0.454
2.8	0.490	0.034	0.054	0.456
4.0	0.478	0.010	0.053	0.469

Part 2 - $K_3 = 5$

$K_2 = 0.01$

t^1	y	β	y_1	y_2	y_3
0	1.000	1.000	0.000	0.000	0.000
3	0.253	0.242	0.741	0.001	0.005
6	0.149	0.130	0.840	0.002	0.009
9	0.109	0.085	0.878	0.002	0.011
12	0.088	0.060	0.897	0.002	0.013
15	0.075	0.044	0.908	0.002	0.015
18	0.067	0.034	0.915	0.002	0.016
21	0.061	0.027	0.920	0.002	0.017
24	0.057	0.021	0.924	0.002	0.017
27	0.054	0.017	0.926	0.002	0.018
30	0.052	0.014	0.928	0.002	0.018
33	0.050	0.011	0.930	0.002	0.018
36	0.048	0.009	0.931	0.002	0.019

$K_2 = 0.1$

0	1.000	1.000	0.000	0.000	0.000
1	0.505	0.476	0.477	0.007	0.011
2	0.350	0.283	0.612	0.011	0.028
3	0.278	0.184	0.669	0.012	0.041
4	0.239	0.125	0.697	0.013	0.051
5	0.215	0.087	0.714	0.013	0.058
6	0.200	0.061	0.724	0.014	0.063
12	0.170	0.009	0.742	0.014	0.074

$K_2 = 1$

0	1.000	1.000	0.000	0.000	0.000
0.3	0.772	0.735	0.200	0.019	0.009
0.6	0.640	0.529	0.286	0.038	0.036
0.9	0.559	0.377	0.325	0.050	0.066
1.2	0.508	0.268	0.344	0.056	0.092
1.5	0.474	0.191	0.354	0.060	0.112
1.8	0.452	0.136	0.359	0.063	0.126
2.1	0.437	0.097	0.362	0.064	0.137
2.4	0.426	0.070	0.364	0.065	0.146
2.7	0.418	0.050	0.365	0.066	0.151

3.0	0.413	0.036	0.365	0.066	0.156
3.3	0.409	0.026	0.366	0.067	0.159
4.2	0.403	0.009	0.366	0.067	0.163

K₂ = 10

0	1.000	1.000	0.000	0.000	0.000
0.1	0.910	0.873	0.058	0.027	0.005
0.2	0.840	0.731	0.074	0.063	0.023
0.3	0.786	0.601	0.077	0.088	0.048
0.4	0.744	0.491	0.077	0.104	0.075
0.5	0.712	0.401	0.075	0.114	0.099
0.6	0.687	0.327	0.074	0.120	0.120
0.7	0.667	0.267	0.072	0.123	0.138
0.8	0.651	0.219	0.071	0.125	0.153
0.9	0.638	0.180	0.070	0.127	0.166
1.0	0.628	0.148	0.069	0.128	0.176
1.1	0.619	0.122	0.068	0.128	0.185
1.2	0.612	0.100	0.067	0.129	0.192
1.3	0.607	0.083	0.067	0.129	0.198
1.4	0.602	0.068	0.066	0.129	0.202
1.5	0.599	0.056	0.066	0.129	0.206
1.6	0.595	0.047	0.066	0.129	0.210
1.7	0.593	0.039	0.065	0.129	0.213
2.5	0.584	0.009	0.064	0.129	0.223

APPENDIX C

EXPERIMENTAL AND COMPUTED PRODUCT DISTRIBUTIONS FOR
SELECTED REAL SYSTEMS

APPENDIX C

EXPERIMENTAL AND COMPUTED PRODUCT DISTRIBUTIONS FOR
SELECTED REAL SYSTEMS

1. Methanol (A) + Propylene Oxide (B) at 45°C. Refs: Lay⁽²⁶⁾ and Pecorini
and Banchemo⁽³⁴⁾

P₁ = monopropylene glycol methyl ether

P₂ = dipropylene glycol methyl ether

Time, hrs	Catalyst Concentration	β ₀	γ ₀	γ ₁		γ ₂	
				Experim'l	Calcu'd	Experim'l	Calcu'd
∞	0.152 mols NaOH/l	0.10	0.90	0.10	0.10	0.00	0.00 ⁽²⁶⁾
∞	0.180	0.16	0.85	0.15	0.15	0.00	0.00 ⁽²⁶⁾
∞	0.350	0.94	0.149	0.736	0.736	0.115	0.115 ⁽²⁶⁾
7.625	0.5 wt.%NaOH	0.20	0.853	0.145	0.146	0.002	0.001 ⁽³⁴⁾
3.325	0.5	0.20	0.900	0.098	0.099	0.002	0.001 ^(")
11.567	0.5	0.20	0.852	0.144	0.147	0.004	0.001 ^(")
3.000	0.8	0.20	0.869	0.129	0.130	0.002	0.001 ^(")
6.700	0.8	0.20	0.840	0.159	0.158	0.001	0.002 ^(")
3.559	0.8	0.20	0.879	0.119	0.120	0.002	0.001 ^(")
8.700	0.8	0.20	0.832	0.167	0.166	0.001	0.002 ^(")
2.033	0.8	0.20	0.899	0.099	0.100	0.002	0.001 ^(")
4.467	0.8	0.50	0.651	0.342	0.340	0.007	0.009 ^(")

2. Monopropylene Glycol Methyl Ether (A) + Propylene Oxide (B) at 60°C.
Ref: Lay⁽²⁶⁾

P₁ = dipropylene glycol methyl ether

P₂ = tripropylene glycol methyl ether

P₃ = tetrapropylene glycol methyl ether and higher products

All data at infinite time.

Catalyst Concentration, Mols/l	β	y_0	y_1		y_2		y_3	
			Expt'l	Calc'd	Expt'l	Calc'd	Expt'l	Calc'd
0.215	0.333	0.75	0.222	0.215	0.026	0.032	-	0.003
0.278	0.500	0.59	0.323	0.311	0.087	0.083	-	0.016
0.272	0.645	0.525	0.343	0.337	0.109	0.111	0.023	0.027
0.253	0.87	0.431	0.362	0.361	0.162	0.154	0.045	0.054
0.305	1.50	0.255	0.337	0.346	0.23	0.24	0.18	0.16

3. 1,3-butanediol (A) + Acetic Acid (B) at 50°C. Ref: Nerdel and Remmets⁽³³⁾

P_1 = mono-ester

P_2 = di-ester

All data at infinite time

y_0	y_1		y_2	
	Experimental	Calculated	Experimental	Calculated
0.214	0.452	0.448	0.334	0.338
0.247	0.457	0.455	0.296	0.298
0.272	0.458	0.458	0.270	0.271
0.316	0.454	0.456	0.230	0.228
0.372	0.444	0.446	0.184	0.182
0.443	0.418	0.422	0.139	0.135
0.530	0.376	0.380	0.094	0.090
0.749	0.228	0.229	0.023	0.022

4. 1,4-butanediol (A) + Acetic Acid (B) at 50°C. Ref: Nerdel and Remmets⁽³³⁾

P_1 = mono-ester

P_2 = di-ester

All data at infinite time

y_0	y_1		y_2	
	<u>Experimental</u>	<u>Calculated</u>	<u>Experimental</u>	<u>Calculated</u>
0.112	0.459	0.443	0.429	0.445
0.145	0.469	0.469	0.386	0.386
0.170	0.475	0.482	0.355	0.348
0.216	0.483	0.496	0.301	0.289
0.273	0.501	0.498	0.226	0.230
0.360	0.475	0.479	0.165	0.161
0.465	0.430	0.433	0.105	0.102
0.727	0.250	0.251	0.023	0.022

5. Monoethanolamine (A) + Ethylene Oxide (B) at 10°C. Ref: Potter⁽³⁵⁾

P_1 = diethanolamine

P_2 = triethanolamine

<u>Time, min</u>	<u>y_0</u>	y_1		y_2	
		<u>Experimental</u>	<u>Calculated</u>	<u>Experimental</u>	<u>Calculated</u>
20	0.499	0.401	0.378	0.100	0.123
40	0.320	0.447	0.421	0.233	0.259
60	0.220	0.434	0.404	0.346	0.377
80	0.146	0.377	0.359	0.477	0.495
100	0.106	0.328	0.317	0.566	0.577
120	0.086	0.283	0.290	0.631	0.624
140	0.056	0.241	0.235	0.703	0.709
160	0.039	0.192	0.194	0.768	0.768
180	0.032	0.164	0.173	0.804	0.795
210	0.024	0.125	0.147	0.851	0.829
240	0.022	0.097	0.139	0.881	0.839
300	0.010	0.057	0.086	0.933	0.905

6. Ammonium Hydroxide (A) + Ethylene Oxide (B). Ref: Potter⁽³⁵⁾

P₁ = monoethanolamine

P₂ = diethanolamine

P₃ = triethanolamine

Time, min	Temp., °C	β ₀	y ₀	y ₁		y ₂		y ₃	
				Expt'l	Calc'd	Expt'l	Calc'd	Expt'l	Calc'd
20	10	4.03	0.875	0.080	0.087	0.028	0.031	0.017	0.007
40	10	4.03	0.780	0.105	0.114	0.061	0.073	0.054	0.032
60	10	4.03	0.696	0.110	0.121	0.097	0.106	0.097	0.076
75	10	4.03	0.638	0.110	0.120	0.115	0.123	0.137	0.119
150	10	4.03	0.432	0.084	0.090	0.132	0.134	0.352	0.344
200	10	4.03	0.355	0.077	0.075	0.121	0.120	0.447	0.450
250	10	4.03	0.286	0.069	0.061	0.106	0.101	0.539	0.552
300	10	4.03	0.233	0.060	0.050	0.093	0.085	0.614	0.633
400	10	4.03	0.175	0.038	0.037	0.060	0.065	0.727	0.723
15	20	4.03	0.821	0.094	0.106	0.039	0.055	0.046	0.018
20	20	4.03	0.782	0.105	0.114	0.058	0.072	0.055	0.032
25	20	4.03	0.746	0.110	0.119	0.076	0.088	0.068	0.048
30	20	4.03	0.701	0.112	0.121	0.092	0.105	0.095	0.073
35	20	4.03	0.674	0.114	0.121	0.102	0.113	0.110	0.092
40	20	4.03	0.625	0.114	0.119	0.114	0.126	0.147	0.130
50	20	4.03	0.570	0.109	0.113	0.124	0.136	0.197	0.182
60	20	4.03	0.522	0.102	0.106	0.136	0.139	0.240	0.233
70	20	4.03	0.471	0.095	0.098	0.139	0.138	0.295	0.294
90	20	4.03	0.390	0.086	0.082	0.135	0.127	0.389	0.401
150	20	4.03	0.250	0.062	0.053	0.099	0.090	0.589	0.607
210	20	4.03	0.177	0.048	0.038	0.071	0.065	0.704	0.720
300	20	4.03	0.119	0.032	0.025	0.050	0.044	0.799	0.811
20	30	4.03	0.589	0.112	0.115	0.125	0.133	0.174	0.163
40	30	4.03	0.377	0.079	0.080	0.128	0.125	0.416	0.419
60	30	4.03	0.254	0.059	0.054	0.092	0.091	0.595	0.601
85	30	4.03	0.179	0.045	0.038	0.062	0.066	0.714	0.717
120	30	4.03	0.119	0.032	0.025	0.040	0.044	0.809	0.811
150	30	4.03	0.089	0.025	0.019	0.036	0.033	0.850	0.859
∞	Room	0.25	0.805	0.097	0.110	0.059	0.062	0.039	0.023
∞	Room	0.50	0.702	0.113	0.121	0.096	0.104	0.089	0.073
∞	Room	1.00	0.538	0.104	0.108	0.139	0.138	0.219	0.215
∞	Room	1.50	0.394	0.083	0.083	0.129	0.128	0.394	0.395
∞	Room	2.00	0.258	0.063	0.055	0.100	0.093	0.579	0.594
∞	Room	2.50	0.187	0.048	0.040	0.075	0.069	0.690	0.704
∞	Room	3.00	0.109	0.035	0.023	0.045	0.041	0.811	0.827
∞	Room	4.00	0.029	0.017	0.006	0.024	0.011	0.930	0.954

7* Carbon Tetrachloride (A) + Hydrogen Fluoride (B). Ref: McBee et al. (27)

P₁ = fluorotrichloromethane

P₂ = dichlorodifluoromethane (Freon-12)

Temp., °C	y ₀	y ₁		y ₂	
		Experimental	Calculated	Experimental	Calculated
300	0.21	0.46	0.47	0.33	0.32
290	0.07	0.21	0.35	0.72	0.58
300	0.06	0.22	0.33	0.72	0.61
290	0.02	0.56	0.21	0.42	0.77
305	0.11	0.34	0.41	0.55	0.48

8. Propylene (A) + Chlorine (B). Ref: Groll and Hearne (17)

P₁ = monochloropropylene

P₂ = dichloropropylene

P₃ = trichloropropylene

Time, sec	T, °C	β ₀	y ₀	y ₁		y ₂		y ₃	
				Expt'l	Calc'd	Expt'l	Calc'd	Expt'l	Calc'd
0.27	525	0.77	0.537	0.317	0.331	0.121	0.103	0.025	0.029
0.41	525	0.59	0.549	0.347	0.327	0.091	0.100	0.013	0.024
0.56	528	0.48	0.632	0.296	0.288	0.055	0.068	0.018	0.012
0.95	525	0.33	0.748	0.217	0.216	0.025	0.032	0.010	0.004
0.82	510	0.54	0.578	0.318	0.315	0.089	0.088	0.015	0.020

9. Benzene (A) + Chlorine (B). Ref: Mason et al. (30)

P₁ = monochlorobenzene

P₂ = dichlorobenzene

Temp. °C	y_0	y_1		y_2		y_3	
		<u>Expt'l</u>	<u>Calc'd</u>	<u>Expt'l</u>	<u>Calc'd</u>	<u>Expt'l</u>	<u>Calc'd = 0</u>
450	0.652	0.321	0.312	0.027	0.036	0.000	
450	0.675	0.282	0.294	0.043	0.031	0.000	
450	0.722	0.225	0.256	0.022	0.022	0.031	
450	0.618	0.346	0.338	0.036	0.044	0.000	
450	0.620	0.343	0.336	0.037	0.044	0.000	
450	0.717	0.237	0.260	0.046	0.023	0.000	
450	0.863	0.092	0.132	0.026	0.005	0.019	
450	0.617	0.346	0.339	0.037	0.045	0.000	
450	0.623	0.345	0.334	0.032	0.043	0.000	
450	0.614	0.359	0.341	0.027	0.045	0.000	
450	0.618	0.340	0.338	0.042	0.044	0.000	
450	0.667	0.302	0.301	0.031	0.033	0.000	
450	0.782	0.168	0.205	0.035	0.013	0.015	
450	0.401	0.447	0.469	0.152	0.130	0.000	
450	0.499	0.433	0.418	0.068	0.083	0.000	
450	0.738	0.240	0.243	0.022	0.019	0.000	
440	0.633	0.331	0.327	0.036	0.040	0.000	
450	0.608	0.363	0.345	0.035	0.047	0.000	

APPENDIX D

EXPERIMENTAL DATA

APPENDIX D

EXPERIMENTAL DATA

1. Preparation of Known Ethanolamine Mixtures

Mixture	5	6	7
Wt. MEA, g	0.8440	1.0366	1.0441
Wt. DEA, g	0.4425	1.0800	0.3981
Wt. TEA, g	0.2925	0.5029	0.
Volume after water added, cc	71.5	73.4	142.4
[MEA], gmols/l	0.1930	0.231	0.1200
[DEA], gmols/l	0.0589	0.1400	0.0266
[TEA], gmols/l	0.0274	0.0459	0.
Amine normality	0.2793	0.4169	0.1466

2. Correlation of pH Against True Hydroxyl Ion Concentration of Known Mixtures 5-7

Mixture	5	6	7
pH	10.58	10.68	10.39
[HMEA ⁺], gmols/l	0.0168	0.01771	0.01323
[DEAH ⁺], gmols/l	0.00165	0.00346	0.00100
[HTEA ⁺], gmols/l	0.00005	0.00007	0.
[OH ⁻], gmols/l	0.01851	0.0212	0.01423

3. Conditions for the Experimental Runs

Run	1A	2	3
Volume NH_4OH , cc	60.2	60.2	60.2
Gmols NH_4OH	0.1770	0.1770	0.1770
Wt. EtO stock, g	23.40	23.20	22.00
Wt. EtO, g	6.75	6.70	6.35
Gmols EtO	0.1531	0.1520	0.1441
x_{A_0}	0.536	0.538	0.551
Reaction time, min	10.5	22.6	37.5
Average reaction temp. °C	20.6	20.2	20.1
Reaction time at 20°C, for $\Delta E = 17000 \text{ cal/gmol}$, min	11.2	23.0	37.5
β_0	0.865	0.859	0.815
$[A]_0$, gmols/l	2.12	2.125	2.16

4. Determination of Amine Normality of Reaction Mixes

Run	1A	2	3
Aliquot, cc	10.0	5.0	2.0
Total base normality	0.674	1.749	0.855
Aliquot of NH_3 blank, cc	0.95	0.94	0.92
Ammonia normality	0.200	1.118	0.033
Amine normality	0.474	0.631	0.822

5. Numerical Evaluation of Constants in Equation (3.104)

Run	1A	2	3
pH of reaction mix	10.82	10.89	10.95
$[\text{OH}^-]$, gmols/l	0.0256	0.0282	0.0305
$[\text{NH}_4^+]$, gmols/l	0.0001402	0.000710	0.00001941
$\Sigma [A_i\text{H}^+]$, gmols/l	0.0255	0.0275	0.0305

6. Numerical Evaluation of Density Equation

	<u>Known Mixture</u>			<u>Reaction Mixture</u>		
	5	6	7	1A	2	3
Wt. of bottleful of liquid, g	10.3604	10.3745	10.3404	10.3242	10.2878	10.4214
Temp., °C	29.1	29.0	28.9	28.7	28.6	28.6
Wt. at 28.5°C	10.3625	10.3163	10.3419	10.3251	10.2884	10.4220
Excess wt. over water or NH ₄ OH at 28.5°C, mg	22.3	36.1	1.7	(1)	33.2	84.0

(1) Value was negative and taken as indicating the absence of triethanolamine.

APPENDIX E

EXPERIMENTAL AND COMPUTED REACTION MIXES; TIME INCLUDED,
FOR SELECTED REAL SYSTEMS

APPENDIX E

EXPERIMENTAL AND COMPUTED REACTION MIXES, TIME INCLUDED, FOR SELECTED REAL SYSTEMS

1. Benzene (A) + Chlorine (B) at 450°C Reference: Mason et al (30)

[A] ₀ , gmols/l	Time, min	P ₀	y ₀		β		y ₁		y ₂	
			Expt'l	Calc'd	Expt'l	Calc'd	Expt'l	Calc'd	Expt'l	Calc'd
0.0116	0.020	0.46	0.652	0.612	0.08	0.05	0.321	0.326	0.027	0.062
0.0116	0.010	0.46	0.675	0.691	0.09	0.15	0.282	0.272	0.043	0.038
0.0116	0.050	0.46	0.618	0.577	0.04	0.00	0.346	0.347	0.036	0.075
0.0116	0.020	0.46	0.620	0.612	0.04	0.05	0.343	0.326	0.037	0.062
0.0116	0.010	0.46	0.717	0.691	0.13	0.15	0.237	0.272	0.046	0.038
0.0116	0.200	0.46	0.617	0.576	0.04	0.00	0.346	0.348	0.037	0.076
0.0116	0.100	0.46	0.623	0.576	0.05	0.00	0.345	0.348	0.032	0.076
0.0116	0.0667	0.46	0.614	0.576	0.04	0.00	0.359	0.348	0.027	0.076
0.0116	0.040	0.46	0.618	0.580	0.03	0.01	0.340	0.346	0.042	0.074
0.0116	0.020	0.46	0.667	0.612	0.09	0.05	0.302	0.326	0.031	0.062
0.00885	0.020	0.91	0.401	0.407	0.16	0.17	0.447	0.425	0.152	0.168
0.0104	0.020	0.63	0.499	0.520	0.06	0.09	0.433	0.379	0.068	0.101
0.0130	0.020	0.29	0.738	0.721	0.01	0.02	0.240	0.249	0.022	0.030

2. Propylene (A) + Chlorine (B)

Reference: Groll and Hearne (17)

T, °C	[A] ₀ , gmols/l	Time, sec	P ₀	y ₀		β		y ₁		y ₂		y ₃	
				Expt'l	Calc'd	Expt'l	Calc'd	Expt'l	Calc'd	Expt'l	Calc'd	Expt'l	Calc'd
525	0.0086	0.27	0.77	0.537	0.513	0.08	0.10	0.317	0.332	0.121	0.111	0.025	0.044
525	0.0096	0.41	0.59	0.549	0.568	0.03	0.02	0.347	0.313	0.091	0.090	0.013	0.029
528	0.0103	0.56	0.48	0.632	0.625	0.02	0.00	0.296	0.287	0.055	0.069	0.018	0.018
525	0.0114	0.95	0.33	0.748	0.719	0.02	0.00	0.217	0.234	0.025	0.040	0.010	0.007

3. Carbon Tetrachloride (A) + Hydrogen Fluoride (B)

Reference: McBee et al (27)

T, °C	[A] ₀ , gmols/l	Time, hrs	P ₀		y ₀		β		y ₁		y ₂	
			Expt'l	Calc'd	Expt'l	Calc'd	Expt'l	Calc'd	Expt'l	Calc'd	Expt'l	Calc'd
300	0.079	0.000198	1.14	0.36	0.21	0.02	0.02	0.46	0.37	0.33	0.28	
290	0.061	0.000196	1.77	0.21	0.07	0.12	0.09	0.21	0.33	0.72	0.46	
300	0.060	0.000218	1.83	0.20	0.06	0.17	0.08	0.22	0.32	0.72	0.48	
290	0.062	0.000139	1.72	0.25	0.02	0.32	0.21	0.56	0.34	0.42	0.41	

4. Methanol (A) + Propylene Oxide (B) at 45°C

Reference: Pecorini and Banchero (34)

[A]₀ = 18.34 gmols/l P₀ = 0.200 Catalyst concentration: 0.8 wt. per cent NaOH

Time, hrs	y ₀		β		y ₁		y ₂	
	Expt'l	Calc'd	Expt'l	Calc'd	Expt'l	Calc'd	Expt'l	Calc'd
4.76*	0.853	0.851	0.05	0.05	0.145	0.146	0.002	0.001
2.06*	0.900	0.909	0.10	0.11	0.098	0.090	0.002	0.000
7.22*	0.852	0.828	0.05	0.03	0.144	0.170	0.004	0.002
3.00	0.869	0.885	0.07	0.09	0.129	0.114	0.002	0.001
6.70	0.840	0.832	0.04	0.03	0.159	0.166	0.001	0.002
3.56	0.879	0.873	0.08	0.07	0.119	0.126	0.002	0.002
8.70	0.832	0.819	0.03	0.02	0.167	0.179	0.001	0.002
2.03	0.899	0.911	0.10	0.11	0.099	0.089	0.002	0.000

* Data taken at 1.6 x the given times, for 0.5 wt. per cent NaOH. Pecorini found k₁ ∞ [NaOH].

5. Ammonium Hydroxide (A) + Ethylene Oxide (B)
 a. At 10°C

Reference: Potter (35)

$$[A]_0 = 1.294 \text{ gmols/l} \quad \beta_0 = 4.03$$

Time, min	y_0		β		y_1		y_2		y_3	
	Expt'l	Calc'd	Expt'l	Calc'd	Expt'l	Calc'd	Expt'l	Calc'd	Expt'l	Calc'd
20	0.875	0.880	3.85	3.83	0.080	0.084	0.028	0.029	0.017	0.006
40	0.780	0.780	3.65	3.63	0.105	0.114	0.061	0.072	0.054	0.034
60	0.696	0.695	3.44	3.45	0.110	0.121	0.097	0.103	0.097	0.081
75	0.638	0.640	3.28	3.32	0.110	0.119	0.115	0.118	0.137	0.123
200	0.355	0.361	2.37	2.39	0.077	0.076	0.121	0.112	0.447	0.451
250	0.286	0.301	2.14	2.10	0.069	0.063	0.106	0.097	0.539	0.539

b. At 20°C

(1) $[A]_0 = 0.831 \text{ gmols/l}$
 Correlation 1: alone

$$\beta_0 = 4.03$$

Reference: Potter (35)

Correlation 2: with present experimentation

Time, min	y_0		β		y_1		y_2		y_3	
	Expt'l	Calculated Corr1	Expt'l	Calculated Corr1	Expt'l	Calculated Corr1	Expt'l	Calculated Corr1	Expt'l	Calculated Corr1
15	0.821	0.829	3.72	3.73	0.094	0.100	0.039	0.053	0.047	0.018
20	0.782	0.782	3.65	3.63	0.105	0.110	0.058	0.073	0.056	0.035
25	0.746	0.738	3.57	3.54	0.110	0.115	0.076	0.091	0.068	0.056
30	0.701	0.697	3.45	3.45	0.112	0.116	0.092	0.105	0.096	0.081
35	0.674	0.660	3.38	3.36	0.114	0.115	0.102	0.116	0.111	0.109
40	0.625	0.626	3.25	3.27	0.114	0.112	0.114	0.124	0.147	0.138
50	0.570	0.565	3.09	3.10	0.109	0.106	0.124	0.132	0.198	0.197
60	0.522	0.513	2.94	2.95	0.102	0.098	0.136	0.133	0.240	0.256
70	0.471	0.467	2.78	2.80	0.095	0.091	0.139	0.131	0.295	0.310
90	0.390	0.394	2.51	2.52	0.086	0.077	0.135	0.120	0.389	0.409

(2) Present experimentation

Correlation 1: alone
 Correlation 2: with Potter's data

Run	1A		2		3	
Correlation	1	2	1	2	1	2
[A] ₀ , gmols/l	2.12	2.125	2.125	2.16	2.16	2.16
β ₀	0.865	0.859	0.859	0.815	0.815	0.815
Time, min	11.2	23.0	23.0	37.5	37.5	37.5
y ₀ , Experimental	0.90	0.87	0.87	0.84	0.84	0.84
Calculated	0.94	0.93	0.88	0.87	0.83	0.82
β, Experimental	0.73	0.67	0.67	0.63	0.54	0.49
Calculated	0.77	0.75	0.67	0.63	0.54	0.49
y ₁ , Experimental	0.08	0.09	0.09	0.09	0.11	0.10
Calculated	0.06	0.06	0.09	0.09	0.11	0.10
y ₂ , Experimental	0.03	0.04	0.04	0.04	0.04	0.04
Calculated	0.01	0.01	0.03	0.04	0.06	0.06
y ₃ , Experimental	0.00	0.01	0.01	0.01	0.02	0.02
Calculated	0.00	0.00	0.00	0.01	0.01	0.02

c. At 30°C

[A]₀ = 0.831 gmols/l

β₀ = 4.03

Reference: Potter (35).

Time, min	y ₀		β		y ₁		y ₂		y ₃	
	Expt'l	Calc'd	Expt'l	Calc'd	Expt'l	Calc'd	Expt'l	Calc'd	Expt'l	Calc'd
20	0.589	0.580	3.15	3.17	0.112	0.121	0.125	0.127	0.174	0.172
40	0.377	0.378	2.45	2.49	0.079	0.086	0.128	0.118	0.416	0.418
60	0.254	0.270	2.01	1.96	0.059	0.062	0.092	0.091	0.595	0.577

APPENDIX F

METHODS OF SOLUTION OF EQUATIONS IMPLICIT IN THE UNKNOWNNS

Consider a set of k real variables, $x_1, \dots, x_1, \dots, x_k$ and n real functions, $f_1(\vec{x}), \dots, f_j(\vec{x}), \dots, f_n(\vec{x})$, defined on these variables. The $\{x_i\}$ define an independent variable space and the f_j can be represented by a set of n surfaces in a space of $k+1$ dimensions; such surfaces are called response surfaces. We will be concerned here with two problems associated with response surfaces:

Problem (a). If f_j is minimized by a single set of values of the independent variables, what is the x -vector corresponding to this minimum?

Problem (b). When $n = k$, for which unique x -vector are all the f_j equal to zero?

1. Definition of Deviation

Before treating the problems above, it is worthwhile to consider a special case which appears frequently throughout the study to follow.

Assume that a set of response surfaces exists, so that for a given x -vector, a certain y -vector obtains:

$$\begin{aligned}
 y_1 &= \phi_1(x_1, \dots, x_i, \dots, x_k) \\
 \vdots \\
 y_j &= \phi_j(x_1, \dots, x_k) \\
 \vdots \\
 y_l &= \phi_l(x_1, \dots, x_k) \\
 \vec{y} &= (y_1, \dots, y_j, \dots, y_l)
 \end{aligned}
 \tag{F.1}$$

If the natures of these response surfaces are not known beforehand, they can be determined only by some experimental procedure. The x-vector is chosen, and an experimental \hat{y} -vector measured. In general, owing to experimental error, y_j will not equal \hat{y}_j . Let m experiments be made. Although the ϕ_j are not known, the experimental data give some picture of the nature of the response surfaces. Assume that at this point, approximations to the ϕ_j are proposed, using the experimental data as a guide. In general, for the q'th run,

$$y_{jq} = f_j(x_{1q}, \dots, x_{pq}; \beta_1, \dots, \beta_m, \dots, \beta_p) + \Delta_{jq}(x_{1q}, \dots, x_{pq}) \quad (F.2)$$

where f_j = proposed approximation to ϕ_j
 $(\beta_1, \dots, \beta_p)$ = parameters of the approximation
 Δ_{jq} = an error term induced by the inability of the f_j to represent the true response surface.

The purpose of the parameters in the approximation is to introduce a flexibility into f_j to give it a better chance to approximate ϕ_j over the range of interest and reduce Δ_{jq} . As a matter of fact, if $p \geq lm$, the Δ_{jq} can all be reduced to zero, and the f_j will be able to describe exactly the experimental response surface. If $\hat{y} \equiv \vec{y}$, as is sometimes the case, the true response surface can be represented, at least at the experimental points, by the use of sufficiently many β_n . For this reason, when testing the validity of an approximation to ϕ , p should not be too large.

In general, the nature of the true response surface is not known, and hence we cannot find the best β -vector to use in Equation (F.2). On the other hand, it is possible to obtain a best fit to the experimental

surface and in this way obtain best estimates, $\{b_n\}$, of the $\{\beta_n\}$.

$$\begin{aligned} \hat{y}_{jq} &= f_j(x_{1q}, \dots, x_{kq}; b_1, \dots, b_p) \pm d_{jq}(x_{1q}, \dots, x_{kq}) \\ &= y_{jqP}(\bar{b}) \pm d_{jq} \quad (q=1, \dots, m) \end{aligned} \quad (F.3)$$

where y_{jqP} = predicted value of y_j , for the q 'th run
 d_{jq} = deviation of y_j , for the q 'th run .

The deviation is a measure of the inability of the functions f_j to represent the experimental response surface and, if experimental error is small, the true response surface as well. In Equation (F.3), the deviation is equated to the absolute difference between y_p and \hat{y} .

$$d = |\hat{y} - y_p| \quad (F.4)$$

The deviation may be defined more generally than this, however. Any function of \hat{y} and y , whose absolute value increases as $|\hat{y} - y_p|$ increases may be chosen as the deviation. For instance, the following definitions of deviation are also acceptable:

$$d = (\hat{y} - y_p)^2 \quad (F.5)$$

$$d = (|\hat{y} - y_p|)^m, \quad m \geq 1 \quad (F.6)$$

$$d = \left| \ln \frac{\hat{y}}{y_p} \right| = |\ln \hat{y} - \ln y_p|, \quad \hat{y}, y_p > 0 \quad (F.7)$$

$$d = \frac{(|\hat{y} - y_p|)}{|\hat{y}|} \quad (F.8)$$

For a series of runs, we may simply add the deviations of the individual runs, as in Equation (F.9), or apply positive weighting

factors, dependent on the estimated accuracy or the importance of the particular run, as in Equation (F.10).

$$d_j = \sum_{q=1}^m d_{jq} \tag{F.9}$$

$$d_j = \sum_{q=1}^m w_q d_{jq} \tag{F.10}$$

where w_q = weighting factor for the q'th run .

Similar considerations apply to the several dependent variables. In general, the overall deviation, D, for l variables defined by m runs, is

$$D = \sum_{q=1}^m \sum_{j=1}^l w_{jq} d_{jq} \tag{F.11}$$

where w_{jq} = weighting factor for the j'th variable in the q'th run and where d_{jq} can be given by any of several equations, of which (F.4) through (F.8) are typical. Whenever a set of parameters is estimated by minimizing the overall deviation, this deviation must be defined explicitly, as the best values of the $\{b_n\}$ will normally change when the definition of D is modified.

When the experimental data have been collected and the functions f_j decided upon, D may be treated as a dependent variable itself, a function of the parameters $\{b_n\}$. It is desired to find those values of the $\{b_n\}$ which correspond to a minimum on the response surface D. This, the final problem in fitting data to a model or equation, is merely a special case of Problem (a) above.

2. Methods to be Used in Solving the Problem

We now come to a discussion of several methods useful in the solution of Problems (a) and (b) above. Although these procedures can be used to solve the general problem given by Equation (F.3), we will assume, for simplicity, that $l = 1$, and that a single response surface is under consideration. In the equations and discussion to follow, the variable subscript j will be dropped.

a) Least Squares

In Section A, we considered the problem of fitting an approximate function, f , to a set of experimentally determined points, $\{\hat{y}_q\}$. There are two reasons why the fit should not be expected to be perfect; first, because f is not an exact representation of the true dependence ϕ ; and second, because experimental errors would deny us the true responses, $\{y_q\}$, even if the values of the independent variables were known exactly.

If the experimental errors are as likely to be positive as negative and if the distribution of y is not truncated near the region under investigation, the experimental error is normally distributed in that neighborhood and obeys Equation (F.12).⁽⁹⁾

$$P\{|y_q - \hat{y}_q| > a\} = \frac{h}{\sqrt{\pi}} e^{-h^2 a^2} \quad (F.12)$$

= probability of an experimental error greater than a

where h = precision constant .

Let us use Equation (F.5) to define overall deviation. With unit weighting,

$$D = \sum_{q=1}^m \left(\frac{\hat{y}_q}{\sigma_q} - \frac{y_q}{\sigma_q} \right)^2 \quad (F.13)$$

It can be shown that if the errors are normally distributed, the probability of obtaining the observed value \hat{y}_q is a maximum when D , as defined in Equation (F.13), is minimized. We cannot expect the error occasioned by the inability of f to represent ϕ to be unbiased, but if it is small, the distribution criterion is essentially met.

As we have noted, D is an explicit function of the $\{b_n\}$. At the minimum,

$$\frac{\partial D}{\partial k_m} = 0 \quad (m=1, \dots, p) \quad (\text{F.14})$$

The partial derivatives are functions of the $\{b_n\}$. Equation (F.14) can sometimes be solved directly for the parameters; more frequently the iterative methods applicable to Problem (b) above will be required.

b) Newton's Method

This method is used to treat certain cases of Problem (b): for example, the solution of the p Equations (F.15) for the $\{x_n\}$.

$$\begin{aligned} g_1(x_1, \dots, x_m, \dots, x_p) &= 0 \\ \vdots \\ g_r(x_1, \dots, x_p) &= 0 \\ \vdots \\ g_p(x_1, \dots, x_p) &= 0 \end{aligned} \quad (\text{F.15})$$

Assume that we have evaluated, at the point $(x_1^{(k)}, \dots, x_p^{(k)})$, all the functions and their p^2 partial derivatives with respect to the independent variables. These latter terms may be obtained either by direct differentiation or, for complicated g_r , by the use of difference methods.

$$\left. \frac{dg_r}{dx_m} \right|_{(x_1^{(k)}, \dots, x_p^{(k)})} = \gamma_{rn} \sim \frac{g_r(x_1^{(k)}, \dots, x_{m-1}^{(k)}, x_m + \Delta, x_{m+1}^{(k)}, \dots, x_p^{(k)}) - g_r(x_1^{(k)}, \dots, x_p^{(k)})}{\Delta} \quad (F.16)$$

where Δ = small increment in x_n
 k = iteration number *

Expanding the functions in a Taylor series about $(x_1^{(k)}, \dots, x_p^{(k)})$,

$$g_r(x_1^{(k+1)}, \dots, x_p^{(k+1)}) = g_r(x_1^{(k)}, \dots, x_p^{(k)}) + \sum_{m=1}^p \gamma_{rn} (x_m^{(k+1)} - x_m^{(k)}) + \dots \quad (F.17)$$

$(r=1, \dots, p)$.

Choose the $(x_1^{(k+1)}, \dots, x_p^{(k+1)})$ so that, if the $\{\gamma_{rn}\}$ are constant, and the higher-order terms negligible,

$$g_r(x_1^{(k+1)}, \dots, x_p^{(k+1)}) = 0 \quad (r=1, \dots, p) \quad (F.18)$$

If the higher-order terms are neglected, substitution of Equation (F.18) into (F.17) gives

$$\sum_{n=1}^p \gamma_{rn} x_n^{(k+1)} = \sum_{m=1}^p \gamma_{rn} x_m^{(k)} - g_r(x_1^{(k)}, \dots, x_p^{(k)}) \quad (r=1, \dots, p). \quad (F.19)$$

Equation (F.19), being linear, can readily be solved for the coordinates of the new point. The iteration is continued until the $\{g_r\}$ are sufficiently small or the $\{x_n\}$ sufficiently close upon repeated iteration.

This method works best when the initial guesses, $\{x_1^{(1)}, \dots, x_p^{(1)}\}$, at the $\{x_n\}$ are sufficiently close to the roots of Equations (F.15) and when the g_r are relatively smooth; otherwise convergence difficulties may be encountered.

c) Functional Fit

It is sometimes the case that only a very small portion of a response surface is being studied; for instance, the immediate neighborhood of a minimum. If much of the surface has been covered experimentally, it is likely that there are too few data points near the minimum to justify or allow the use of the complete approximation (F.2). A more empirical approach is required. When the minimum of the surface is being searched for, a second-degree polynomial representation of the region near the extremum is frequently employed. It is understood that only the experimental points near the minimum should be used to determine the polynomial coefficients, and that this representation cannot be expected to describe more distant areas of the surface.

The first-degree functional fit is no less powerful. Consider the set of equations

$$g_r(x_1, \dots, x_n, \dots, x_r, \dots, x_p) = x_r \quad (r=1, \dots, p) \quad (F.20)$$

If $g_r(x_1, \dots, x_p)$ is replaced by $x_r^{(k+1)}$ ($x_1^{(k)}, \dots, x_p^{(k)}$), the roots of these equations are the limit points of an iterative solution. Suppose that the functional forms of the g_r are unknown but that, given the $\{x_n\}$, the values of the functions, $\{g_r\}$, can somehow be found. This is the case for certain graphical procedures. Over small ranges of $\{x_n\}$, the g_r can be assumed to be linear transformations. If the $\{g_r\}$ can be computed for p sets of $\{x_n\}$, the coefficient matrix can be found and the roots determined. For the s^{th} run,

$$g_r(x_{1s}, \dots, x_{ns}, \dots, x_{ps}) = a_{1r}x_{1s} + a_{2r}x_{2s} + \dots + a_{pr}x_{ps} \quad (F.21)$$

$$(r, s = 1, \dots, p)$$

where $|a_{ij}|$ = coefficient matrix .

d) Creep

There are many problems in fitting which do not admit the use of least squares to find the $\{b_n\}$ of Equation (F.3). If the deviation to be minimized is not defined by Equation (F.13), the very theory behind least squares does not apply. And even if the errors are normally distributed and the squared deviation is to be minimized, the function f may be so complex that the differentiations indicated by Equation (F.14) are burdensome. In fact, f may not be an explicit mathematical function. It is in such situations that the creep method is most useful, for, in spite of its crudeness, it is the most generally applicable approach to the study of extrema of response surfaces.

A guess at the true $\{b_n\}$ is made and D is computed. Then, each element of the b -vector in turn is subjected to the following treatment.

- (a) b_n is raised, and the new D computed.
- (b) If the new D is less than the response to the unmodified b_n , the higher value of b_n is retained; if not,
- (c) b_n is lowered below its original value, and the new D computed.
- (d) If the new D is less than the response to the unmodified b_n , the lower value of b_n is retained; if not, the unmodified b_n is retained. Step (a) is then carried out for b_{n+1} .

When all the $\{b_n\}$ have been treated in this way, the entire procedure is repeated, starting with b_1 . As the solution proceeds, "favorable" adjustments, those which reduce D , are retained, and finally at least a local minimum of the response surface is reached. If small enough increments are made in the $\{b_n\}$, the problem can be considered solved when no changes in the fitting constants occasion a reduction in D . Frequently, for efficiency, it is helpful to use large increments at first, and then reduce them when this grid becomes too coarse.

One deficiency of this method has already been hinted at; only local minima will be found. In fact, the method may give some trivial solution rather than the desired one if the first guesses at the $\{b_n\}$ are particularly errant. Another difficulty can be encountered if this method is applied on a digital computer. If the response surface is flat or nearly so in the region under study, the changes in D caused by changes in the $\{b_n\}$ may be very small, and possibly too small to be recognized by the computer. Then minima will be indicated in the middle of a plateau when the true minimum is some distance away. However, in most cases, creep serves as an effective, if lengthy, method of finding extrema of response surfaces.

e) Steepest Descent

The method of Steepest Descent, an extension of the creep method, requires fewer steps to reach the region of the minimum. (5,29)

It is convenient, in describing this method, to let (b_1, \dots, b_p) be the coordinates of a point in a space of $p+1$ dimensions, as described above. As in the creep method, an initial guess at the $\{b_n\}$ is made,

defining a point, $\vec{b}^{(1)}$. An initial step size, $\alpha^{(1)}$, is also selected. The derivatives of D with respect to each of the $\{b_n\}$ at $\vec{b}^{(1)}$ are computed, using direct differentiation or, more frequently, difference methods. Let

$$\left. \frac{\partial D}{\partial b_n} \right|_{\vec{b}^{(1)}} = \delta_m^{(1)} \quad (\text{F.22})$$

Let $E^{(k)}$ be the norm of $(1+b_n^{(k)2})\delta_n^{(k)}$.

$$E^{(k)} = \|(1+b_n^{(k)2})\delta_n^{(k)}\| = \left(\sum_{m=1}^p ((1+b_n^{(k)2})\delta_m^{(k)})^2 \right)^{1/2} \quad (\text{F.23})$$

Let $E_n^{(k)}$ be the negative of the normalized $(1+b_n^{(k)2})\delta_n^{(k)}$

$$E_n^{(k)} = - \frac{(1+b_n^{(k)2})\delta_n^{(k)}}{E^{(k)}} \quad (\text{F.24})$$

The solution procedure is as follows

- (a) Compute $E_n^{(1)}$.
- (b) $b_n^{(2)} = b_n^{(1)} + \alpha^{(1)} E_n^{(1)}$ ($n = 1, \dots, p$). The vector $\vec{b}^{(2)} - \vec{b}^{(1)}$ points in the direction of steepest descent of the response surface in the metric defined by Equations (F.23) and (F.24).
- (c) Compute $D^{(2)}$, the deviation at $\vec{b}^{(2)}$.
- (d) If $D^{(2)}$ is greater than $D^{(1)}$, the step size is too large. Quarter $\alpha^{(1)}$ and repeat Step (b); otherwise, continue.
- (e) Compute $E_n^{(2)}$.
- (f) The $E_n^{(k)}$ are normalized vectors in the metric defined by Equations (F.23) and (F.24). The cosine of the angle

between them is given by

$$\cos \theta = \sum_{m=1}^P E_m^{(1)} E_m^{(2)}. \quad (\text{F.25})$$

This is the angle between the direction of steepest descent from $\vec{b}^{(1)}$ and that from $\vec{b}^{(2)}$. Marquardt suggests quartering $\alpha^{(1)}$ and going to Step (b) if θ is greater than 90° ; Boberg prefers to keep the original $\vec{b}^{(2)}$ and reduce $\alpha^{(2)}$. The author concurs with the latter, for $\vec{b}^{(2)}$ is probably closer to the desired \vec{b} than $\vec{b}^{(1)}$, as $D^{(2)}$ must be less than $D^{(1)}$ if Step (f) is reached.

- (g) Compute $\alpha^{(2)}$. Boberg and the present work uses Equation (F.26); Marquardt recommends (F.27).

$$\alpha^{(2)} = \alpha^{(1)} (1 + 0.5 \cos^3 \theta) \quad (\text{F.26})$$

$$\alpha^{(2)} = \alpha^{(1)} (0.5 + \cos^4 \theta) \quad (\text{F.27})$$

- (h) Raise the iteration number by one and go to Step (b).

The continuation of the descent by further iteration is obvious.

The method of Steepest Descent is more efficient than the creep method because the independent variables are changed more intelligently. However, unless α is severely lowered near the minimum, the $\{b_n\}$ oscillate about the best values. Frequently, steepest descent is used to reach the vicinity of the minimum, and then some other method, such as functional fit or creep, is employed to study this region and determine the best values of the fitting constants.

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