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ANALYSIS OF BACKMIXING AND MASS TRANSFER IN SOLVENT EXTRACTION COLUMNS

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Based on a M.S. thesis submitted to Iowa State University

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Analysis of backmixing and mass transfer in solvent extraction columns

by

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NOMENCLATURE

A	Pulse amplitude, ft
Af	Pulse velocity, ft/sec
$A_1,\ldots,A_4$	Constants
a	Interfacial area, ft^2/ft^3
$a_1,\ldots,a_4$	Constants
α	Adjustable exponent in Equation 94, dimensionless
α'	Constants
β	Miyauchi's backmixing correlation factor relates to the liquid motion instability
β'	Constant
b	A proportionality constant for the diffusion of component A through a solution of A and B
$b_1,\ldots,b_8$	Constants
C	Total molal concentration of components A and B, $C = C_A+C_B$
C_{BM}	Logarithmic mean concentrations of B on each side of the liquid film, $C_{BM} = \dfrac{C_{B2}-C_{B1}}{\ln \dfrac{C_{B2}}{C_{B1}}}$
c	Concentration of tracer at z=H at time t
c_o	Concentration of tracer at outlet
D_A	Molecular diffusion coefficient of component A, lb mole.ft^2/sec
D_i	Diffusivity coefficient of solute in phase i, ft^2/sec
D_t	Column internal diameter, ft

d_p	Drop diameter, ft
d_h	Plate hole diameter, ft
Δ	Difference operator defined by e.g., $\Delta x_n = x_{n+1} - x_n$
Δt	Time interval, sec
Δz	Interval of finite difference equation
$\Delta \rho$	Density difference between two phases
E	Difference operator, defined by e.g., $Ex_n = x_{n+1}$
E_i	Axial dispersion coefficient in the ith phase, ft^2/sec
e_i	Backflow ratio, e = interstage mixing flow rate/main flow rate
η	Overall extraction efficiency
F	Extraction factor, $F = L/mG$
f	Pulse frequency, cycle/sec
f_i	Weighting factors, dimensionless
Φ	Correlation factor, dimensionless
γ	Interfacial tension, lb/sec^2
γ'	Constant
G	Light phase flow rate, $G = U_y \rho_y$, lb/sec.ft^2
$\overline{G}$	Interstage mixing flow rate for light phase, $\overline{G} = Afh_y \rho_y$
H	Height of column, ft
h	Height of one stage or plate spacing, ft
h', h''	Height of first and last stage, respectively
h_i	Holdup fraction of phase i, dimensionless

h'_i, h''_i	Holdup fraction of phase i for first and last stage, respectively
$(HTU)_i$	Height of a transfer unit based on i-phase, ft
$(HTU)_{oi}$	Overall height of a transfer unit, based on i-phase, ft
$(HTU_{oi})_T$	Overall true height of a transfer unit based on i-phase, ft, $(HTU_{oi})_T = U_i/K_{oi}a$
$(HTU_{oi})_p$	Plug flow or apparent overall height of a transfer unit based on i-phase, ft
$(HTU_{oi})_M$	Measured overall height of a transfer unit based on i-phase
$(HTU_{oi})_D$	Overall height of diffusion unit based on i-phase, ft
J_z	Quantity of tracer transferred per unit area per unit time
k_i	Mass transfer coefficient of i-phase for concentrated solution, lb/sec.ft^2 or ft/sec
K_{oi}	Overall mass transfer coefficient of i-phase, for concentrated solution, lb/sec.ft^2 or ft/sec
k'	Numerical coefficient, dimensionless
ℓ	Film thickness
$\bar{\ell}$	Effective film thickness
L	Heavy phase flow rate, lb/sec.ft^2
$\bar{L}$	Interstage mixing flow rate for heavy phase, $\bar{L} = Afh_x\rho_x$
l_i	Length of region near the i-phase outlet, ft
m	Distribution coefficient, $m = y/x^*$
m_1, m_2, m_3	Constants
μi	Viscosity of phase i, lb/ft.sec

N	Total number of stages
n	Number of nth stage
NP_i	Peclet number in phase i using $(HTU_{oi})_p$ for characteristic length, $NP_i = U_i(HTU_{oi})_p/E_i$
$(NTU)_i$	Number of transfer units based on i-phase
$(NTU)_{oi}$	Overall number of transfer units for i-phase
$(NTU_{oi})_T$	Overall true number of transfer units for i-phase
$(NTU_{oi})_p$	Plug flow or apparent overall number of transfer units based on i-phase
$(NTU_{oi})_M$	Measured overall number of transfer units for i-phase
$(NTU_{oi})_D$	Overall number of dispersion units based on i-phase
P_i	Peclet number of phase i, $P_i = U_iH/E_i$
$(PB)_i$	Overall Peclet group for phase i
Q	Molar of solute transferred per unit time
Q_A	The rate of mole of solute A diffusing per unit time, mole/sec
Re	Reynolds number, $Re = U_i\mu_i d_p/\rho_i$
ρ_i	Density of phase i, lb/ft^3
S	Cross section area of column, ft^2
s	Plate free area fraction
Sc	Schmidt number, $Sc = \mu_i/\rho_i D_i$
Sh	Sherwood number, $Sh = \rho_i d_p/D_i$
σ_t^2	Variance of tracer residence distribution, sec^2
t	Time, sec

u_A, u_B	Velocity of components A and B, respectively
U_i	Superficial velocity of phase i, ft/sec
X	Dimensionless solute concentration in heavy phase
x, x_s	Mole fraction of solute in x-phase at the mixing-cup and near the interface, respectively
x^*	Mole fraction of solute in x-phase at equilibrium with the concentration y in the y-phase
x_{11}	Concentration jump from x_{in} at the inlet
x_{BM}	Logarithmic mean molar concentrations of B on each side of the liquid film, $x_{BM} = \dfrac{x_{B2} - x_{B1}}{\ln \dfrac{x_{B2}}{x_{B1}}}$
y, y_s	Mole fraction of solute in y-phase at the mixing-cup and near the interface, respectively
y^*	Y-phase concentration in equilibrium with the concentration x in the other phase
Y	Dimensionless solute concentration in light phase
z	Distance from heavy phase inlet nozzle, ft
Z	Dimensionless distance from heavy phase inlet, $Z = z/H$

ABSTRACT

A critical survey of the published literature concerning; modelling of liquid-liquid extraction columns, mass transfer studies in extraction towers and the influence of backmixing on concentration profiles, extraction efficiency and the number of transfer units has been made to determine the most accurate correlations for computing the true number of transfer units or the true overall mass transfer coefficients in backmixed solvent extraction columns. These parameters are of great significance and are very useful in the design and performance evaluation of solvent extraction columns.

Several approximate correlations of these parameters as a function of column geometry, operating conditions, and physical properties of the liquid systems involved have been developed and it is possible to use mathematical models in the interpretation and analysis of experimental data to determine which correlations appear to be most accurate and easiest to use.

The results of the data analysis, together with the best possible estimate of the extraction efficiency were applied to a differential backmixing model to obtain concentration profiles in an extraction column.

INTRODUCTION

The measurement of mass transfer coefficients, especially for extraction columns, has been the subject of much research over the past forty years. In spite of this effort, the complexity of the problem is so great that the reliability of predicted mass transfer rates is still far from satisfactory. In the correlations for different systems to be presented in the present work, experimental results frequently deviate by as much as 25 percent from the recommended correlations.

In the past thirty years there has also been growing awareness of the part played by axial mixing or backmixing in extraction column performance. It is a particular case of nonideal flow in which a random movement of fluid is superimposed on the main flow and may occur either in the direction of or opposite to the direction of the main flow. In early research work on extraction columns the extraction efficiencies reported often included both mass transfer rates and backmixing effects.

Pratt (34), Geankoplis and Hixson (7), and Gier and Hougen (10) were among the earliest workers to recognize the effects of axial mixing upon extraction efficiency. In their studies and in subsequent work, it has been necessary to consider the manner in which concentration profiles in a column vary from the profiles predicted by simple mass transfer or equilibrium theories.

While the last fifteen years have yielded considerable theoretical advances in the description of axial mixing and relevant design procedures (30), comparatively little attention has been paid to reducing the axial mixing by reconsidering the basic construction of extraction equipment. Misek, as cited in (20), has reported that axial mixing effects can account for up to 90% of the installed height of large diameter agitated extraction columns. Under these conditions, consideration of the axial mixing characteristics of extractors is just as important as the more usual concepts of mass transfer coefficient and interfacial area. Several efforts have been made to reduce axial mixing in the design of some contactors, e.g., by using baffles or distributor plates.

In early work, the concept of the height of a transfer unit and the height equivalent to a theoretical stage, based on entry and exit concentrations, were commonly used. These parameters were introduced when plug flow was considered a reasonable assumption for the flow pattern inside a counter current column. Later, by recognizing the nonideality of this flow, the mass transfer efficiency has been recognized as being strongly dependent on the column construction because of the effect of column geometry on the identity of the flow within the column. However, mass transfer rates are still sometimes given without a warning about possible scale-up problems. To improve this situation a more detailed approach is necessary. The mass transfer coefficients should be calculated from actual concentrations inside the column, and the nonideality of the flow should be expressed by some other means. A true mass transfer coefficient, based on a proper description of flows inside a column, will not be dependent on column dimensions. Scale-up should be considerably improved as soon as the design equations realistically represent the processes involved.

The mass transfer process and the influence of back-mixing in a liquid-liquid extraction column may be represented by various mathematical models. These mathematical models enable one to analyze column performance as a function of various operating conditions. Two categories of mathematical models have been used to describe the axial mixing in extractors. Of these, the diffusion model relates to differentially continuous columns in which longitudinal back-diffusion is superimposed upon plug flow of both phases. This leads to a fourth-order differential equation which can be solved analytically for the case of a linear equilibrium relationship to give the concentration profiles in the form of a sum of exponentials. The equations may also be solved numerically by using a digital computer. The other model describes the backmixing by a discrete backward flow of the phases between stages. This leads to a fourth-order difference equation, the general analytical solution to which gives the concentration profiles for the linear equilibrium case as a sum of power functions involving the number of stages. Again, for more complicated equilibrium relationships, one may use digital simulation to compute the concentration profiles.

Scope and Objectives of the Present Study

The present work is concerned with longitudinal mixing and its influence on the efficiency of an extractor. Mathematical models are used for the interpretation and analysis of experimental data to find the most accurate correlations for evaluating the extraction efficiency, the true number of transfer units and the true overall mass transfer coefficients. A computer program was written to compute unsteady state concentration profiles and was run for a 7 and a 27 stage backmixing column.

LITERATURE REVIEW

Due to the extensive amount of research in mass transfer and nonideal flow in liquid-liquid extraction columns, it is not feasible to review all of the work published in the past forty years. A brief review of the major research efforts most closely related to the present work is given in the following paragraphs.

Diffusion and Mass Transfer

According to the Maxwell-Stefan concept, upon which most analyses of diffusion in liquid-liquid extraction are based, the resistance to diffusion of a component A through a solution of A and B is assumed to be proportional to the relative velocity of A with respect to B, $u_A - u_B$; to the distance $d\ell$ through which the diffusion occurs; and to the number of molecules of A and B in the path of the diffusion, in turn proportional to the concentrations C_A and C_B. The resistance must be overcome by a concentration gradient in the direction of diffusion, dC_A. Thus,

$$dC_A = -bC_A C_B (u_A - u_B) d\ell \tag{1}$$

If one component, say B, is stationary then $u_B = 0$ and Equation 1 becomes

$$dC_A = -bC_AC_Bu_Ad\ell \qquad (2)$$

At steady-state conditions, let Q_A be the amount of A diffusing per unit time across an area S so that

$$Q_A = C_Au_AS \qquad (3)$$

then,

$$dC_A = \frac{-bQ_AC_Bd\ell}{S} \qquad (4)$$

Further, define a diffusion coefficient as

$$D_A = \frac{1}{b(C_A+C_B)}$$

so that Equation 4 can be written,

$$dC_A = -\frac{Q_AC_Bd\ell}{SD_A(C_A+C_B)} \qquad (5)$$

Then assume that the volume of the solution is an additive function of the volumes of the constitutients. Under these conditions

$$C_A+C_B = \text{constant}$$

and,

$$dC_A = -dC_B$$

Equation 5 can then be written as,

$$dC_A = -dC_B = -\frac{Q_AC_Bd\ell}{SD_AC} \qquad (6)$$

or,

$$CD_A \int_{C_{B_1}}^{C_{B_2}} \frac{dC_B}{C_B} = \frac{Q_A}{S} \int_{\ell_2}^{\ell_1} d\ell \qquad (7)$$

Integrating Equation 7 and utilizing the relations

$$C_{B_1} + C_{A_1} = C_{B_2} + C_{A_2}$$

$$(\ell_2 - \ell_1) = \ell$$

$$C_A = X_A C$$

$$C_{BM} = X_{BM} C$$

gives the result,

$$Q_A = \frac{D_A SC}{X_{BM}\ell} (X_{A_1} - X_{A_2}) \qquad (8)$$

The quantity D_A is a molecular diffusion coefficient. In most cases of practical importance in liquid-liquid extraction mass transfer occurs as a result of both molecular and eddy diffusion and one defines an "effective" or "fictitious" film thickness $\underline{\ell}$ which is sufficient to account for the total resistance to mass transfer. Further, a mass transfer coefficient k may be defined as,

$$k = \frac{D_A}{X_{BM}\underline{\ell}} \qquad (9)$$

so that Equation 8 may be written,

$$Q_A = kSC(X_{A_1} - X_{A_2}) \tag{10}$$

Mass Transfer in Differential Extraction Systems

When the concept of a mass transfer coefficient, as introduced in Equation 10 is applied to liquid-liquid extraction one considers that there is a mass transfer resistance in each of the two immiscible liquid phases and that there is a fictitious film on each side of the interface. The film thickness on each side of the interface is sufficient to account for the total resistance to mass transfer in that phase. The rate of transfer of solute then becomes,

$$dQ = k_x dSC(x-x_s) = k_y dSC(y_s-y) \tag{11}$$

In most practical situations it is impossible to approach the interface sufficiently closely to measure x_s or y_s accurately and so the true film driving forces $(x-x_s)$ and (y_s-y) cannot be obtained.

If the equilibrium curve is a straight line so that at all concentrations encountered y_s in proportional to x_s then

$$y_s = mx_s \tag{12}$$

and a concentration y* may be defined as that concentration in equilibrium with x, the bulk concentration in the x-phase so that

$$y^* = mx \tag{13}$$

or, analogously, define x* such that,

$$y = mx^* \tag{14}$$

One may then write

$$dQ = K_{ox} dSC(x-x^*) = K_{oy} dSC(y^*-y) \tag{15}$$

where K_{ox} and K_{oy} are called the overall mass transfer coefficients. Then by combining Equations 11 through 15 the relations between individual coefficients and overall coefficients are found to be

$$K_{ox} = \frac{1}{\frac{1}{k_x} + \frac{1}{mk_y}} \tag{16}$$

and

$$K_{oy} = \frac{1}{\frac{1}{k_y} + \frac{m}{k_x}} \tag{17}$$

The choice of which coefficient to use is customarily made by determining the controlling resistance. For example, if the equilibrium distribution strongly favors the y-phase, then m will be large and, if k_x and k_y are of comparable order of magnitude, then $\frac{1}{mk_y}$ is small and K_{ox} approaches k_x and the major resistance to transfer is in the x-phase.

Although an overall coefficient should not be used for systems with a curved equilibrium line, reference to the literature shows that such a coefficient is often the only one reported. It is almost impossible in two-fluid contactors to measure x_s and y_s experimentally and thus to calculate k_x and k_y, directly from data on the rate of mass transfer between phases. Usually only x and y can be measured and the individual resistances must be estimated indirectly.

A justification for the use of overall coefficients is the lack of precision of most data on mass transfer. This lack of precision is not caused by carelessness, but by the difficulty of obtaining data on concentrations and velocities in a device such as a solvent extraction column.

Number of Transfer Units in a Tower-Concentrated Solution

From the previous discussion the use of overall coefficients is difficult. The concept of the "height of a transfer unit" first advocated by Chilton and Colburn (3) is more often used. It may be derived by reference to Figure 1. From a balance on a differential height of column

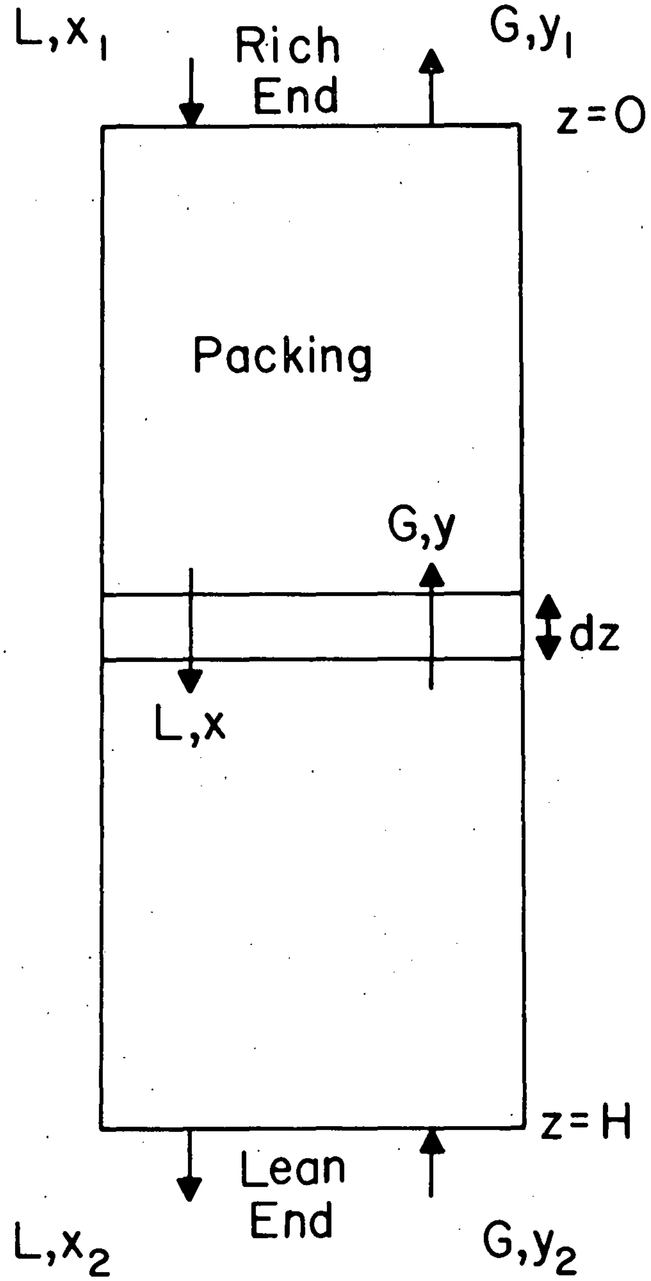

Figure 1. Diagram of a solvent extraction column

one may write,

$$dQ = d(Lx) = k_x aSC(x-x_s)dz \tag{18}$$

where Q = moles of solute transferred per unit time, a is the interfacial area per unit volume of the tower and S is the cross section area. The total flow-rate, L, may vary along the length of the tower but the solute free flow rate L(1-x) will remain relatively constant. Also, the mass transfer coefficient, k_x, includes a term $(1-x)_{im}$ which also varies throughout the column as shown in Equation 8. The quantity $k_x(1-x)_{im}$ is more likely to remain constant. Making these two changes in Equation 18 and rearranging terms gives

$$\frac{(1-x)_{im}dx}{(1-x)(x-x_s)} = \frac{k_x a(1-x)_{im}SCdz}{L} \tag{19}$$

Since the terms $(1-x)_{im}$ and $(1-x)$ are usually near unity, the left-hand portion of Equation 19 is essentially the concentration change dx per unit of concentration difference $(x-x_s)$ causing the change. It is a measure of the difficulty of the extraction and the integral has been named the number of transfer units (NTU). The number of transfer units, when multiplied by an experimentally determined quantity called the height of a transfer unit (HTU) gives the height of the tower. Thus,

$$H = (HTU)(NTU) \tag{20}$$

and from Equations 19 and 20,

$$(NTU)_x = \int_{x_2}^{x_1} \frac{(1-x)_{im}dx}{(1-x)(x-x_s)} = \int_0^H \frac{dz}{HTU} = \frac{H}{(HTU)_x} \tag{21}$$

So the mass transfer coefficient and the HTU are related by the expression

$$(HTU)_x = \frac{L}{k_x a(1-x)_{im} CS} \tag{22}$$

As was discussed in the explanation of the use of mass transfer coefficients, the practical problems of obtaining true equilibrium interfacial concentrations has also led to the use of overall mass transfer coefficients in the computation of the number of transfer units. Thus it is common practice to use overall mass transfer coefficients and overall concentration gradients. With these changes, Equations 21 and 22 become,

$$(NTU)_{ox} = \int_{x_2}^{x_1} \frac{(1-x)_{om}dx}{(1-x)\ln(x-x^*)} = \frac{H}{(HTU)_{ox}} \tag{23}$$

and

$$(HTU)_{ox} = \frac{L}{K_{ox}a(1-x)_{om}C_{xm}S} \tag{24}$$

Weigand (48) has found that, if (1-x*) and (1-x) differ by no more than a factor of two then the use of an arithmetic average rather than a logarithmic average for $(1-x)_{om}$ leads to error of not more than 1.5 per cent. So, using the relation,

$$(1-x)_{om} = \frac{(1-x^*)+(1-x)}{2} \tag{25}$$

gives the equation

$$(NTU)_{ox} = \int_{x_2}^{x_1} \frac{dx}{x-x^*} + \frac{1}{2}\ln\left(\frac{1-x_2}{1-x_1}\right) \tag{26}$$

and the first term of Equation 26 can be found by plotting a curve of $1/x-x^*$ vs. x and integrating graphically between x_1 and x_2.

For the case of a straight equilibrium line which passes through the origin and for a straight operating line (L/G = constant), Colburn (4) has solved the resulting finite difference equation to obtain

$$(NTU)_{ox} = \frac{\ln\{(1-F)[(x_2-y_2/m)/(x_1-y_2/m)]+F\}}{1-F} \tag{27}$$

where F is called the extraction factor, L/mG.

SEPARATION BY DISCRETE STAGES

A large proportion of industrial separations are performed in equipment in which the interphase contacting is done countercurrently in stages. The two phases are intimately mixed and then separated and led independently to the adjacent stages. The contact between the phases as they move through the device is intermittent rather than continuous.

In an ideal, or equilibrium, stage, the phases are mixed long enough so that the streams leaving the stage are in equilibrium, and the phases are mixed so that there are no gradients of concentration in them. But in a real stage, there may not be sufficient contact between the phases to bring the streams into equilibrium. The overall efficiency η is defined as the ratio of the number of ideal stages to the number of real stages:

$$\eta = \frac{N_{ideal}}{N_{real}} \tag{28}$$

Bennett and Myers (2) describe the following relation between the number of stages and the number of transfer units for the case of straight equilibrium, and operating lines,

$$N_{ideal} = \left(\frac{F-1}{\ln F}\right)(NTU)_{ox} \tag{29}$$

Substituting for $(NTU)_{ox}$ from Equation 27 gives

$$N_{ideal} = \frac{\ln\{(1-F)[(x_2-y_2/m)/(x_1-y_2/m)]+F\}}{\ln(1/F)} \qquad (30)$$

and one can find N_{real} from Equation 28,

$$N_{real} = N_{ideal}/\eta \qquad (31)$$

MODELLING OF LIQUID-LIQUID EXTRACTION COLUMNS

A variety of attempts have been made to design liquid-liquid extraction columns utilizing available correlations for dropsize, holdup of dispersed phase, flooding velocity, mass transfer coefficients and axial mixing effects. Such correlations, in many cases, are presently based on very limited data and thus their use, while technically correct, lacks experimental verification.

Before a simulation study of the design or performance of a liquid-liquid extraction column can be confidently carried out, a suitable model representing the physical processes occurring in the column must be developed.

In the simplest model it is assumed that solute is transferred between two immiscible phases flowing counter-currently in plug flow. The model can be made more accurate by assuming that there is backmixing or longitudinal dispersion in each phase.

The recognition of backmixing as an important factor in the design of liquid-liquid extraction columns is now firmly established but its use requires that additional process parameters be known. Two mathematical models which include backmixing are available. The first model assumes that there are individual stages in the column and is called a stagewise model. The second approach is based on a continuous or a differential concept and is called a diffusion model.

The development of both models and experimental verification of their usefulness have been extensively treated in the literature over the past twenty years but despite the mass of published material, the ability to design extraction columns or to predict column performance has not become commonly accepted.

Stagewise Backmixing Model

This model has been introduced by Sleicher (40) and developed by many other authors, such as Miyauchi and Vermeulen (32), and Hartland and Mecklenburgh (13).

A typical section of a countercurrent column for which a stagewise analysis has been applied is shown diagrammatically in Figure 2, along with a phase disengaging section at each end. The heavy phase flows from the top and is contacted with the light phase which rises from the bottom. In addition to the main flows, two hypothetical flows in the opposite direction of the main flow are used to represent backmixing. Accommodation is made for backmixing in each phase by the inclusion of the backmixing coefficients e_x and e_y defined by

$$e_x = \overline{L}/L \quad \text{and} \quad e_y = \overline{G}/G$$

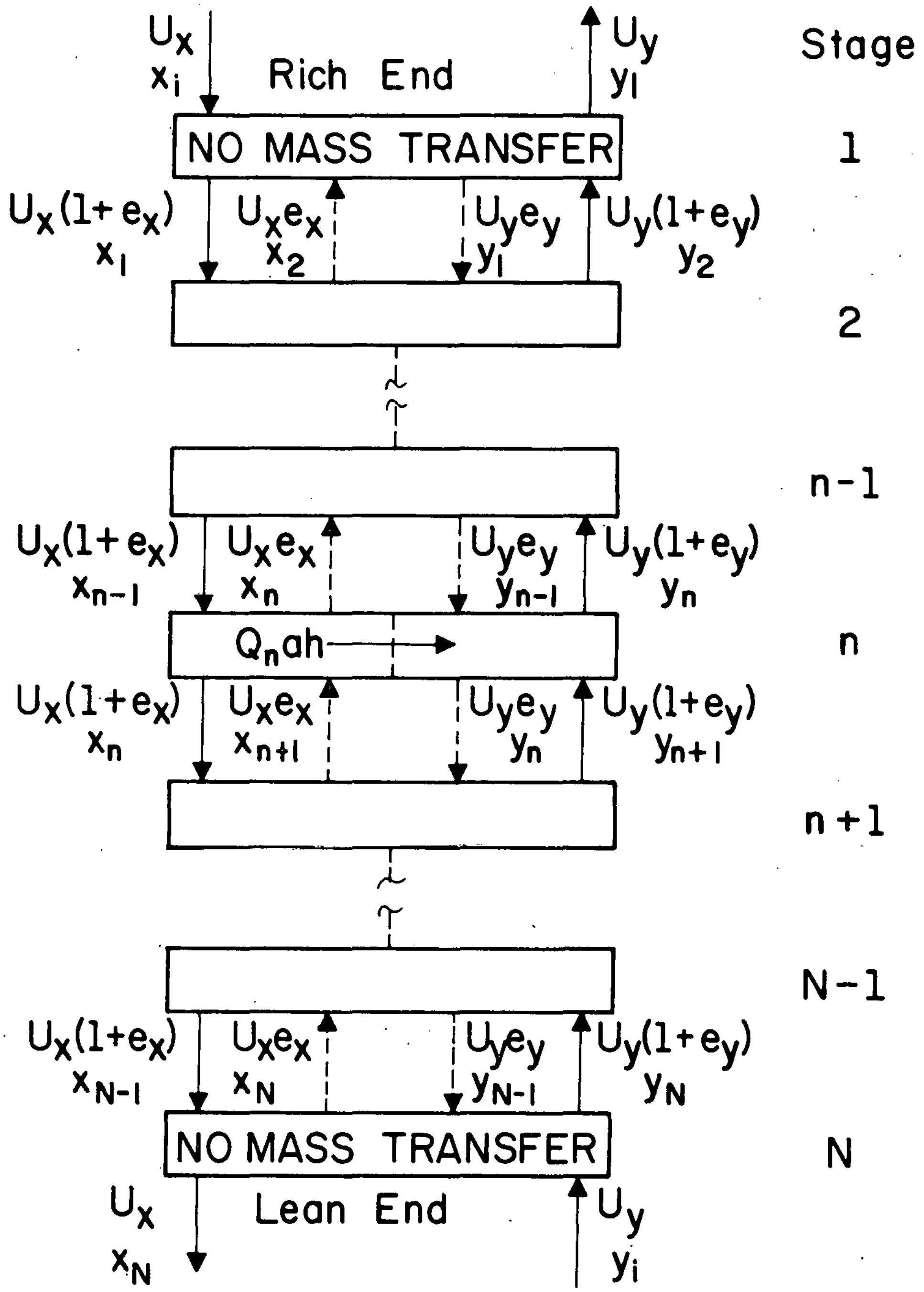

Figure 2. Diagrammatic representation of stagewise backmixing model

where e_x represents the fraction of the heavy phase flow $\overline{L}$ which is flowing between stages in an opposite direction to the bulk heavy phase flow and e_y is defined similarly for the light phase.

The following assumptions are used to construct the material balance equations:

1. e_x and e_y are constants, independent of the stage number and solute concentration.
2. The volume of each stage is constant and of this volume a constant fraction h_x is heavy phase and a constant fraction h_y is light phase, such that $h_x + h_y = 1$.
3. At each end of the column is a phase disengagement section represent by an unmixed stage in which it is assumed that no mass transfer occurs.
4. One component only is being transferred between phases according to the linear equilibrium relationship:

   $$y = mx^* + b$$

   Where y is the concentration of solute in the light phase and x^* the concentration of solute in the heavy phase which would be in equilibrium with y.

5. Mass transfer occurs according to the equation:

   $$Q_n = k_{ox}(x_n - x_n^*)$$

   Where Q_n is the rate of mass transfer in stage n and k_{ox} is the mass transfer coefficient per unit interfacial area based on x-phase, and it is independent of stage number.
6. Volume changes due to solute transfer are considered negligible.
7. The stages are assumed perfectly mixed, the concentration inside each being equal to its exit concentration.

Steady state solution

A material balance on the heavy phase around stage n gives

$$U_x(1+e_x)x_{n-1} - U_x(1+2e_x)x_n + U_x e_x x_{n+1} - Q_n ah = 0 \tag{32}$$

Where h is the height of a stage. In a similar manner, a solute balance on the organic phase around stage n gives:

$$U_y(1+e_y)y_{n+1} - U_y(1+2e_y)y_n + U_y e_y y_{n-1} + Q_n ah = 0 \tag{33}$$

There is no mass transfer at the end stages (Q_n=0), and also no backflow leaves the column. Therefore, the boundary condition at the top (n=1) will be

$$U_x x_{in} - U_x(1+e_x)x_1 + U_x e_x x_2 = 0$$

$$x_1 = \frac{x_{in} + e_x x_2}{1+e_x} \tag{34}$$

$$U_y(1+e_y)y_2 - U_y e_y y_1 - U_y y_1 = 0$$

$$y_1 = y_2 \tag{35}$$

At the bottom, n = N:

$$U_x(1+e_x)x_{N-1} - U_x e_x x_N - U_x x_N = 0$$

$$x_N = x_{N-1} \tag{36}$$

$$U_y y_{in} - U_y(1+e_y)y_N + U_y e_y y_{N-1} = 0$$

$$y_N = \frac{y_{in} + e_y y_{N-1}}{1+e_y} \tag{37}$$

Equations 32 and 33 may be put in dimensionless form by introducing the dimensionless compositions X and Y:

$$X = \frac{x-1/m(y_{in}-b)}{x_{in}-1/m(y_{in}-b)}$$

$$Y = \frac{1/m(y-y_{in})}{x_{in}-1/m(y_{in}-b)}$$

Hence Equations 32 and 33 become

$$(1+e_x)X_{n-1} - (1+2e_x)X_n + e_x X_{n+1} = (NTU_{ox})_{T1}(X_n-Y_n) \tag{38}$$

$$e_y Y_{n-1} - (1+2e_y) Y_n + (1+e_y) Y_{n+1}$$

$$= -(NTU_{ox})_{T1} F (X_n - Y_n) \qquad (39)$$

Where $F = U_x/mU_y$ and $(NTU_{ox})_{T1} = k_{ox}ah/U_x = (NTU_{ox})/N$ is the number of the true transfer units per stage based on the x-phase. Equations 38 and 39 can be put into finite difference form using the difference operator Δ, where $\Delta X_n = X_{n+1} - X_n$. If Y is eliminated, a 4th-order difference equation in X results. Expressed in E operator form, where $E = 1+\Delta$, the equation is

$$\{e_x(1+e_y)(E-1)^4 - [(1+e_y)(1+(NTU_{ox})_{T1})$$

$$- e_x(1-(NTU_{ox})_{T1}F)](E-1)^3$$

$$- [1+(NTU_{ox})_{T1}(e_xF+e_y-F+2)](E-1)^2$$

$$- (NTU_{ox})_{T1}(1-F)(E-1)\}X_n = 0 \qquad (40)$$

The solution of Equation 40 gives the X profile and the combination of this result with Equation 39 gives the Y-profile, as follows:

$$X_n = A_1 + A_2 d_2^n + A_3 d_3^n + A_4 d_4^n \qquad (41)$$

$$Y_n = A_1 + A_2 a_2 d_2^n + A_3 a_3 d_3^n + A_4 a_4 d_4^n \qquad (42)$$

Where the constants A_i are determined by the four boundary conditions (34), (35), (36), and (37). The a_i will be:

$$a_i = F\left[\frac{1-e_x(d_i-1)}{d_i+e_y(d_i-1)}\right] \qquad (43)$$

The d_i in Equations 41 and 42 are the roots of the equation

$$(d-1)^3 - \alpha'(d-1)^2 - \beta'(d-1)-\gamma' = 0 \qquad (44)$$

in which

$$\alpha' = \frac{(1+(NTU_{ox})_{T1})}{e_x} - \frac{(1-(NTU_{ox})_{T1}F)}{(1+e_y)}$$

$$\beta' = (NTU_{ox})_{T1}[1/e_x+F/(1+e_y)] + \frac{1+(NTU_{ox})_{T1}(1-F)}{e_x(1+e_y)}$$

$$\gamma' = \frac{(NTU_{ox})_{T1}(1-F)}{e_x(1+e_y)}$$

Hartland and Mecklenburgh (13) have given the full analytical solutions to the stagewise case by evaluating all of the roots of Equation (44). However, the resulting equations are complex and difficult to use for design purposes where the number of stages is required. Calculation of the exit concentrations from Equations 41 and 42 in order to find the total number of stages is not convenient for rapid design purposes. A simplified approximate solution for calculating the exit concentrations X and Y, and the number of stages has been given by Pratt (35) who examined the characteristics of the roots of Equation 44 and used their unique properties to eliminate the more insignificant terms in the solution. With this simplification, Pratt's approximate solution is

$$N = \frac{\log \dfrac{a_4(d_2-1)(d_4-d_3)(F-Y_{out})}{F^2(d_3-1)(d_4-d_2)(1-Y_{out})}}{\log d_4} \tag{45}$$

If the outlet X-phase composition is specified, the corresponding value of Y_{out} is given by the overall material balance

$$Y_{out} = F(1-X_{out}) \tag{46}$$

Pratt found that Equation 45 is of adequate accuracy for most design purposes if four or more actual stages are required, even with very high backmixing ratios.

The stagewise model reduces to other recognized models at extreme values of e_x, e_y and N. When $e_x = e_y = 0$ it becomes the theoretical stage model with no backmixing. When e_x and $e_y \to \infty$ or N=1 the model reduces to one perfectly mixed stage. When $N \to \infty$ at finite e_x and e_y it becomes the differential model with no backmixing. When N, e_x and $e_y \to \infty$ and e_x/N and e_y/N remain finite it becomes the differential model with backmixing. Such relations have been shown by Hartland and Mecklenburgh (13).

Differential Backmixing Model

The differential model has been studied by Eguchi and Nagata (6), Miyauchi and Vermeulen (33), Sleicher (41) and Hartland and Mecklenburgh (13).

With reference to Figure 3 a solute mass balance over the element dz for the x and y phases yields the following set of differential equations based on assumptions will be mentioned later. In general the material balance equation is:

In - Out = Accumulation

At steady state it becomes,

In - Out = 0

For the x-phase the equation is,

$$E_x \frac{dx}{dz}\bigg|_{z+dz} - E_x \frac{dx}{dz}\bigg|_z + U_x x\bigg|_z - U_x x\bigg|_{z+dz}$$

$$- K_{ox} a(x-x^*)dz = 0$$

Dividing both sides by dz and taking the limit gives

$$E_x \frac{d^2x}{dz^2} - U_x \frac{dx}{dz} - K_{ox} a(x-x^*) = 0 \qquad (47)$$

and when converted to dimensionless form it becomes,

$$\frac{1}{p_x} \frac{d^2X}{dZ^2} - \frac{dX}{dZ} - (NTU_{ox})_T (X-Y/m) = 0 \qquad (48)$$

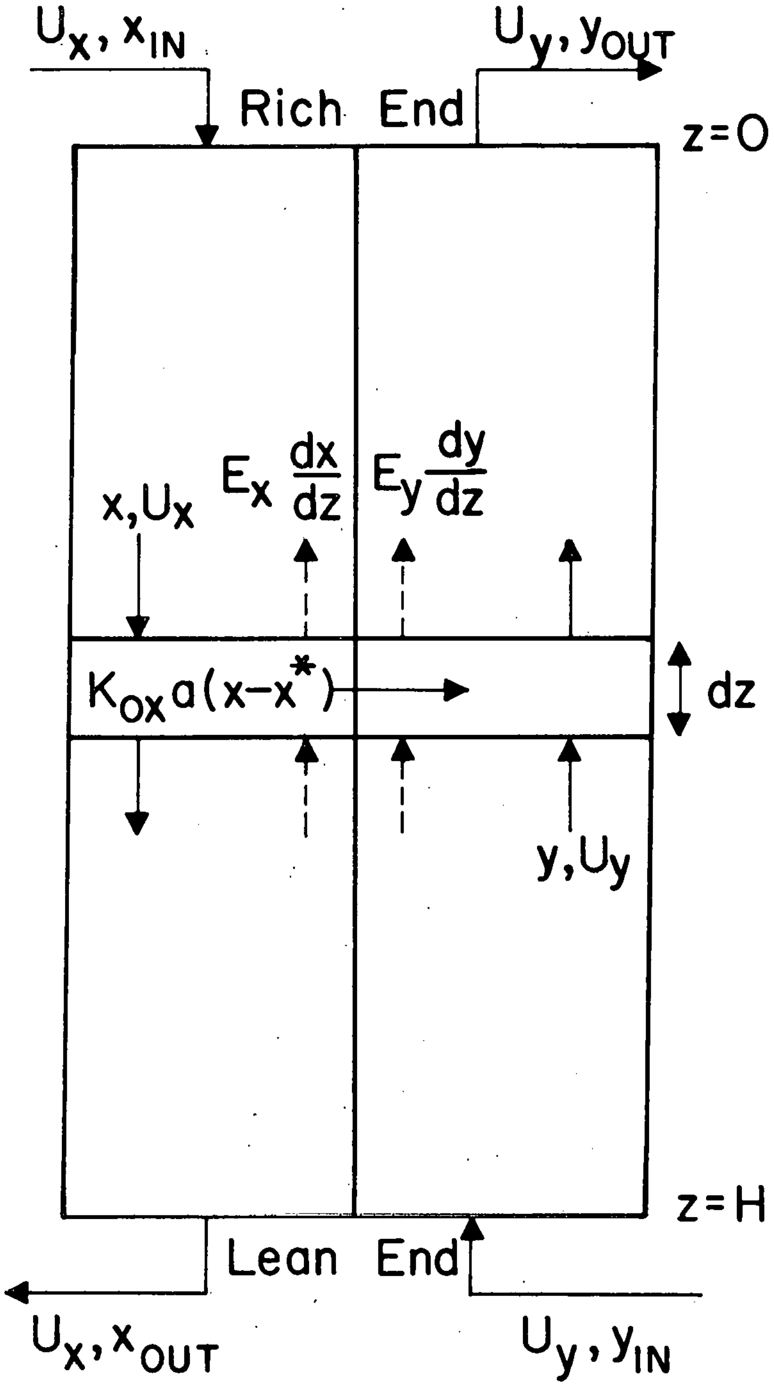

Figure 3. Schematic representation of differential backmixing model

where $(NTU_{ox})_T = K_{ox}aH/U_x$ is the true number of transfer units, $P_x = U_xH/E_x$ and $P_y = U_yH/E_y$ are the Peclet numbers for the x and the y phases, respectively, $F = U_x/mU_y$ is the extraction factor, $X = x/y_{in}$, $Y = y/y_{in}$, $Z = z/H$ and $y = mx^*$. Similarly, for the y phase:

$$E_y \frac{d^2y}{dz^2} + U_y \frac{dy}{dz} + K_{ox}a(x-x^*) = 0 \qquad (49)$$

or:

$$\frac{1}{P_y} \frac{d^2Y}{dZ^2} + \frac{dY}{dZ} + (NTU_{ox})_T(X-Y/m) = 0 \qquad (50)$$

The boundary conditions are obtained by taking balances around the ends of the contactor. Neglecting concentration changes at both outlets, the boundary conditions are the familiar equations of Danckwerts:

$$\begin{aligned} &\text{At } Z = 0 \quad dX/dZ = P_x(X-X_{in}) \quad \text{and} \quad dY/dZ = 0 \\ &\text{At } Z = 1 \quad dX/DZ = 0 \qquad\qquad\quad \text{and} \quad dY/dZ = P_y(1-Y) \end{aligned} \qquad (51)$$

<u>Steady state solution</u>

Combining Equations 48 and 50 and rearranging in dimensionless form, the result is the following differential equation representing the solute concentration in the x phase as a function of height:

$$\frac{d^4X}{dZ^4} - (P_x-P_y)\frac{d^3X}{dZ^3} - (P_x(NTU_{ox})_T + P_xP_y + P_y(NTU_{ox})_TF)\frac{d^2X}{dZ^2} - (NTU_{ox})_TP_xP_y(1-F)\frac{dX}{dZ} = 0 \tag{52}$$

The general solution to Equation (52) is,

$$X = A_1e^{m_1Z} + A_2e^{m_2Z} + A_3e^{m_3Z} + A_4 \tag{53}$$

where m_1, m_2, m_3 and m_4 are the roots of the equation,

$$m[m^3-(P_x-P_y)m^2-(P_x(NTU_{ox})_T+P_xP_y+P_y(NTU_{ox})_TF)m - (NTU_{ox})_TP_xP_y(1-F)] = 0 \tag{54}$$

By using a digital computer program based on Equations 52 and 51 one can find concentration profiles in the x phase.

In the special case where there is no axial mixing, E_x and E_y are assumed to be negligible, and from Equations 47 and 49 one can obtain

$$\frac{d^2X}{dZ^2} - (NTU_{ox})_T(F-1)\frac{dX}{dZ} = 0 \tag{55}$$

The boundary conditions for this case are,

At $Z = 0$ $\quad X = X_{in}$

At $Z = 1$ $\quad X = 0$

And hence the model becomes a plug flow model.

When E_x and $E_y \to \infty$ there is complete mixing in both phases and Equation 52 reduces to that of a stirred tank.

Comparison of the Differential and Stagewise Model

With the availability of the design Equations 45 and 46 it would appear desirable to interpret and present backmixing data for stagewise models rather than differential models. However, there is a real need in differential columns for reliable mass transfer data, in the form of true values of (NTU) or (K_{ox}) and (a) before the design of these contactors can be put on a satisfactory theoretical basis.

Hartland and Mecklenburgh (13) related the differential and stagewise models by using the first and second order finite difference equations of the form

$$
\begin{aligned}
&X = X_n \qquad Y = Y_n \qquad Z = n/N \\
&dX/dZ = (X_{n+1}-X_{n-1})N/2 \\
&dY/dZ = (Y_{n+1}-Y_{n-1})N/2 \qquad\qquad (56) \\
&d^2X/dZ^2 = N^2(X_{n+1}-2X_n+X_{n-1}) \\
&d^2Y/dZ^2 = N^2(Y_{n+1}-2Y_n+Y_{n-1})
\end{aligned}
$$

Substitution of these equations in the differential Equations 48 and 49 and comparison of the result with Equations 38 and 39 for the stagewise model gives

$$\frac{e_x}{N} + \frac{1}{2N} = \frac{1}{P_x} \quad \text{and} \quad \frac{e_y}{N} + \frac{1}{2N} = \frac{1}{P_y} \qquad (57)$$

When N, e_x and $e_y \to \infty$ so that e_x/N and e_y/N remain finite, then

$$e_x/N = 1/P_x \quad \text{and} \quad e_y/N = 1/P_y \qquad (58)$$

Thus under these conditions the differential and the stagewise models are identical.

A complete list of the identities needed to convert a stagewise process into a differential one is given in Table 1 (13).

Table 1. Conversion of stagewise equation governing back-mixing to the equivalent differential equation

$N\to\infty$	Finite N
$e_x/N = 1/P_x$	$e_x/N + 1/2N = 1/P_x$
$e_y/N = 1/P_y$	$e_y/N + 1/2N = 1/P_y$
$n/N = Z$	$n/N = Z$
$N(NTU_{ox})_{T1} = (NTU_{ox})_T$	$(NTU_{ox})_{T1} = (NTU_{ox})_T/N$
$(NTU_{ox})_{T1} = 0$	

THE EFFECT OF AXIAL MIXING ON THE CONCEPT OF NUMBER OF TRANSFER UNITS IN PULSED PERFORATED PLATE COLUMNS

Since the conception of the pulsed column (46) in 1935 and its successful application in contacting highly corrosive, dangerously radioactive liquids and in the extraction and separation of metals from solutions in the atomic energy industry in 1949 (38), a great deal of experimental effort has been expended, principally for the purpose of evaluating column performance for design and scale-up. Backmixing has a substantial effect upon the operation of these mass transfer devices, because it leads to:

1. A decrease in concentration driving force and an adverse effect on the mass transfer rate between phases. This is illustrated in Figure 4 in which the broken curves represent the concentration profiles in the feed and the solvent phase for a particular case without axial mixing and the solid curves represent the same case with axial mixing. There are concentration jumps at the points where feed and solvent enter. Figure 5 shows the distribution diagram with operating lines B'J' for the case of axial mixing and A'C' for the case of piston flow ($E_y = 0$, $E_x = 0$). It follows from this graph that, as the degree of longitudinal

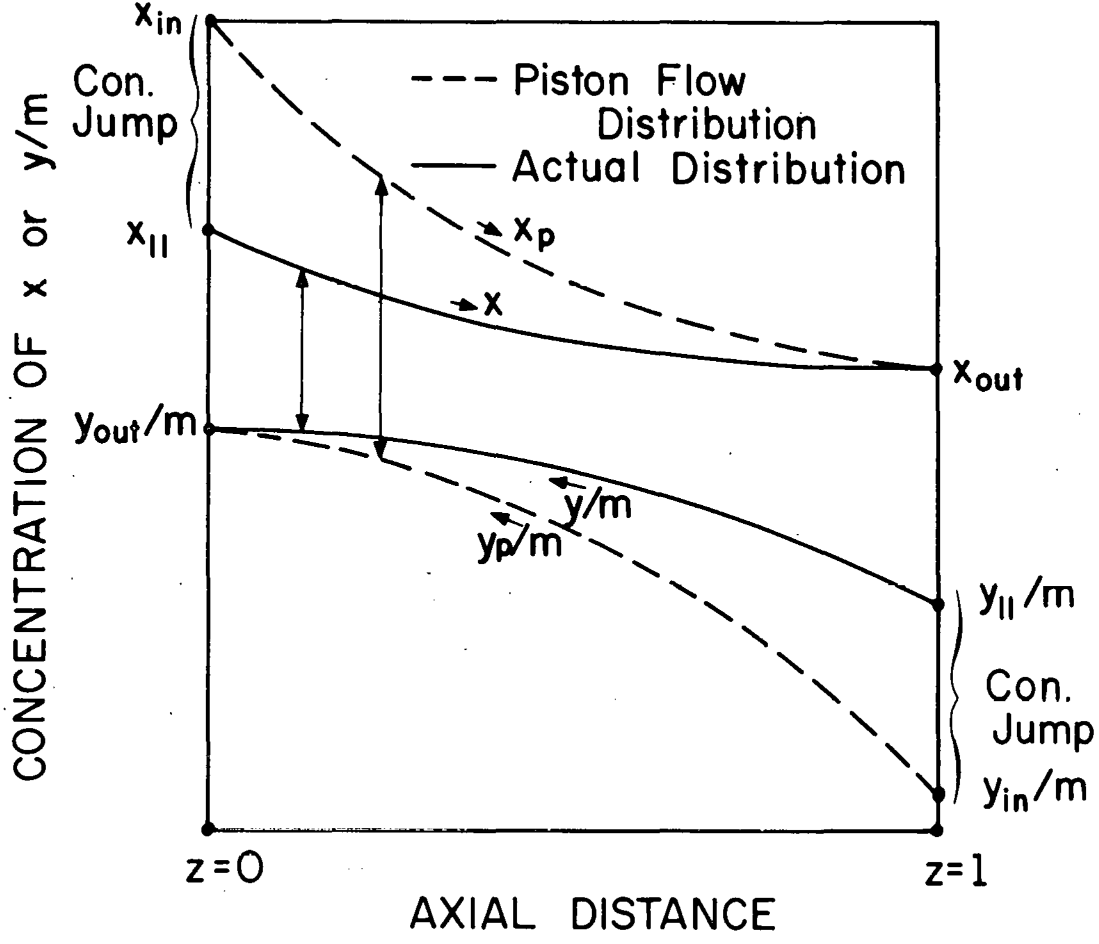

Figure 4. Concentration distribution in extraction column for piston flow and actual flow

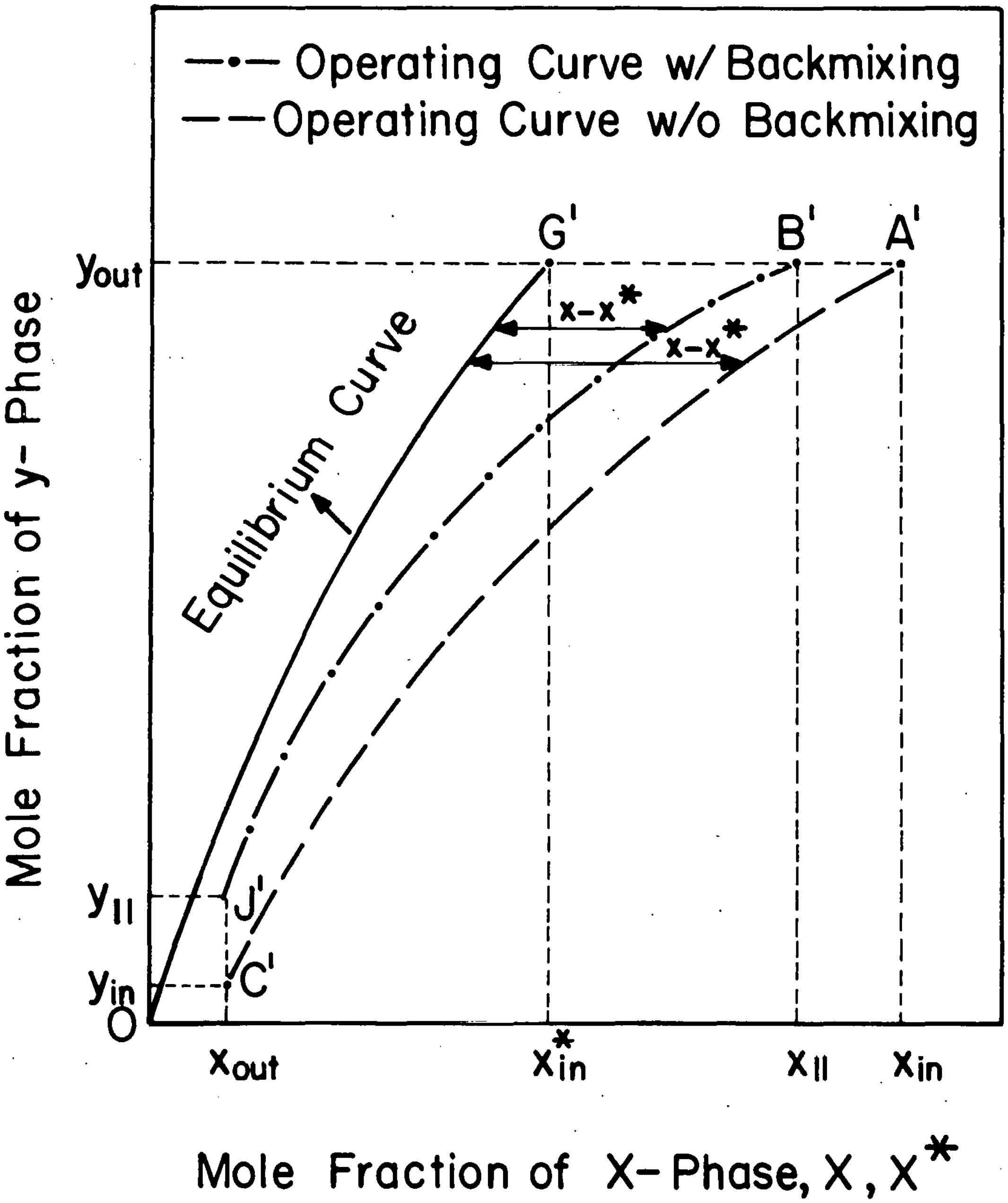

Figure 5. Concentration profiles in both phases and corresponding distribution diagram with operating line

mixing increases, the driving force (x-x*), based on the x-phase concentration, for example, decreases and the operating line approaches the equilibrium line until they coincide and the indicated degree of separation is no longer possible with a column of finite height.

2. A decline in extraction efficiency, because, as cited in part 1, axial mixing reduces the mass transfer rate between phases and thus the result is a decrease in efficiency.
3. It is clear that in the case of axial mixing the height of the column has to be increased to arrive at the same degree of separation.
4. With backmixing present, the concept of HTU and NTU are somewhat clouded because HTU and NTU become a function of the contactor length and of the backmixing coefficients. Hartland and Mecklenburgh (14) showed theoretically that

$$(HTU_{ox})_p = \frac{E_x/U_x+E_y/U_y+U_x/K_{ox}a}{1-l_x/H-l_y/H+E_x/U_xH+E_y/U_yH} \qquad (59)$$

In which l_y is the length of the region near the y phase outlet and l_x is the length of the region near the x phase outlet. From Equation (59) it is obvious that the HTU increases with increased backmixing. For low backmixing and large contactor length Equation (59) may be written in the form

$$(\mathrm{HTU}_{ox})_p = \frac{U_x}{K_{ox}a} \tag{60}$$

and one can think in terms of a constant HTU. The above process has been practically shown in Figure 6 by Hartland and Mecklenburgh (14).

Therefore, for design calculation for pulse columns with backmixing, it is necessary to separate the mass transfer coefficients and backmixing coefficients in the simulation model.

In the analysis of longitudinal dispersion in a continuous column Miyauchi and Vermeulen (33) introduced three different NTU's for mass transfer:

1. The true NTU, which arises from the original definition of the height of a transfer unit proposed by Chilton and Colburn (3):

$$(\mathrm{NTU}_{ox})_T = K_{ox}aH/U_x \tag{61}$$

$$(\mathrm{NTU}_{ox})_T(\mathrm{HTU}_{ox})_T = H \tag{62}$$

where K_{ox} is the true overall mass transfer coefficient based on the x phase, a is the interfacial area, H is the length of column and U_x the superficial velocity of the x phase.

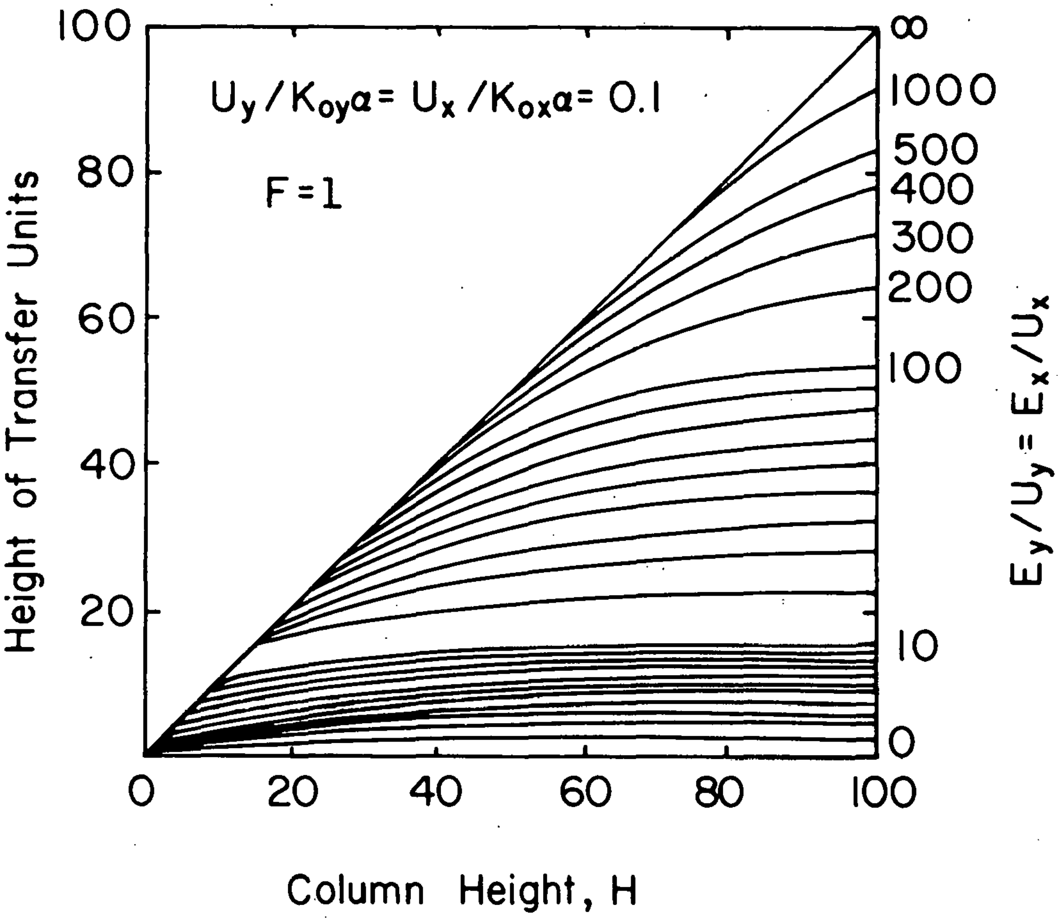

Figure 6. Variation of height of a transfer unit with contactor length for different backmixing coefficients such that $E_y/U_y = E_x/U_x$ when $U_y/K_{oy}a = U_x/K_{ox}a = 0.1$ and $F = 1$

2. The plug flow or apparent NTU defined in terms of the end concentration of the x phase for a dilute solution (straight operating and equilibrium lines),

$$(NTU_{ox})_p = \int_{x_{out}}^{x_{in}} \frac{dx}{x-x^*} \tag{63}$$

where x* is the x concentration in equilibrium with the concentration in the other phase and $y = mx^*$.

As mentioned before, the logarithmic mean driving force is appropriate for dilute solution, thus:

$$(NTU_{ox})_p = \frac{x_{in}-x_{out}}{(x-x^*)_{ln}} \tag{64}$$

But $y = mx^*$, therefore:

$$(NTU_{ox})_p = \frac{1}{((y_{out}-y_{in})/m(x_{in}-x_{out}))-1} \ln \frac{(y_{in}-mx_{out})}{y_{out}-mx_{in}} \tag{65}$$

$$(NTU_{ox})_p (HTU_{ox})_p = H \tag{66}$$

3. The measured NTU, which is similar to the $(NTU_{ox})_p$ but is based on the true operating curve, i.e., the actual concentration profile measured in the column. It includes the backmixing effect. In Figure 4 the concentration profile for phase x and

phase y as measured by Geankoplis and coworkers (7, 8, 22) and by Gier and Hougen (10) are shown. The measured NTU may be expressed in terms of the distance between the curves, i.e., x - y/m:

$$(NTU_{ox})_M = \int_{x_{out}}^{x_{11}} \frac{dx}{x-x^*} = \int_{x_{out}}^{x_{11}} \frac{dx}{x-y/m} \qquad (67)$$

As shown in Figure 4, x_{11} is the "concentration jump" from x_{in}.

In general, one will find that $(NTU_{ox})_T \geq (NTU_{ox})_M \geq (NTU_{ox})_p$ because both $(NTU_{ox})_p$ and $(NTU_{ox})_M$ include the effect of longitudinal mixing in each phase. Also, $(HTU_{ox})_p \geq (HTU_{ox})_M \geq (HTU_{ox})_T$.

To compute $(NTU_{ox})_p$, $(NTU_{ox})_M$, and $(NTU_{ox})_T$ for a pulse column from experimental concentration values, Smoot and Babb (42) obtained experimental data in which concentration values were measured in terms of a differential backmixing model. The systems studied in this investigation were methyl isobutyl ketone-acetic acid-water (M.I.K.-HAC-H_2O), and trichloroethane-acetone-water (T.C.E.-Acetone-H_2O).

Solute transfer was from the organic phase to the aqueous phase, and hence, the Equations (47), (49) and (52) become

$$E_x \frac{d^2x}{dz^2} - U_x \frac{dx}{dz} + K_{ox}a(x^*-x) = 0 \qquad (68)$$

$$E_y \frac{d^2y}{dz^2} + U_y \frac{dy}{dz} - K_{ox}a(x^*-x) = 0 \qquad (69)$$

$$\frac{d^4X}{dZ^4} - (P_x-P_y)\frac{d^3X}{dZ^3} - (P_x(NTU_{ox})_T + P_xP_y + P_y(NTU_{ox})_T F)\frac{d^2X}{dZ^2} - (NTU_{ox})_T P_x P_y (1-F)\frac{dX}{dZ} = 0 \qquad (70)$$

where $F = U_x/mU_y$.

An integration of Equation (68) yields the true NTU as:

$$\frac{1}{U_x} K_{ox}a \int_0^H dz = \int_{x_{11}}^{x_{out}} \frac{dx}{x^*-x} + \frac{E_x}{U_x}\int_0^H \frac{1}{x-x^*}\frac{d^2x}{dz^2}\, dz \qquad (71)$$

This is equivalent to

$$(NTU_{ox})_T = (NTU_{ox})_M + \text{Correction Term}$$

Smoot and Babb (42) commented that the numerical integration of the second derivative (d^2x/dz^2) in Equation 71 is highly inaccurate and therefore the graphical integration of the above integral is not a good way to calculate the true NTU. Consequently, a simple method is to assume different values of $(NTU_{ox})_T$ and calculate the concentration profile using the differential backmixing model (Equations 70 and 51). By a numerical integration for each profile $(NTU_{ox})_M$ is evaluated and then by using these data and a machine interpolation, the true NTU value which corresponds to the measured NTU value can be obtained. These results have been summarized in Table 2. The backmixing coefficients (E_x and E_y) are determined either by a steady state tracer injection method or by some type of unsteady injection at the inlet such as the delta or impulse injection technique.

Table 2. Summary of experimental and calculated data

Run No.	Cartridge No.[a]	H,Ft.	A,Ft.	f,Hr.$^{-1}$	U_x Ft./Hr.	U_y Ft./Hr.	E_x Sq.Ft./Hr.	E_y Sq.Ft./Hr.	$(NTU_{ox})_P$	$(NTU_{ox})_M$	$(NTU_{ox})_T$
					Methyl Isobutyl Ketone-Acetic Acid-Water						
1	1	1.96	0.0833	4200	42.0	27.2	5.24	3.84	1.70	2.76	2.45
2	1	1.96	0.0833	4200	27.0	42.0	7.27	1.20	2.84	5.30	5.42
3	1	1.96	0.0833	1800	42.0	42.0	4.39	0	1.05	1.27	1.27
4	1	1.96	0.0833	1800	27.0	27.2	4.69	0	1.18	1.52	1.50
5	1	1.96	0.0421	1800	42.0	27.2	3.67	0	0.75	0.86	0.84
6	1	1.96	0.0421	1800	27.0	42.0	5.08	0	1.54	1.54	1.66
7	1	1.96	0.0421	4500	27.0	27.2	6.23	0	1.07	1.70	1.66
8	1	1.96	0.0421	4200	42.0	42.0	5.68	0	0.91	1.04	1.05
9	1	1.96	0.0421	4200	27.0	27.2	6.07	0	1.02	1.35	1.35
10	2	1.96	0.0421	4200	27.0	42.0	8.53	0	1.50	1.25	1.41
11	2	1.96	0.0421	4200	42.0	27.2	6.14	0	0.65	0.84	0.81
12	2	1.96	0.0421	1800	42.0	42.0	5.15	0	0.92	0.98	0.99
13	2	1.96	0.0421	1800	27.0	27.2	5.51	0	0.99	1.07	1.09
14	2	1.96	0.0833	4200	27.0	27.2	7.87	1.61	2.00	5.16	4.38
15	2	1.96	0.0833	4200	42.0	42.0	7.37	2.60	1.78	2.76	2.60
16	2	1.96	0.0833	1800	42.0	27.2	4.76	0	0.686	0.82	0.80
17	2	1.96	0.0833	1800	27.0	42.0	6.60	0	1.34	1.41	1.54
18	3	1.97	0.0833	4200	42.0	42.0	4.79	1.62	2.29	3.58	3.31
19	3	1.97	0.0833	4200	27.0	27.2	5.12	1.60	2.65	5.05	4.41
20	3	1.97	0.0833	1800	27.0	42.0	4.29	0	1.79	2.01	2.10
21	3	1.97	0.0833	1800	42.0	27.2	3.09	0	0.99	1.25	1.19
22	3	1.97	0.0421	4200	42.0	27.2	4.00	0	0.97	1.10	1.05
23	3	1.97	0.0421	4200	27.0	42.0	5.55	0	1.73	1.99	2.11
24	3	1.97	0.0421	1800	42.0	42.0	3.35	0	1.35	1.21	1.21
25	3	1.97	0.0421	1800	27.0	27.2	3.38	0	1.36	1.54	1.52

[a] Cartridge characteristics are given in Table 3.

Table 2 (Continued)

Run No.	Cartridge No.[a]	H,Ft.	A,Ft.	f,Hr.$^{-1}$	U_x Ft./Hr.	U_y Ft./Hr.	E_x Sq.Ft./Hr.	E_y Sq.Ft./Hr.	$(NTU_{ox})_p$	$(NTU_{ox})_M$	$(NTU_{ox})_T$
26	4	1.97	0.0421	4200	42.0	42.0	5.62	0	1.10	1.26	1.26
27	4	1.97	0.0421	1800	27.0	42.0	5.03	0	1.52	1.35	1.44
28	4	1.97	0.0421	1800	42.0	27.2	3.63	0	0.74	0.71	0.70
29	4	1.97	0.0421	4200	27.0	27.2	6.0	0	1.47	1.33	1.33
30	4	1.97	0.0833	4200	27.0	42.0	7.19	2.10	2.99	5.79	5.92
31	4	1.97	0.0833	4200	42.0	27.2	5.18	2.54	1.88	2.94	2.55
32	4	1.97	0.0833	1800	42.0	42.0	4.34	0	1.09	1.10	1.10
33	4	1.97	0.0833	1800	27.0	27.2	4.64	0	1.18	1.25	1.25
34	4	1.97	0.0833	4200	27.0	27.2	6.31	2.60	2.56	7.04	5.95
35	4	1.97	0.0833	5400	27.0	27.2	6.91	3.29	3.08	11.54	9.30
36	4	1.97	0.0833	3000	27.0	27.2	5.58	0	1.38	1.91	1.84
37	4	1.97	0.0421	1800	27.0	27.2	4.42	0	1.04	1.10	1.11
38	4	1.97	0.0421	5400	27.0	27.2	6.57	0	1.36	1.95	1.86
39	4	1.97	0.0421	3000	27.0	27.2	5.31	0	1.08	1.17	1.18
40	4	1.97	0.0625	4200	27.0	27.2	6.18	0	1.34	2.10	2.00
41	2	2.00	0.0833	4200	27.0	28.0	7.90	1.61	2.18	4.65	4.06
42	2	2.00	0.0833	3000	27.0	28.0	7.00	1.61	1.29	1.67	1.67
43	2	2.00	0.0833	5400	27.0	28.0	8.70	0	2.82	12.50	8.81
44	2	2.00	0.0421	4200	27.0	28.0	7.55	0	1.02	1.23	1.26
45	2	2.71	0.0833	4200	27.0	28.0	7.93	1.61	2.88	5.89	5.01
46	2	2.71	0.0833	3000	27.0	28.0	7.02	0	1.62	2.85	2.64
47	2	2.71	0.0421	4200	27.0	28.0	7.52	0	1.59	1.58	1.56
48	2	3.27	0.0833	4200	27.0	28.0	7.93	0	3.64	15.57	11.07
49	2	3.27	0.0833	3000	27.0	28.0	7.02	0	2.14	3.44	3.13
50	2	3.27	0.0421	4200	27.0	28.0	7.54	0	1.66	2.50	2.36
51	2	3.93	0.0833	3000	27.0	28.0	7.02	0	2.57	4.42	3.94
52	2	3.93	0.0421	4200	27.0	28.0	7.54	0	2.00	2.56	2.42

Table 2 (Continued)

Run No.	Cartridge No.[a]	H,Ft.	A,Ft.	f,Hr.$^{-1}$	U_x Ft./Hr.	U_y Ft./Hr.	E_x Sq.Ft./Hr.	E_y Sq.Ft./Hr.	$(NTU_{ox})_P$	$(NTU_{ox})_M$	$(NTU_{ox})_T$
					1,1,2-Trichoroethane-Acetone-Water						
53	4	2.08	0.0833	4200	52.1	71.5	9.85	0	3.38	3.41	4.47
54	4	2.08	0.0833	4200	6.84	54.1	8.02	0	1.62	1.69	1.88
55	4	2.08	0.0833	2400	68.4	71.5	7.12	0	1.52	1.56	1.72
56	4	2.08	0.0833	2400	52.1	54.1	7.39	0	1.46	1.46	1.66
57	4	2.08	0.0421	4200	68.4	71.5	8.30	0	1.47	1.51	1.69
58	4	2.08	0.0421	4200	52.1	54.1	8.00	0	1.65	1.58	1.84
59	4	2.08	0.0421	2400	52.1	71.5	7.65	0	1.94	1.89	2.22
60	4	2.08	0.0421	2400	68.4	54.1	6.23	0	1.37	1.34	1.44
61	4	2.08	0.0833	4200	52.1	46.0	9.06	0	2.02	2.06	2.45
62	4	2.08	0.0833	6000	52.1	46.0	10.0	0	4.20	3.81	4.95
63	4	2.08	0.0421	2400	52.1	54.1	7.03	0	1.55	1.54	1.75
64	4	2.08	0.0421	6000	52.1	54.2	9.80	0	1.98	2.02	2.45

Table 3. Pulsed column cartridges performed by Smoot and Babb (42)

Cartridge No.	Plate Spacing, Ft.	Plate Hole Diam. Ft.	Plate Free Area, %	Column Diam., Ft.
1	0.183	0.0052	23	0.167
2	0.183	0.0104	23	0.167
3	0.132	0.0052	23	0.167
4	0.132	0.0104	23	0.167

EVALUATION OF THE BACKMIXING COEFFICIENTS

The steady state method consists of injecting a steady and continuous stream of tracer at some point and measuring the resultant steady state concentration profile of back-mixed tracer along the column. Mathematically the steady state method can be expressed by

$$J_z = -E_x \frac{dc}{dz} + U_x c \qquad (72)$$

Assuming that fluid velocity is uniform across the column and eddy diffusivity is constant, integration of Equation 72 for steady state conditions yields

$$\ln \frac{c}{c_0} = \frac{U_x}{E_x} z + B \qquad (73)$$

where c_0 is the concentration of tracer in the column outlet and B is constant of integration. Thus, a plot of $\ln \frac{c}{c_0}$ vs. distance (z) will give a line with a slope equal U_x/E_x.

In the impulse method (5) dye tracers are used (a dye for the x phase insoluble in the y phase and a dye for the y phase insoluble in the x phase). Continuous recording of dye concentration in the flows of both phases passing from the column are accomplished by a photocolorimeter and a recording potentiometer.

In the delta injection technique, the tracer is introduced into either the x phase or the y phase at a distance l from the inlet. Concentrations of the phase containing tracer are obtained at a distance (l+z) from the inlet at various times after tracer injection. The simplest way to describe this change is to calculate the variance of the concentration curve by using the formula presented by Levenspiel and Smith (25). The variance is defined as

$$\sigma_t^2 = \frac{\int_0^\infty t^2 c dt}{\int_0^\infty c dt} - \left(\frac{\int_0^\infty t c dt}{\int_0^\infty c dt}\right)^2 \tag{74}$$

It is related to the dispersion coefficient as follows,

$$\sigma_t^2 = 1/U_x^4 (8E_x^2 + 2E_x U_x z) \tag{75}$$

This formula was derived for the dispersion model assuming there is no mass transfer and that all the solute was introduced into the column in the same time. Differentiation of Equation 75 with respect to the height z gives

$$\frac{d\sigma_t^2}{dz} = \frac{2E_x}{U_x^3} \tag{76}$$

If σ_t^2 is plotted against z, the dispersion coefficient E_x may easily be calculated from the slope. To calculate the parameters e_x or e_y for the stagewise model, Miyauchi and Vermeulen (32) recommend an empirical formula:

$$\frac{E_x}{U_x z} = \frac{N}{(N-1)(2N+1)} + \frac{2e_x}{2N-1} \qquad (77)$$

which comes from an analysis of the stagewise and the differential models and the conditions under which they are mathematically equal. Combining Equations 76 and 77 gives,

$$\frac{d\sigma_t^2}{dz} = \frac{2z}{U_x^2}\left[\frac{N}{(N-1)(2N+1)} + \frac{2e_x}{2N-1}\right] \qquad (78)$$

from which e_x may be calculated. Also, for evaluating the dispersion coefficient, Miyauchi and Vermeulen (32) have presented the following equation:

$$\frac{E_i/h_i}{Afh} = \frac{U_i/Afh_i}{2\beta-(1/N)} + \frac{1}{\beta} \qquad (79)$$

where h_i is the volume fraction of phase i and h is the axial height of one compartment. β is defined as a superficial number of perfectly mixed plates in each compartment and is commonly between 1 and 2. β is given by the equation

$$\beta = 0.57(D_t^2\ h)^{1/3}/(d_h/s) \qquad (80)$$

In which d_h is hole diameter of perforation and s is the fraction of total free hole area.

RESULTS AND DISCUSSION

In order to obtain the true NTU or the true overall mass transfer coefficient for a Purex plant-size column from existing data, the only possible method at present is to determine the $(NTU_{ox})_T$ from experimental data on small size pulse columns and use this information for scale-up to large columns. Unfortunately, such experiments even on small size columns are very few. Only a limited amount of work in this area has been done by Smoot and Babb (42), Kagan, et al. (20), Miyauchi, et al. (31), Angelino and Molinier (1), Thornton (45), and Logsdail and Thornton (26). On the other hand, the plug flow NTU's are much easier to measure and to calculate because they only require that the end concentrations in the column to be known.

$(NTU_{ox})_p$ or $(HTU_{ox})_p$ values have been reported by a number of workers. Of particular interest is the data source on $(HTU_{ox})_p$ and $(NTU_{ox})_p$ from the Purex Technical Manual (36) for various Purex plant-size columns. The data were obtained from full-scale or nearly full-scale testing of prototypes of the Purex plant columns with "cold" tests conducted at the Hanford Laboratories and "hot" pilot plant tests conducted at Oak Ridge National Laboratory.

Here we analyze the literature data on NTUs (Table 2) reported by Smoot and Babb (42), and attempt to establish a relationship between $(NTU_{ox})_T$ and $(NTU_{ox})_p$ in order to estimate the true number of transfer units or column efficiency, which is defined as $\eta = \frac{(NTU_{ox})_p}{(NTU_{ox})_T}$.

The Effect of Dispersed Phase Flow Rate on Column Efficiency

The effect of U_y on $1/\eta$ is somewhat clouded because the various cartridges used have several variables which change simultaneously and it is difficult to determine a unique relationship between U_y and $1/\eta$. The effect of U_y appears to be very slight, as shown in Table 4.

Influence of Continuous Phase Flow Rate on Column Efficiency

As shown in Table 5, the effect of U_x is appreciable. With decreasing U_x, $1/\eta$ decreases and thus η increases.

The Effect of Combined or Total Flow Rate on Column Efficiency

The effect of U_x+U_y on $1/\eta$ at constant U_y/U_x is shown in Table 6. At high values of Af, with increasing U_x+U_y, $1/\eta$ decreases but at low values of Af the effect of U_x+U_y may be negligible.

Table 4. Selected data from Table 2 for system A.[a] Effect of U_y

Cartridge No.	Af	U_x	U_y	$1/\eta = (NTU_{ox})_T/(NTU_{ox})_p$
1	70	42.0	27.2	1.44
2	70	42.0	42.0	1.46
3	70	42.0	42.0	1.44
4	70	42.0	27.2	1.36
1	35	42.0	42.0	1.15
2	35	42.0	27.2	1.25
3	35	42.0	27.2	1.08
4	35	42.0	42.0	1.145
1	30	42.0	42.0	1.20
2	30	42.0	27.2	1.16
3	30	42.0	27.2	1.20
4	30	42.0	42.0	1.00
1	15	42.0	27.2	1.12
2	15	42.0	42.0	1.07
3	15	42.0	42.0	0.97
4	15	42.0	27.2	0.95

---

[a] System A - MIBK - HAC - H_2O.

Table 5. Selected data from Table 2 for system A.[a] Effect of U_x

Cartridge No.	Af	U_x	U_y	$1/\eta = (NTU_{ox})_T/(NTU_{ox})_p$
1	70	42.0	27.2	1.44
2	70	27.0	27.2	2.19
3	70	27.0	27.2	1.66
4	70	42.0	27.2	1.36
1	35	27.0	27.2	1.32
2	35	42.0	27.2	1.25
3	35	42.0	27.2	1.08
4	35	27.0	27.2	1.136
1	30	27.0	27.2	1.27
2	30	42.0	27.2	1.16
3	30	42.0	27.2	1.20
4	30	27.0	27.2	1.06
1	15	42.0	27.2	1.12
2	15	27.0	27.2	1.10
3	15	27.0	27.2	1.11
4	15	42.0	27.2	0.95

[a] System A - MIBK - HAC - H_2O.

Table 6. Selected data from Table 2 for system A.[a] Effect of U_x+U_y

Cartridge No.	Af	U_y/U_x	U_y+U_x	$1/\eta = (NTU_{ox})_T/(NTU_{ox})_p$
2	70	1.0	54.2	2.19
2	70	1.0	84.0	1.46
3	70	1.0	54.2	1.66
3	70	1.0	84.0	1.44
1	35	1.0	54.2	1.32
1	35	1.0	84.0	1.15
4	35	1.0	54.2	1.136
4	35	1.0	84.0	1.145
1	30	1.0	54.2	1.27
1	30	1.0	84.0	1.20
4	30	1.0	54.2	1.06
4	30	1.0	84.0	1.00
2	15	1.0	54.2	1.10
2	15	1.0	84.0	1.07
3	15	1.0	54.2	1.11
3	15	1.0	84.0	0.97

[a] System A - MIBK - HAC - H_2O.

Influence of U_y/U_x on Column Efficiency

As shown in Table 7, at constant U_x+U_y and at high values of Af, $1/\eta$ increases with increasing U_y/U_x but at low values of Af, this effect is insignificant.

The Effect of Frequency and Amplitude on Column Efficiency

From data shown in Table 8 and also in Figure 7, it can be seen that $(NTU_{ox})_T$ increases sharply with increasing A and with increasing f, and approaches almost a constant value when the column is operating in the emulsion region. From data in Table 8 and Figure 8 it can be concluded that $1/\eta$ increases very rapidly with increasing f and with increasing A.

For system B (T.C.E. - Acetone - H_2O) from Table 9, and Figures 9 and 10, one can see that as a result of the large density difference between phases and the high distribution coefficient little effect of f and A was observed on $(NTU_{ox})_T$ and $1/\eta$ over the range studied. Because of the large difference in density the organic droplets fall rapidly through the column with little or no mixing in the aqueous phase. Consequently, longitudinal mixing in this system has a small effect on the column performance. This effect assumes some importance when one attempts to generalize results obtained on only a few physical systems.

Table 7. Selected data from Table 2 for system A.[a] Effect of U_y/U_x

Cartridge No.	Af	U_y/U_x	U_y+U_x	$1/\eta = (NTU_{ox})_T/(NTU_{ox})_p$
1	70	0.648	69.2	1.44
1	70	1.55	69.2	1.90
4	70	0.648	69.2	1.36
4	70	1.55	69.2	1.98
2	35	0.648	69.2	1.25
2	35	1.55	69.2	1.085
3	35	0.648	69.2	1.08
3	35	1.55	69.2	1.22
2	30	0.648	69.2	1.16
2	30	1.55	69.2	1.15
3	30	0.648	69.2	1.20
3	30	1.55	69.2	1.17
1	15	0.648	69.2	1.12
1	15	1.55	69.2	1.08
4	15	0.648	69.2	0.95
4	15	1.55	69.2	0.95

[a] System A - MIBK - HAC - H_2O.

Table 8. Selected data from Table 2 for system A.[a] Effect of frequency and amplitude

Cartridge No.	U_y/U_x	U_y+U_x	A	f	$(NTU_{ox})_T$	$1/\eta = (NTU_{ox})_T/(NTU_{ox})_p$
4	1.0	54.2	1	30	1.25	1.06
4	1.0	54.2	1	50	1.84	1.33
4	1.0	54.2	1	70	5.95	2.32
4	1.0	54.2	1	90	9.30	3.02
4	1.0	54.2	.5	30	1.11	1.07
4	1.0	54.2	.5	50	1.18	1.09
4	1.0	54.2	.5	70	1.33	1.136
4	1.0	54.2	.5	90	1.86	1.37
4	1.0	54.2	.75	70	2.0	1.149
2	1.037	55	1	50	1.67	1.29
2	1.037	55	1	70	4.06	1.86
2	1.037	55	1	90	8.81	3.12
2	1.037	55	.5	70	1.26	1.23

[a] System A - MIBK - HAC - H_2O.

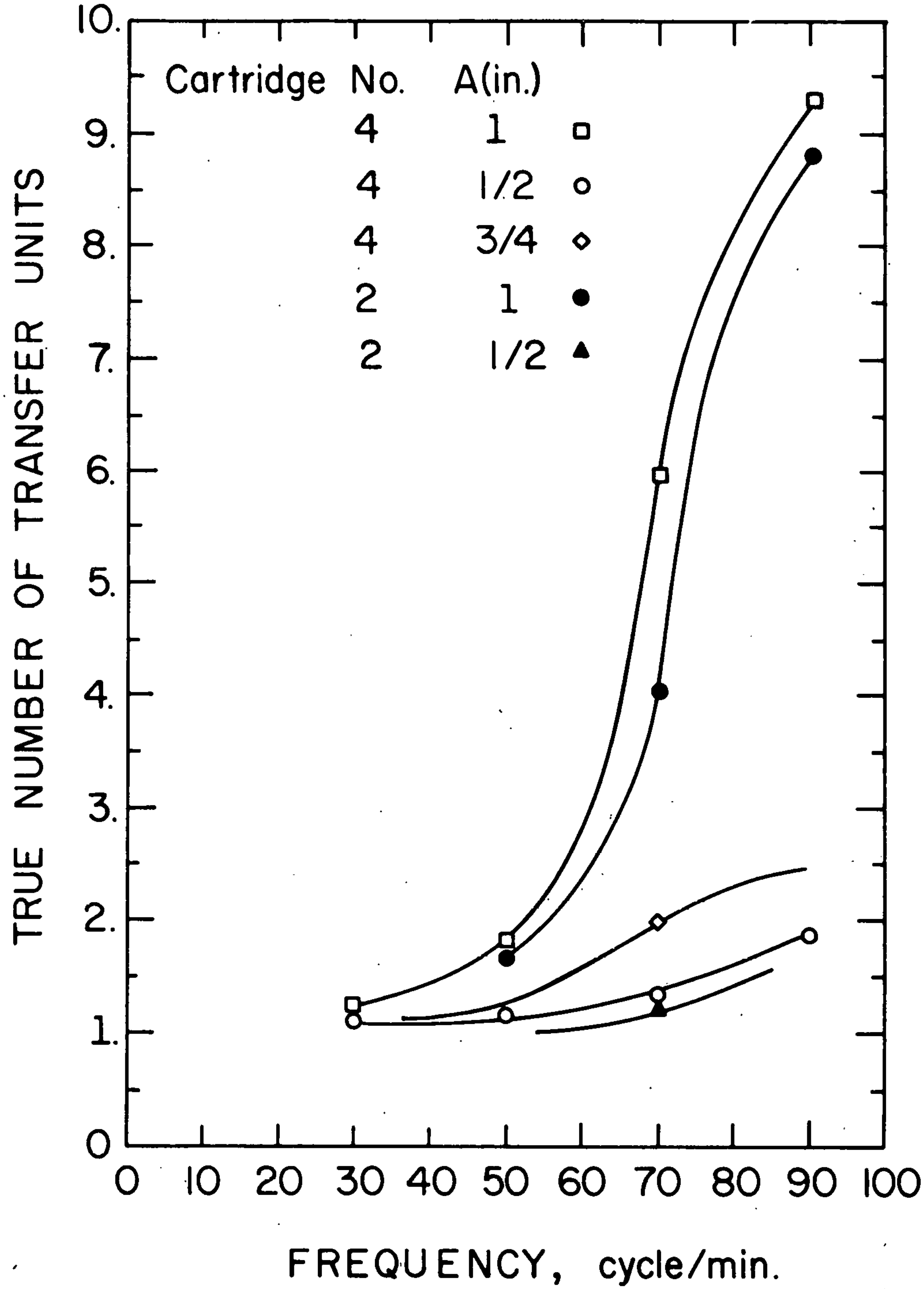

Figure 7. Effect of frequency and amplitude on the true number of transfer units for the MIBK - HAC - H_2O system

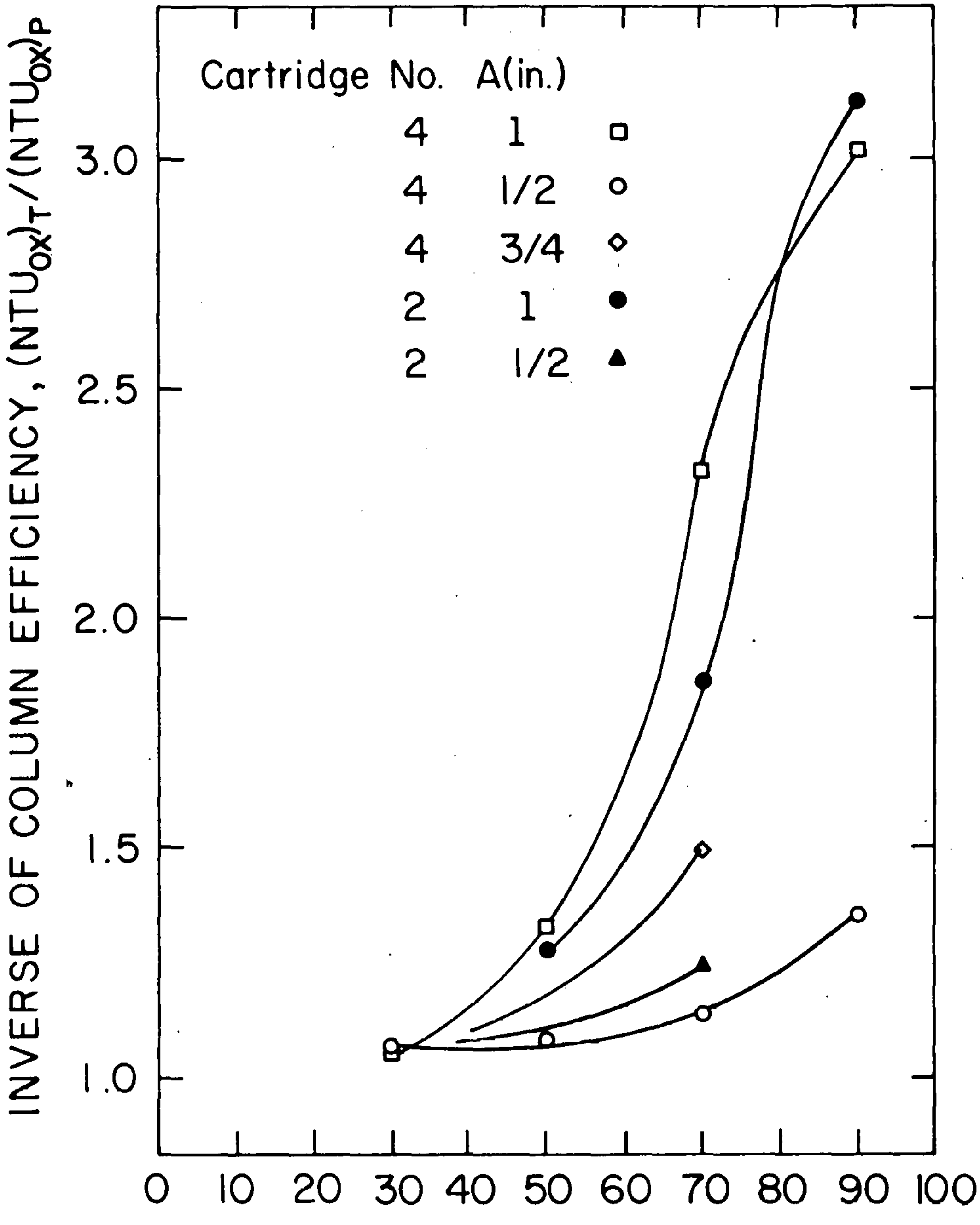

Figure 8. Effect of frequency and amplitude on the inverse of column efficiency for the MIBK - HAC - H_2O system

Table 9. Selected data from Table 2 for system B.[a] Effect of frequency and amplitude

Cartridge No.	U_y/U_x	U_y+U_x	A	f	$(NTU_{ox})_T$	$1/\eta = (NTU_{ox})_T/(NTU_{ox})_P$
4	1.04	106.2	.5	40	1.75	1.13
4	1.04	106.2	.5	70	1.84	1.115
4	1.04	106.2	.5	100	2.45	1.237
4	1.04	106.2	1	40	1.66	1.137

[a] System B - 1,1,2 T.C.E. - Acetone - H_2O.

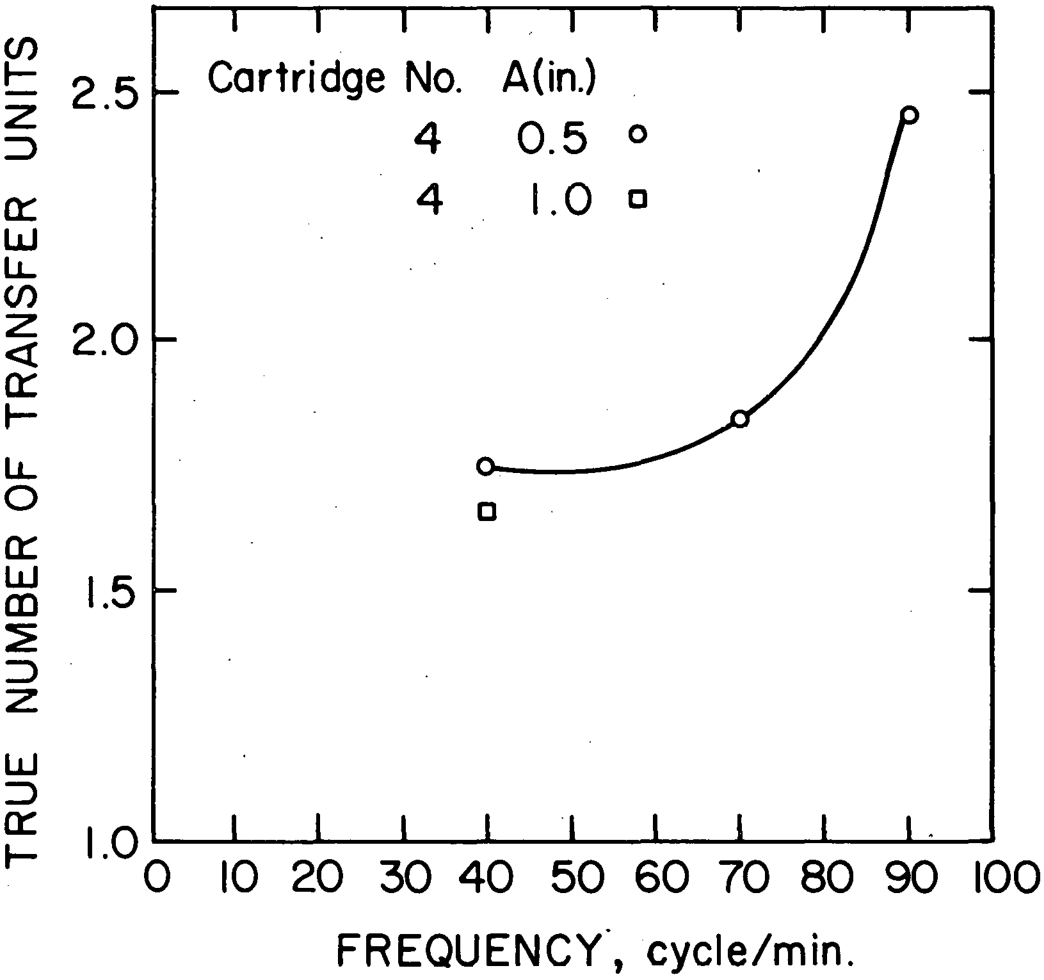

Figure 9. Effect of frequency and amplitude on the true number of transfer units for the 1,1,2 T.C.E. - acetone - H_2O system

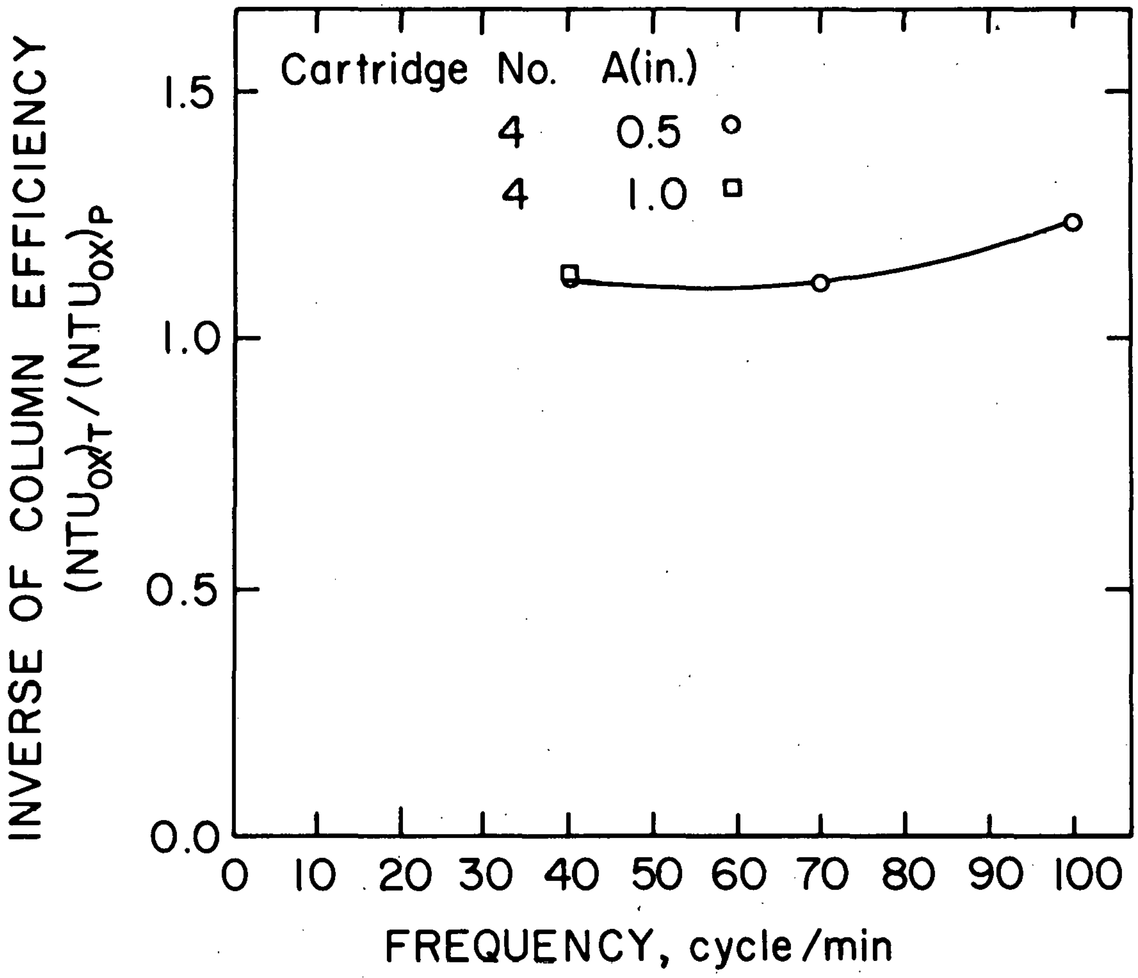

Figure 10. Effect of frequency and amplitude on the inverse of column efficiency for the 1,1,2 T.C.E. - acetone - H_2O system

Since Af (the amplitude-frequency product) expresses the pulse velocity in feet per hour, it might be assumed that $1/\eta$ is a function of Af rather than A and f independently.

The Effect of Cartridge Number on Column Efficiency

Smoot and Babb (42) introduced different cartridges for different columns. Each cartridge had the following variables: plate hole diameter (d_h), plate free area (s), plate spacing (h), and column diameter (D_t). The four different cartridges are listed in Table 3. From Tables 10 and 3 it appears that $1/\eta$ changes as cartridge number varies according to the possible expression,

$$1/\eta \ \alpha (h)^a (d_h)^b \tag{81}$$

where a and b are positive numbers which must be determined experimentally.

The Effect of Column Height on the Number of Transfer Units and Column Efficiency

As shown in Figure 11, a variation of the column height from 2 to 4 feet causes an effect on $(NTU_{ox})_p$. For a greater range of column height this change would be more significant.

Table 10. Selected data from Table 2 for system A.[a] Effect of cartridge number

Cartridge No.	Af	U_y/U_x	U_y+U_x	$1/\eta = (NTU_{ox})_T/(NTU_{ox})_p$
1	70	0.648	69.2	1.44
4	70	0.648	69.2	1.36
1	70	1.55	69.2	1.90
4	70	1.55	69.2	1.98
1	35	1.00	54.2	1.32
4	35	1.00	54.2	1.136
1	35	1.00	84.0	1.15
4	35	1.00	84.0	1.145
1	30	1.00	54.2	1.27
4	30	1.00	54.2	1.06
1	30	1.00	84.0	1.20
4	30	1.00	84.0	1.00
1	15	0.648	69.2	1.12
4	15	0.648	69.2	0.95
1	15	1.55	69.2	1.07
4	15	1.55	69.2	0.95

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[a] System A - MIBK - HAC - H_2O.

Table 11. Selected data from Table 2 for system A.[a] Effect of column height on the number of transfer units and column efficiency

Cartridge No.	H	U_y/U_x	U_y+U_x	A	f	$(NTU_{ox})_p$	$(NTU_{ox})_T$	$1/\eta$
2	2.0	1.037	55	0.5	70	1.02	1.26	1.23
2	2.71	1.037	55	0.5	70	1.59	1.56	0.98
2	3.27	1.037	55	0.5	70	1.66	2.36	1.42
2	3.93	1.037	55	0.5	70	2.00	2.42	1.21
2	1.96	1.037	55	1	70	2.00	4.38	2.19
2	2.00	1.037	55	1	70	2.18	4.06	1.86
2	2.71	1.037	55	1	70	2.88	5.01	1.74
2	3.27	1.037	55	1	70	3.64	11.07	3.05
2	2.00	1.037	55	1	50	1.29	1.67	1.29
2	2.71	1.037	55	1	50	1.62	2.64	1.63
2	3.27	1.037	55	1	50	2.14	3.13	1.46
2	3.93	1.037	55	1	50	2.57	3.94	1.53

[a] System A - MIBK - HAC - H_2O.

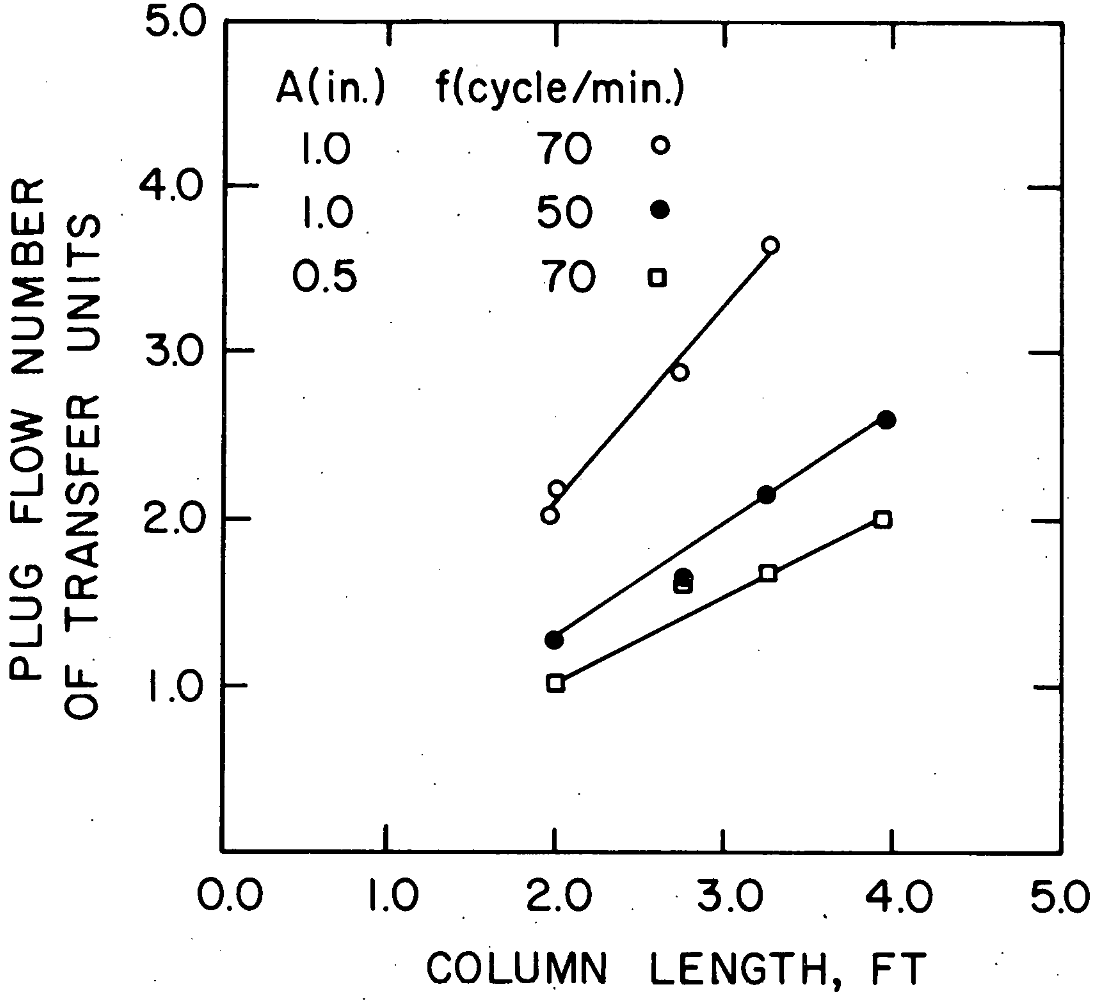

Figure 11. Effect of column height on the plug flow number of transfer units for the MIBK - HAC - H_2O system

As seen from Figure 12 $(NTU_{ox})_T$ tends to increase slightly as the column height is increased. One reason for this slight increase may be that the end effect becomes less significant as column height increases.

The Effect of Column Diameter on Column Efficiency

The number of transfer units (NTU) is also a function of the column diameter due to the channeling effect. However, by using louvre redistributor plates, the present Purex-plant columns show very slight "scale-up" factors, about 1.0 to 1.5 upon going from 3 inch diameter pilot plant columns to full scale units (7 in. to 34 in. diameter). Sege and Woodfield (38) at Hanford, Thornton (45) in England and Rouyer et al. (37) in France have demonstrated this fact. Rouyer, et al. showed that the NTU's are practically the same for small diameter columns (2 in.) and large diameter (4 to 12 in.) columns. They further concluded that pulse columns can be easily scaled up to a limit of at least 39 in. without decreasing the efficiency. However, the minimum possible column diameter for which the diameter has no effect on NTU's may be 2 in. Below 2 inches, the wall effect probably becomes appreciable and the NTU's will be affected.

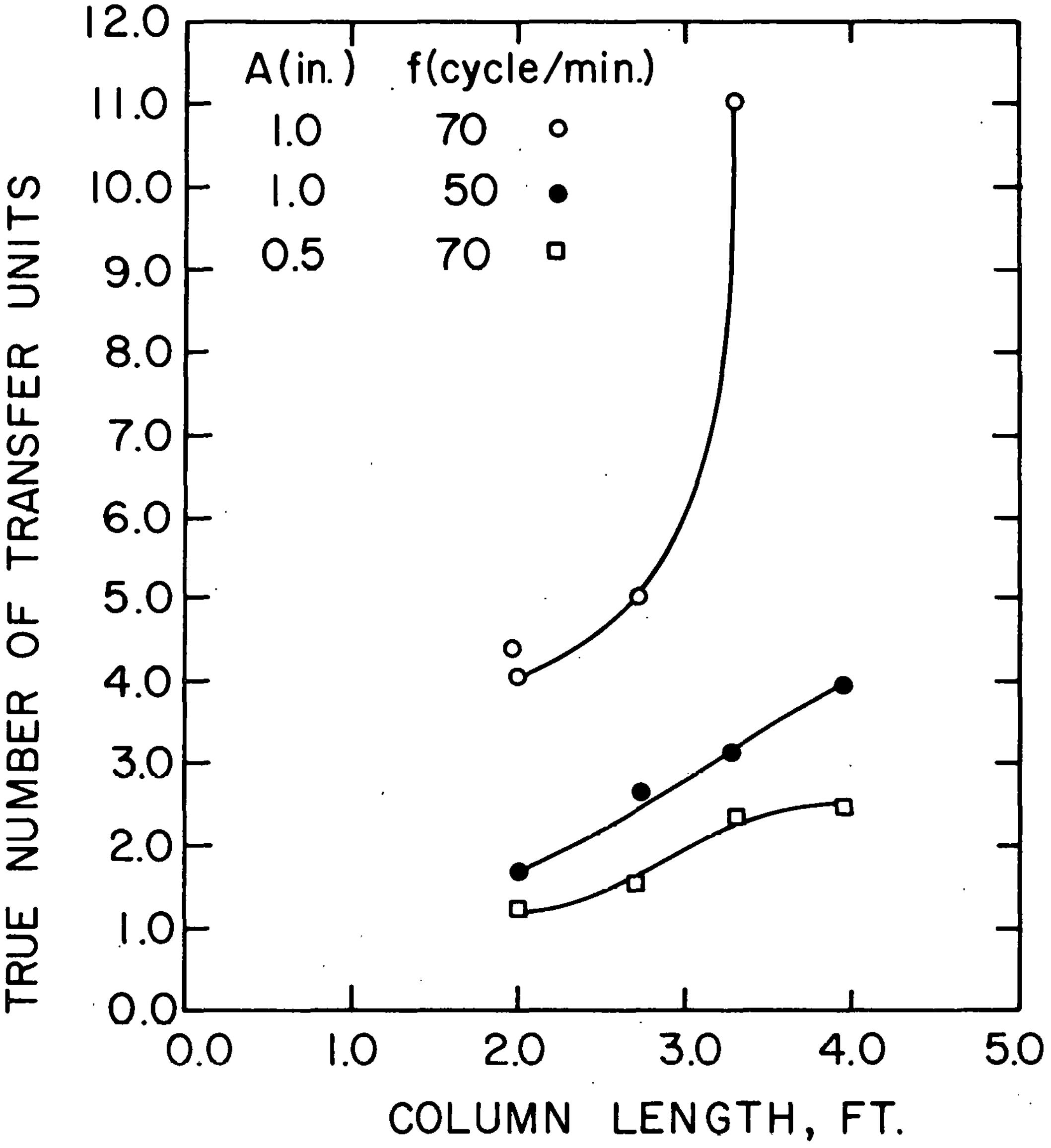

Figure 12. Effect of column height on the true number of transfer units for the MIBK - HAC - H_2O system

General Correlation of Column Efficiency

In developing a correlation equation for the true number of transfer units or extraction efficiency, a dimensional analysis approach would include the following variables,

$$\eta = (Af,\ U_x,\ U_y,\ d_h,\ h,\ m,\ H) \qquad (82)$$

Using the techniques of dimensional analysis to reduce the number of variables yields

$$\eta = (P_x,\ P_y,\ F,\ (NTU_{ox})_T) \qquad (83)$$

or:

$$\eta = (P_x,\ P_y,\ F,\ (NTU_{ox})_p) \qquad (84)$$

where $P_x = U_x H/E_x$ is the Peclet number of x phase, $P_y = U_y H/E_y$ is the Peclet number of y phase, and $F = U_x/mU_y$ is the extraction factor.

As shown in Figure 13, Miyauchi and Vermeulen (33) computed the influence of P_x and $(NTU_{ox})_T$ on the ratio $1/\eta = (NTU_{ox})_T/(NTU_{ox})_p$ at $F = 1.0$ and $P_x = P_y$. The ratio $1/\eta$ increases with decreasing values of the Peclet group, and with increasing $(NTU_{ox})_T$ values. Thus efficiency increases with increasing values of the Peclet group and with decreasing values of the $(NTU_{ox})_T$.

In order to determine an experimental concentration

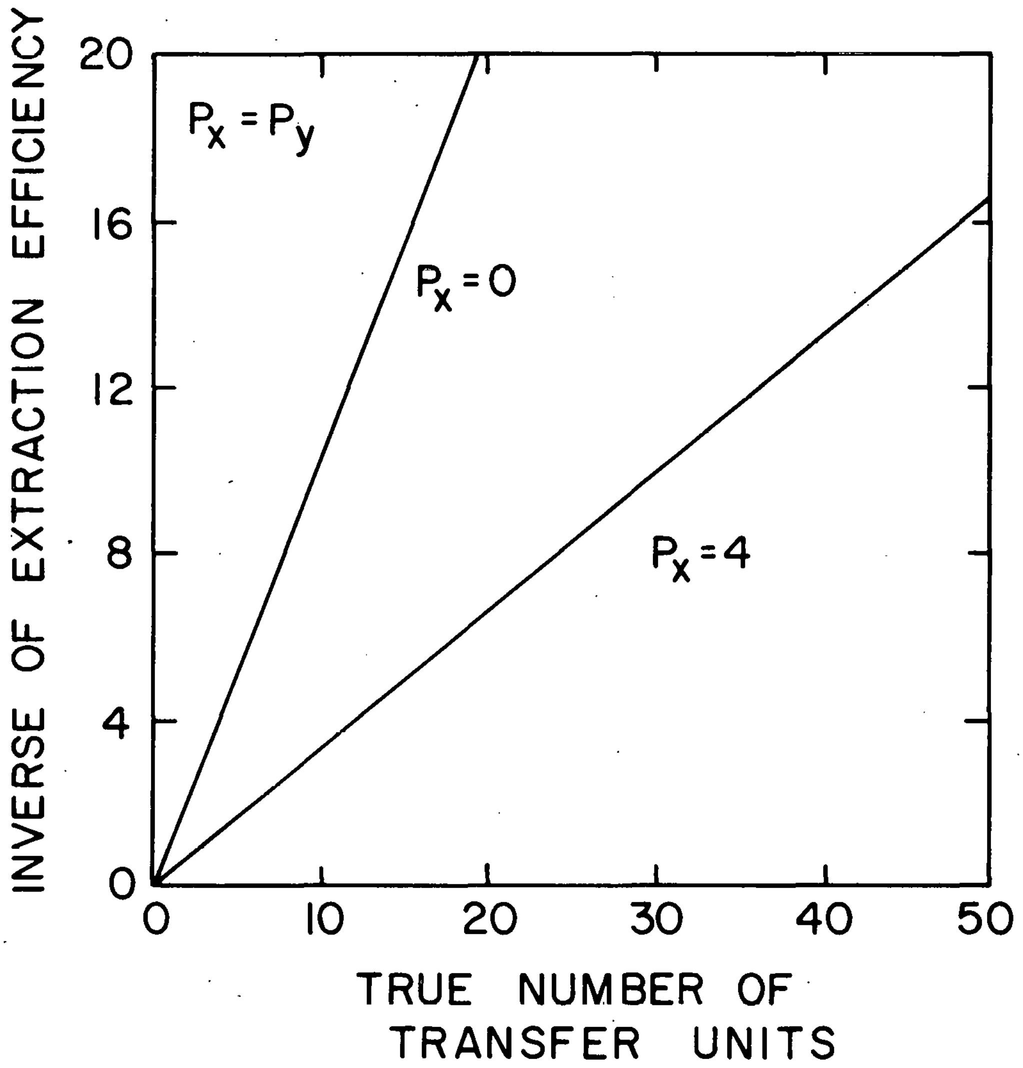

Figure 13. The effect of the inverse of extraction efficiency on the Peclet number P_x

profile, the true number of transfer units, or the overall mass transfer coefficients using the differential model the following assumptions are probably necessary:

1. The solutions involved are dilute and the velocities of the two phases, U_x and U_y are constant throughout the column regardless of the mass transfer which may occur.
2. Concentration gradients in the radial and angular directions can be neglected.
3. The distribution coefficient is constant. However, this offers a major restriction to the applicability of the model, since many systems of interest would not have a constant distribution coefficient.
4. The backmixing coefficients, E_x and E_y, are constant except possibly near the ends of the column.
5. The holdup of both the continuous and the dispersed phases (the volume of each phase per unit volume of the column), h_x and h_y, are constant throughout the column.
6. The product of the mass transfer coefficient and the interfacial area is constant through the column. However, in regions of higher turbulence the interfacial area appears to increase because

when the drops move up the column they are divided repeatedly by the pulsing action which pushes them through the tiny holes of the perforated plates.

SIMPLE AND RAPID METHOD FOR ESTIMATING THE TRUE NUMBER OF TRANSFER UNITS AND EXTRACTION EFFICIENCY

Despite the obvious practical importance of axial backmixing in many applications, few attempts have been made to develop a simple, rapid method for estimating a relationship between $(NTU_{ox})_T$ and $(NTU_{ox})_p$ and the effect of backmixing for purposes of design and experimental interpretation.

The principal purpose of the present section is to describe these correlations briefly, to use the data in Table 2 for testing each method, comparing the results with each other and with experimental results from Table 2 and finally determining the simplest, most accurate and best method for design purposes.

Method 1: Smoot and Babb (42) showed that:

$$(HTU_{ox})_T = \psi(Af,\ U_x,\ U_y,\ d_h,\ h,\ \mu_y,\ \rho_y,\ \Delta\rho,\ \gamma,\ D_y,\ m) \tag{85}$$

By applying the technique of dimensional analysis to the variables of Equation 85 and assuming that the correlation can be represented by an exponential function they obtained the relation:

$$\frac{(HTU_{ox})_T}{h} = b_o\left(\frac{Afd_h\rho_y}{\mu_y}\right)^{b_1}\left(\frac{U_x}{Af}\right)^{b_2}\left(\frac{U_x}{U_y}\right)^{b_3}\left(\frac{d_h}{h}\right)^{b_4}\left(\frac{\gamma}{\mu_y U_y}\right)^{b_5}$$
$$+ \left(\frac{\Delta\rho}{\rho_y}\right)^{b_6}\left(\frac{\mu_y}{\rho_y D_y}\right)^{b_7}\left(\frac{U_x}{mU_y}\right)^{b_8} \qquad (86)$$

Where b_i (i=0 to 8) are constants, h is plate spacing, d_h is sieve-plate hole diameter, μ_y, ρ_y, and γ are viscosity, density, and interfacial tension, respectively. D_y is the molecular diffusivity and $\Delta\rho$ is the density difference between the two phases.

Using the data for M.I.B.K. - HAC - H_2O system in Table 2, the following empirical equation was developed.

$$\frac{(HTU_{ox})_T}{h} = 502\left(\frac{Afd_h\rho_y}{\mu_y}\right)^{-.4}\left(\frac{U_x}{Af}\right)^{.43}\left(\frac{U_x}{U_y}\right)^{.56}\left(\frac{d_h}{h}\right)^{.62} \qquad (87)$$

For this correlation an average deviation of 27% was reported. However, the maximum error in computing $(NTU_{ox})_T$, and hence $(HTU_{ox})_T$, using the mathematical model was estimated to be 20%. The exponents b_5 to b_8 in Equation 86 were not evaluated because of insufficient data. Thus Equation 87 only applies to the systems having values of physical properties similar to M.I.B.K. - HAC - H_2O system. These disadvantages of Equation 87 point up the need for a still better correlation for $(NTU_{ox})_T$ or $(HTU_{ox})_T$ in terms of column parameters.

Method 2: Sleicher (41) presented an algebraic expression which contained several functions of the extraction factor F and gave tables of these functions:

$$\eta = \frac{(NTU_{ox})_p}{(NTU_{ox})_T} = \frac{P_x P_y}{P_x P_y + (NTU_{ox})_T \theta} \qquad (88)$$

where $\theta = aP_x + bP_y + C(P_x P_y)^{.5} - d(P_x + P_y)^{.5} + e(P_x - P_y)\exp(-f(NTU_{ox})_T)$ in which a, b, c, d, e, and f are constants tabulated as functions of F. The number of transfer units in plug flow may be evaluated from the concentrations in the inlet and outlet streams. Then the Colburn equation (page 14, Equation 27), can be used to find

$$(NTU_{ox})_p = \frac{\ln \frac{X}{XF+1-F}}{F-1} \qquad (89)$$

where

$$X = (x_{out} - y_{in}/m)/(x_{in} - y_{in}/m)$$

For F=1 the equation becomes,

$$(NTU_{ox})_p = \frac{1}{X} - 1 \qquad (90)$$

The height of a transfer unit in plug flow can also be estimated from mass transfer correlations or by experimental measurements.

Method 3: Miyauchi and Vermeulen (33) assumed that the behavior of $(NTU_{ox})_p$ in the two limiting cases of mass transfer controlling and of backmixing controlling is consistent with the addition of the reciprocals,

$$\frac{1}{(NTU_{ox})_p} = \frac{1}{(NTU_{ox})_T} + \frac{1}{(NTU_{ox})_D} \tag{91}$$

where $(NTU_{ox})_D$ is the "number of overall dispersion units", with reference to the x phase. It is a function of F, P_x, P_y, and probably also $(NTU_{ox})_T$. It was represented by the general form

$$(NTU_{ox})_D = \frac{\ln F}{F-1} \Phi + (PB)_y \tag{92}$$

in which $(PB)_y$ is the overall Peclet group and is defined by the equation

$$(PB)_y = \left(\frac{F}{f_x P_x} + \frac{1}{f_y P_y}\right)^{-1} \tag{93}$$

where f_x and f_y are weighting factors and are functions of $(NTU_{ox})_T$ and F. The values of f_x and f_y, to a reasonable degree of approximation, are given by

$$f_x = \frac{(NTU_{ox})_T + k'(NTU_{ox})_T^{2\alpha} F^{-.5-\alpha}}{(NTU_{ox})_T + k'(NTU_{ox})_T^{2\alpha} F^{-1.5-\alpha}} \tag{94}$$

$$f_y = \frac{(NTU_{ox})_T + k'(NTU_{ox})_T^{2\alpha} F^{-.5-\alpha}}{(NTU_{ox})_T + k'(NTU_{ox})_T^{2\alpha} F^{+.5-\alpha}} \tag{95}$$

where the constants $\alpha = 0$ and $k' = 6.8$ provide the best results.

The coefficient Φ has been determined from Equations 92 and 93 and a knowledge of the "exact" $(NTU_{ox})_D$. The expression is

$$\Phi = 1 - \frac{.050}{(F(NTU_{ox})_T)^{.5}\ (PB)_y^{.25}} \tag{96}$$

Results of sufficient accuracy, however, may often be obtained by simply setting $\Phi = 1$ according to Miyauchi and Vermeulen (33).

For the case $F = 1$ from the Equations 92, 93, 94, and 95 we conclude that

$$(NTU_{ox})_D = \left(\frac{1}{P_x} + \frac{1}{P_y}\right)^{-1} \tag{97}$$

Method 4: From the Equation 91 one obtains

$$(HTU_{ox})_p = (HTU_{ox})_T + (HTU_{ox})_D \tag{98}$$

where $(HTU_{ox})_D$ is the overall height of dispersion unit. As was shown in Equation 97 for the case, $F = 1$,

$$(HTU_{ox})_D = \left[\frac{1}{P_x} + \frac{1}{P_y}\right]H \tag{99}$$

For the general case, $F \neq 1$ Stemerding and Zuiderweg (44) have found that the $(HTU_{ox})_D$ can be determined from the following equations:

$$(HTU_{ox})_D = \frac{1}{p_o + \frac{.8}{H}\frac{\ln F}{F-1}} \tag{100}$$

where

$$p_o = \frac{\frac{0.1H}{(HTU_{ox})_T} + 1}{\frac{0.1H}{(HTU_{ox})_T} + \frac{p_1}{p_2}} p_1 \tag{101}$$

and

$$\frac{1}{p_1} = \frac{F}{P_x} + \frac{1}{P_y}, \tag{102a}$$

$$\frac{1}{p_2} = \frac{1}{P_x} + \frac{F}{P_y} \tag{102b}$$

Method 5: In all previous methods the Peclet number used is based upon the column length. This can make design of a proposed column a trial and error procedure since the column length would not be known and the correlations can not be solved explicitly for the efficiency.

Watson and Cochran (47) developed simple empirical equations for both single and double phase backmixing. This method of estimating η is useful in design studies since it uses only design parameters or directly measurable quantities.

For backmixing in a single phase x($E_y = 0$ or $P_y = \infty$)

the expression is

$$\eta = 1 - \frac{1}{NP_x + 1 - F + \frac{1}{(NTU_{ox})_p}} \tag{103}$$

The equation for backmixing in both phases is given approximately by the following equation:

$$\eta = 1 - \frac{1}{NP_x + 1 - F + \frac{1}{(NTU_{ox})_p}}$$

$$- \frac{F}{NP_y - 1 + F + \frac{1}{(NTU_{ox})_p}} \tag{104}$$

where $NP_x = (HTU_{ox})_p\ U_x/E_x$, $NP_y = (HTU_{ox})_p\ U_y/E_y$, $F = U_x/mU_y$, and $(NTU_{ox})_p$ can be calculated from Equation 89.

It was reported that the efficiencies estimated by Method 5 do not deviate from the exact values which were tabulated by McMullen, et al. (29) by more than .06 to .07 when

$$(NTU_{ox})_T \geq 2$$

$$\eta \geq .2$$

Therefore column efficiency can be solved for explicitly by this method because the design parameters are not based upon the column length. The required column length can be predicted from the following expression:

$$H = \frac{(NTU_{ox})_p (HTU_{ox})_p}{\eta} \qquad (105)$$

It should be stressed that these correlations for estimating the extraction efficiency and the true number of transfer units require that the following assumptions be satisfied.

1. Constant, uniform operating conditions, including the flow rates, holdup of both phases and the backmixing coefficients.
2. Constant, uniform physical properties, including the distribution coefficient.
3. Solute only transferred from the raffinate (y phase) to the solvent (x phase).

Comparison of the Methods

For comparing the results of the various methods, the data in Table 2 was used. The efficiency and the true number of transfer units were calculated by each method. The best results, which are tabulated in Tables 12, 13, 14 and 15 were obtained from Methods 3 and 5. As can be seen from Tables 14 and 15 the deviations of calculated efficiencies of these two methods are not more than .06-.07. However, as mentioned earlier, Method 3 is very complex and for most design purposes it is difficult to use since it can not be solved

Table 12. Calculation of the true NTU by: (a) using the mathematical model, (b) using Method 3, and (c) using Method 5. Data are selected from Table 2 for System A[a]

Run No.	P_x	P_y	F	NP_x	NP_y	$(NTU_{ox})_p$	$(NTU_{ox})_T$		
							(a)	(b)	(c)
2	7.30	68.6	1.236	2.563	24.15	2.84	5.42	4.84	4.92
6	10.41	0	1.236	6.76	∞	1.54	1.66	1.79	1.78
8	14.5	0	1.923	15.93	∞	0.91	1.05	0.978	0.97
12	15.98	0	1.923	17.37	∞	0.92	0.99	0.98	0.975
13	9.6	0	1.9090	9.70	∞	0.99	1.09	1.11	1.10
15	11.7	31.66	1.923	6.275	17.79	1.78	2.60	2.43	2.43
17	8.02	0	1.236	5.984	∞	1.34	1.54	1.59	1.584
19	10.4	33.4	1.9090	3.920	12.640	2.65	4.41	4.635	4.85
20	12.4	0	1.236	6.93	∞	1.79	2.10	2.08	2.10
22	20.685	0	2.97	21.3	∞	0.97	1.05	1.04	1.02
23	9.584	0	1.236	5.54	∞	1.73	2.11	2.09	2.08
25	15.74	0	1.9090	11.57	∞	1.36	1.52	1.51	1.49
26	14.72	0	1.923	13.38	∞	1.10	1.26	1.2	1.19
29	8.865	0	1.9090	7.577	∞	1.17	1.33	1.365	1.35
30	7.4	25.3	1.236	2.474	13.17	2.99	5.92	5.936	5.74
32	19.0	0	1.923	17.5	∞	1.09	1.10	1.17	1.15
33	11.5	0	1.9090	9.7	∞	1.18	1.25	1.33	1.317
34	8.43	20.61	1.9090	3.3	8.05	2.56	5.95	5.49	5.87
36	9.53	0	1.9090	6.9	∞	1.38	1.84	1.64	1.62
37	12.0	0	1.9090	11.57	∞	1.04	1.11	1.15	1.138
38	8.1	0	1.9090	5.95	∞	1.36	1.86	1.67	1.65
39	10.0	0	1.9090	9.27	∞	1.08	1.18	1.23	1.21
41	6.84	34.8	1.854	3.135	15.95	2.18	4.06	3.98	4.136
42	7.71	34.8	1.854	5.98	26.96	1.29	1.67	1.675	1.684
43	6.20	0	1.854	2.20	∞	2.82	8.81	6.65	6.84
44	7.15	0	1.854	7.01	∞	1.02	1.26	1.20	1.19
45	9.23	47.13	1.854	3.20	16.4	2.88	5.01	5.47	5.54
52	14.00	0	1.854	7.04	∞	2	2.42	2.413	2.35

[a] System A - MIBK - acetic acid - water (at 30°C m = 0.52).

Table 13. Calculation of the true NTU by: (a) using the mathematical model, (b) using Method 2, and (c) using Method 5. Data are selected from Table 2 for System B[a]

Run No.	P_x	P_y	F	NP_x	NP_y	$(NTU_{ox})_p$	$(NTU_{ox})_T$ (a)	$(NTU_{ox})_T$ (b)	$(NTU_{ox})_P$ (c)
53	11.0	0	0.255	3.25	∞	3.38	4.47	4.34	4.41
54	17.74	0	0.442	10.95	∞	1.62	1.88	1.76	1.76
55	19.98	0	0.335	13.15	∞	1.52	1.72	1.62	1.63
56	14.66	0	0.337	10.0	∞	1.46	1.66	1.59	1.60
57	17.14	0	0.335	11.66	∞	1.47	1.69	1.63	1.63
58	13.556	0	0.337	8.21	∞	1.65	1.84	1.74	1.84
59	14.16	0	0.255	7.30	∞	1.94	2.22	2.11	2.20
60	22.84	0	0.442	16.67	∞	1.37	1.44	1.41	1.45
61	11.96	0	0.396	5.92	∞	2.02	2.45	2.33	2.40
62	10.84	0	0.396	2.58	∞	4.20	4.95	5.80	5.38
63	15.41	0	0.337	9.94	∞	1.55	1.75	1.69	1.70
64	11.0	0	0.336	5.585	∞	1.98	2.45	2.31	2.32

[a] System B - 1,1,2 trichloroethane - acetone - water (at 30°C m = 2.86).

Table 14. Calculation of efficiencies by: (a) using the mathematical model, (b) using Method 3, and (c) using Method 5. Data are selected from Table 2 for System A[a]

Run No.	P_x	P_y	F	NP_x	NP_y	$(NTU_{ox})_p$	η		
							(a)	(b)	(c)
2	7.30	68.6	1.236	2.563	24.15	2.84	0.524	0.585	0.577
6	10.41	0	1.236	6.76	∞	1.54	0.927	0.858	0.861
8	14.5	0	1.923	15.93	∞	0.91	0.867	0.93	0.938
12	15.98	0	1.923	17.37	∞	0.92	0.93	0.937	0.943
13	9.6	0	1.9090	9.70	∞	0.99	0.908	0.889	0.898
15	11.17	31.66	1.923	6.275	17.79	1.78	0.685	9.733	0.731
17	8.02	0	1.236	5.984	∞	1.34	0.87	0.843	0.846
19	10.4	33.4	1.9090	3.920	12.640	2.65	0.60	0.57	0.547
20	12.4	0	1.236	6.93	∞	1.79	0.852	0.862	0.85
22	20.685	0	2.97	21.30	∞	0.97	0.924	0.936	0.951
23	9.584	0	1.236	5.54	∞	1.73	0.82	0.826	0.83
25	15.74	0	1.9090	11.57	∞	1.36	0.895	0.90	0.912
26	14.72	0	1.923	13.38	∞	1.10	0.873	0.916	0.925
29	8.865	0	1.9090	7.577	∞	1.17	0.88	0.857	0.867
30	7.4	25.3	1.236	2.474	13.17	2.99	0.501	0.504	0.521
32	19.0	0	1.923	17.50	∞	1.09	0.991	0.932	0.943
33	11.5	0	1.9090	9.70	∞	1.18	0.944	0.887	0.896
34	8.43	20.61	1.9090	3.30	8.05	2.56	0.43	0.466	0.436
36	9.53	0	1.9090	6.90	∞	1.38	0.75	0.84	0.85
37	12.0	0	1.9090	11.57	∞	1.04	0.937	0.904	0.914
38	8.10	0	1.9090	5.95	∞	1.36	0.73	0.813	0.827
39	10.0	0	1.9090	9.27	∞	1.08	0.915	0.88	0.892
41	6.84	34.8	1.854	3.135	15.95	2.18	0.537	0.548	0.527
42	7.71	34.8	1.854	5.98	26.96	1.29	0.77	0.77	0.766
43	6.20	0	1.854	2.20	∞	2.82	0.32	0.423	0.412
44	7.15	0	1.854	7.01	∞	1.02	0.81	0.85	0.86
45	9.23	47.13	1.854	3.20	16.4	2.88	0.57	0.526	0.52
52	14.00	0	1.854	7.04	∞	2	0.82	0.828	0.85

[a] System A - MIBK - acetic acid - water (at 30°C m = 0.52).

Table 15. Calculation of efficiencies by using: (a) the mathematical model, (b) Method 3, and (c) Method 5. Data are selected from Table 2 for System B[a]

Run No.	P_x	P_y	F	NP_x	NP_y	$(NTU_{ox})_p$	η		
							(a)	(b)	(c)
53	11.0	0	0.255	3.25	∞	3.38	0.756	0.779	0.767
54	17.74	0	0.442	10.95	∞	1.62	0.86	0.918	0.917
55	19.98	0	0.335	13.15	∞	1.52	0.884	0.937	0.931
56	14.66	0	0.337	10.0	∞	1.46	0.88	0.917	0.912
57	17.14	0	0.335	11.66	∞	1.47	0.871	0.925	0.923
58	13.55	0	0.337	8.21	∞	1.65	0.897	0.904	0.894
59	14.16	0	0.255	7.30	∞	1.94	0.874	0.893	0.883
60	22.84	0	0.442	16.67	∞	1.37	0.93	0.948	0.944
61	11.96	0	0.396	5.92	∞	2.02	0.84	0.864	0.857
62	10.84	0	0.396	2.58	∞	4.20	0.77	0.725	0.707
63	15.41	0	0.337	9.94	∞	1.55	0.88	0.916	0.911
64	11.0	0	0.336	5.505	∞	1.98	0.825	0.858	0.852

[a] System B - 1,2,2 trichloroethane - acetone - water (at 30°C m = 2.86).

explicitly for the column length or efficiency.

Again, referring to Tables 12, 13, 14 and 15 the values from Methods 3 and 5 are compared with those obtained from the mathematical model. The results are quite accurate. A sample calculation for estimating the true number of transfer units and extraction efficiency by Methods 3 and 5 is given in Appendix A.

SIMULATION STUDY FOR UNSTEADY STATE OPERATION IN BACKMIXING STAGEWISE MODEL

A typical section of a countercurrent column is shown in Figure 14. The heavy phase flows from the top, and it is contacted with the light phase which rises from the bottom. In addition to the main flows, two hypothetical flows in the opposite direction are considered, which represent the backmixing.

Following the assumptions on page 20 and referring to Figure 14 the unsteady state balance for a typical stage n may be written:

In - Out = accumulation

$$L(1+e_x)x_{n-1} - L(1+2e_x)x_n + Le_x x_{n+1} - Q_n ah = hh_x \frac{dx_n}{dt} \tag{106}$$

and:

$$G(1+e_y)y_{n+1} - G(1+2e_y)y_n + Ge_y y_{n-1} + Q_n ah = hh_y \frac{dy_n}{dt} \tag{107}$$

The balances for the first and the last stage differ from Equations 106 and 107 because no backflow leaves the column, and also because there is no mass transfer in the end zones. The corresponding equations are, for the first stage,

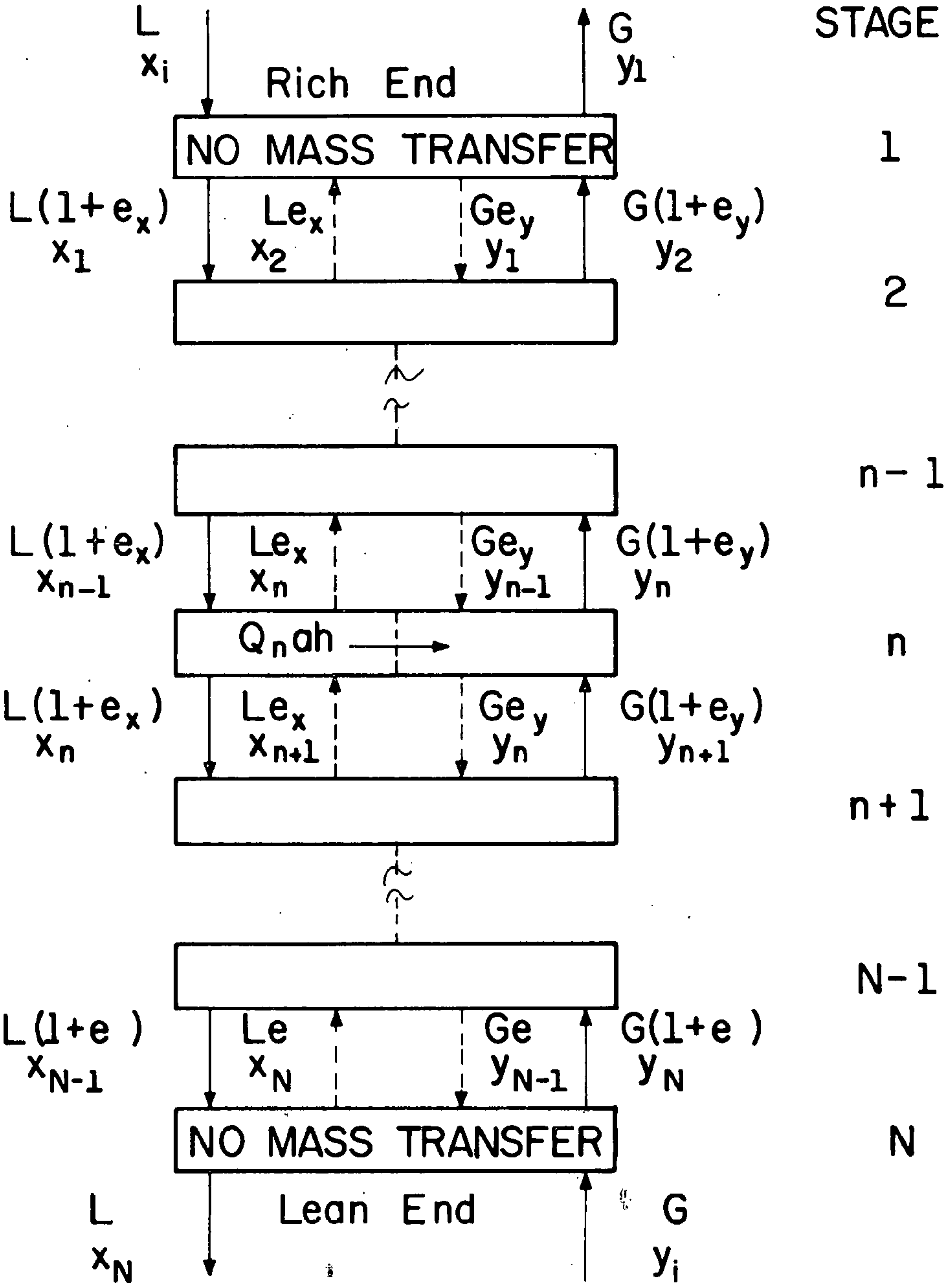

Figure 14. Diagrammatic representation of stagewise backmixing model

$$Lx_{in} - L(1+e_x)x_1 + Le_x x_2 = h'h'_x \frac{dx_1}{dt} \qquad (108)$$

and

$$G(1+e_y)y_2 - Ge_y y_1 - Gy_1 = h'h'_x \frac{dy_1}{dt} \qquad (109)$$

For the last stage,

$$L(1+e_x)x_{N-1} - Le_x x_N - Lx_N = h''h''_x \frac{dx_N}{dt} \qquad (110)$$

and

$$Gy_{in} - G(1+e_y)y_N + Ge_y y_{N-1} = h''h''_y \frac{dy_N}{dt} \qquad (111)$$

In these equations,

$$Q_n = K_{ox}(x_n - x_n^*) \qquad (112)$$

and the equilibrium relationship for small perturbations may be written

$$y_n = mx_n^* \qquad (113)$$

Solution of the Equations

The equations derived in the preceding section are linear with regard to concentration disturbances. Nonlinearities due to flow rate changes can be eliminated by assuming such disturbances to be small perturbations. In this manner the equations may be solved for the concentration profiles in the column by using digital simulation.

Several methods have been developed for the numerical solution of systems of ordinary differential equations. Integration routines for many of these methods have been tested and developed by the Nottingham Algorithm Group as cited in (28). By using these routines, Mcdonald and Wilkinson (28) showed that Gear's method required the minimum running time and was the easiest and the most economical method of solution especially for systems of stiff differential equations.

As an example of the computation of the concentration profiles from the linear ordinary differential equations (Equations 106 through 113), the published data of Mcdonald and Wilkinson (28), shown in Table 16, were used.

Table 16. Parameters used in digital simulation

$L = 0.203$ $G = 0.187$

$e_x = 0.32$ $e_y = 0.01$

$m = 0.73$ $h = 7.45$

$h_x = 0.877$ $h_y = 0.123$

$x_{in} = 0.0693$ $y_{in} = 0.0005$

$K_{ox}a = 0.25$

By using the Gear's method, two Fortran programs were written for the two cases of a 7 and a 27 stage column.

The 7 Stage Column

In this case, 14 first order differential equations were required. The light phase transient concentrations, starting at time = 100 sec. are shown in Figure 15. If the integration is carried out until all the curves are horizontal, all the time derivatives dx_i/dt and dy_i/dt, become zero, then the profile is the steady state one.

The 27 Stage Column

The program structure was modified to solve the 54 first order differential equations required for a 27 stage column. Figure 16 shows the light phase concentration dependence on time at different positions in the column for a feed of constant composition again, starting at time = 100 sec.

Comparison of Figures 15 and 16 shows that the light phase concentration for the 27 stage column is greater than the light phase concentration for the 7 stage column. This is because when the number of stages increase there is greater mass transfer in the column.

Therefore, in computing the concentration profile in a stagewise backmixing column the overall mass transfer coefficient must be known. But in most design problems the mass transfer coefficient is an unknown variable and it must

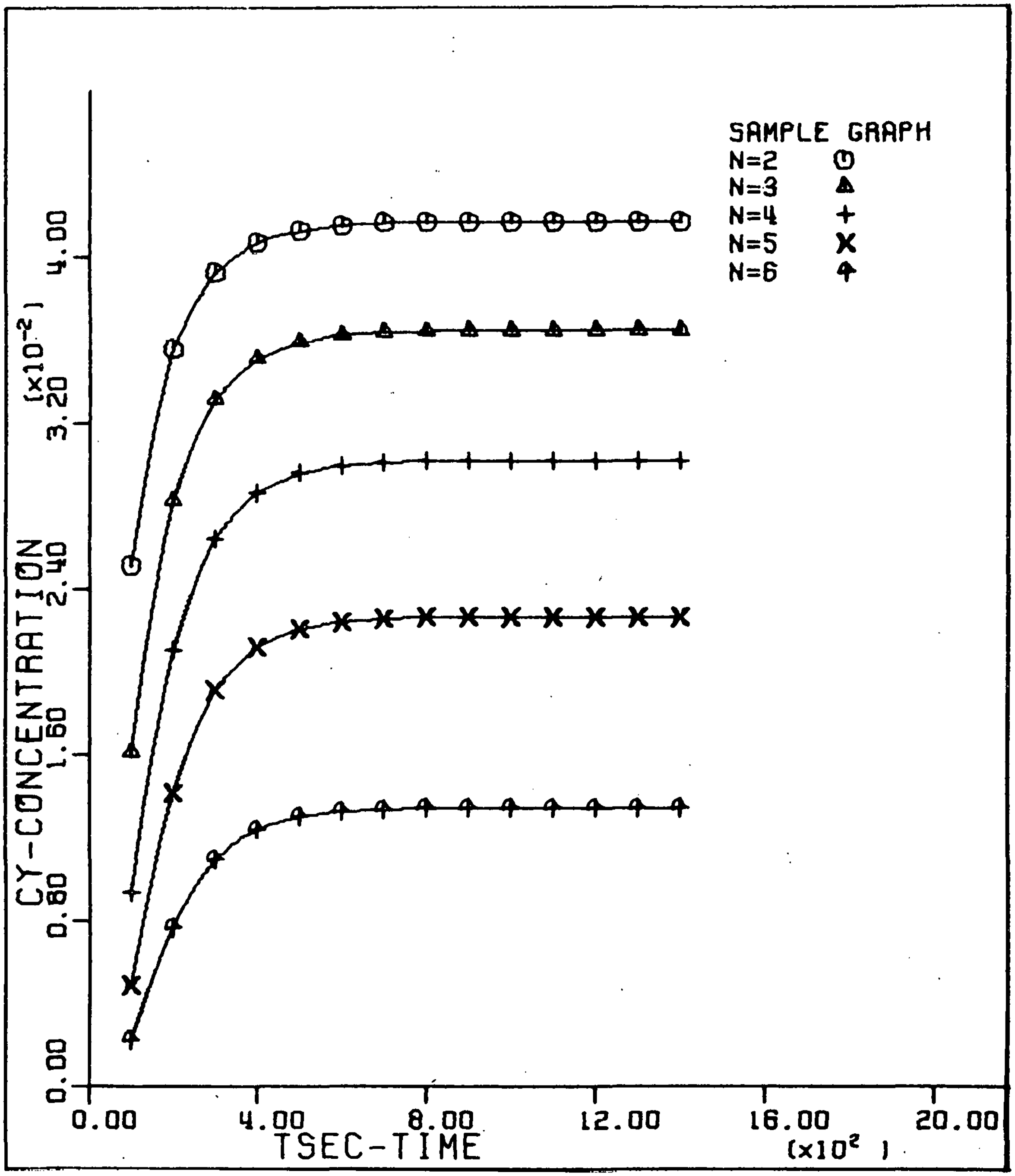

Figure 15. Unsteady state concentration profiles in the 7 stage backmixing column

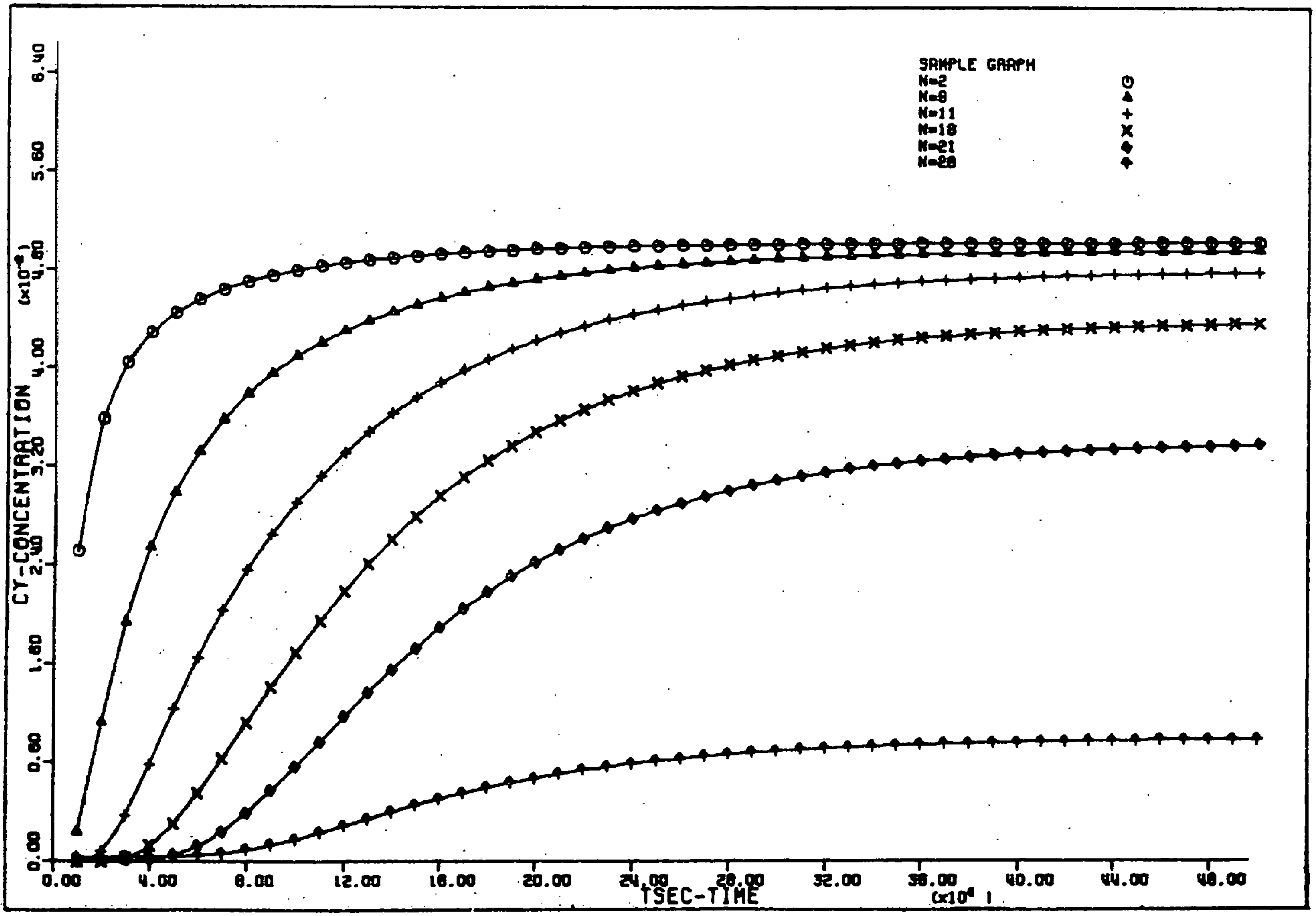

Figure 16. Unsteady state concentration profiles in the 27 stage backmixing column

be measured or else obtained from an existing correlation. The process of finding the overall mass transfer coefficient is not easy because the concentrations between stages are not known. Steiner and Hartland (43) have developed an approximate simplified technique by which one is able to measure the overall mass transfer coefficient.

The mass transfer in a stage j may be written using Equation 106 as

$$K_{ox}ah\int_0^T (x_j-x_j^*)dt = L\int_0^T [(1+e_x)(x_{j-1}-x_j) - e_x(x_j-x_{j+1})]dt - hh_x\int_0^{x_T} dx_j \qquad (114)$$

The last integral on the right-hand side of the Equation (114) is equal to zero if the time interval is so selected that $x_{in} = 0$ at both $t = 0$ and $t = T$. The total mass transfer is the sum of that in all the stages. From Equation 114 the mass transfer coefficient may be expressed as,

$$K_{ox} = \frac{L}{ah}\,\frac{(1+e_x)\int_0^T (x_0-x_n)dt - e_x\int_0^T (x_1-x_{n+1})dt}{\sum_{j=1}^{n}\left(\int_0^T x_j dt - 1/m\int_0^T y_j dt\right)} \qquad (115)$$

To find K_{ox}, the concentration between each stage must be known. As this is impossible in practice, it must be estimated from the end concentrations. Steiner and Hartland showed a reasonably simple way to estimate K_{ox}. They assumed a linear variation in concentration between consecutive control planes as shown in Figure 17. Their approximate formula is

$$K_{ox} = \frac{2L}{ah} \frac{\int_0^T x_o dt - \int_0^T x_n dt}{(n+1)\int_0^T x_n dt + (n-1)\int_0^T x_o dt - \frac{1}{m}[(n+1)\int_0^T y_{n+1} dt + (n-1)\int_0^T y_1 dt]} \quad (116)$$

In this method, constant flows of pure solvents are maintained throughout the column and in a given time an impulse of the solute is added to one of the phases, the concentration dependence with time can be recorded at different points in the column as shown in Figure 18. The area under the curves corresponds to the total amount of solute that still remains in the original phase, or that has been transferred to the other one. By using numerical integration one can find the mass transfer coefficients from Equation 116.

Gear's Method

The choice of the Gear's method (9, 16, 17 and 18) would appear to be logical since these equations, like many encountered in chemical and control engineering, are almost certainly stiff, a situation for which Gear's method is well-suited (23). The Gear integration program is a package

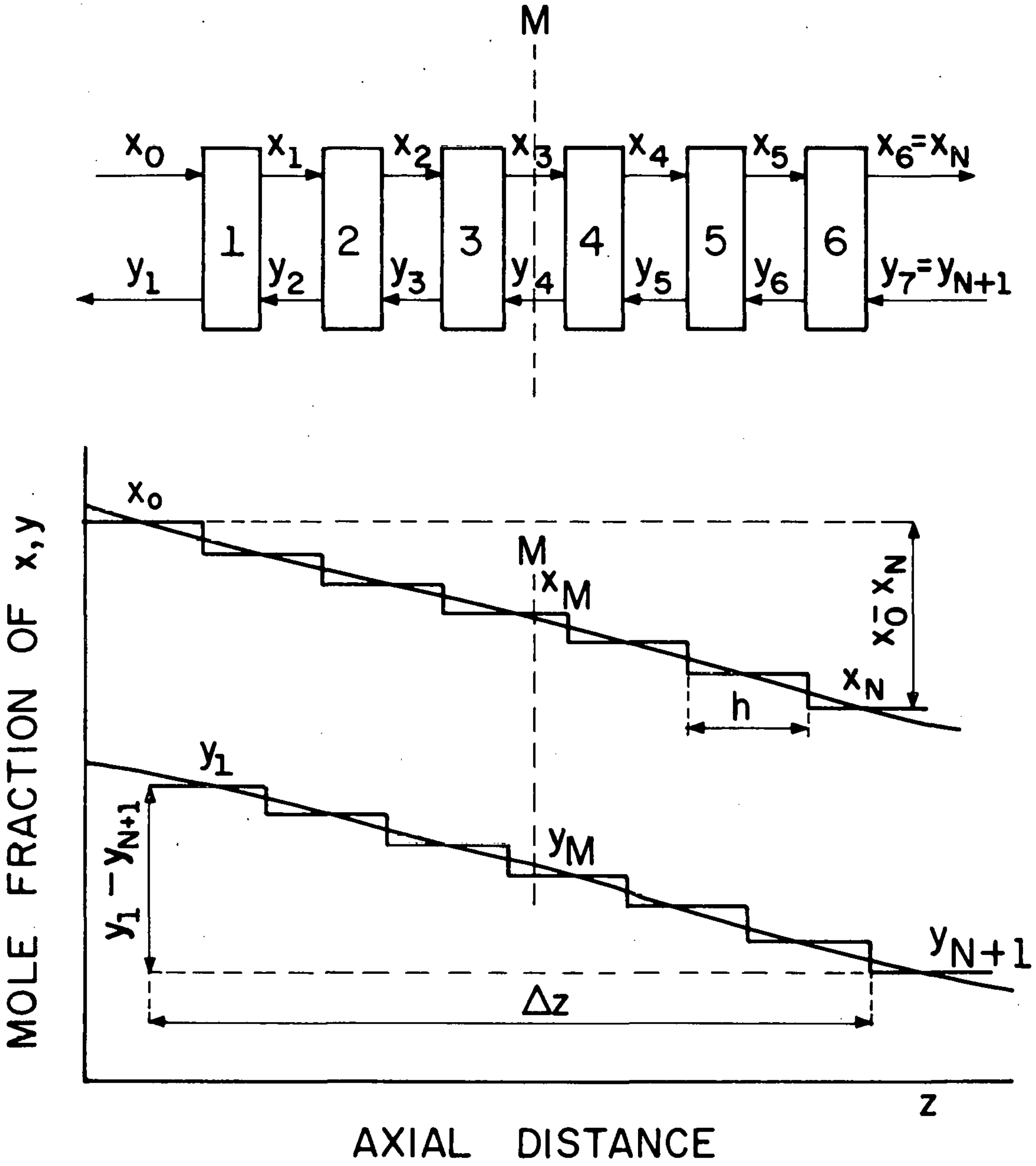

Figure 17. Diagram for derivation of approximate formula for mass transfer coefficients

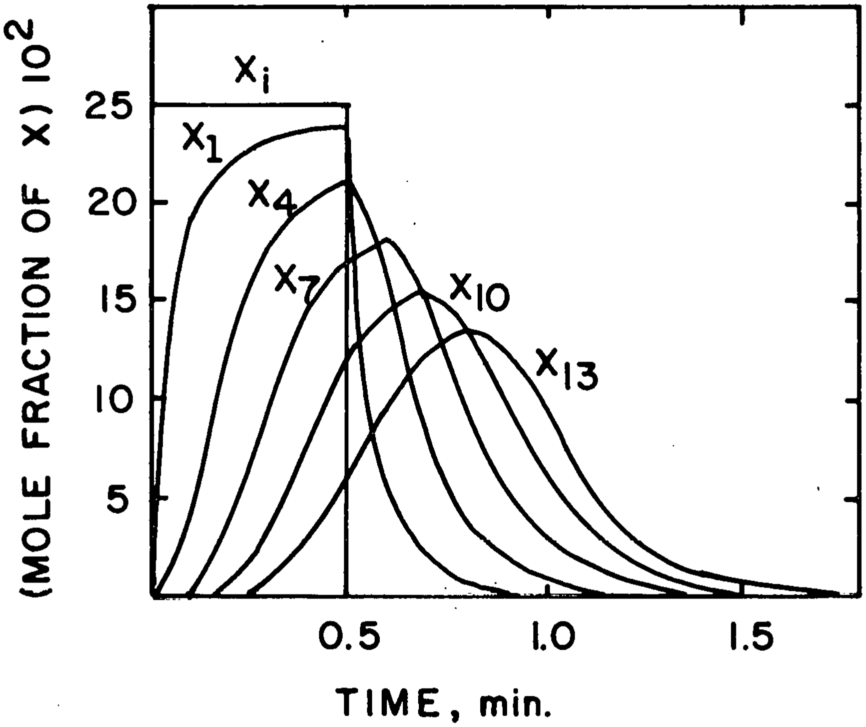

Figure 18. Response of column to a single impulse of solute; stagewise model

of subroutines for the numerical solution of systems of ordinary differential equations, given the initial values. Although particularly well-suited for stiff systems, it can be used generally. The package contains both the implicit Adams method and the backward differentiation formulas, or the methods of C. W. Gear.

The details of this method have been described by Gear (9) and Hindmarsh (16, 17, and 18).

Figure 19 shows the overall structure of the Gear package. It consists of seven subroutines (DRIVE, INTERP, STIFF, COSET, PSET, DEC, and SOL) and three user-supplied routines (CALLING PROGRAM or MAIN PROGRAM, DIFFUN, PEDERV). A downward sloping line from one box to another indicates that the lower routine is called by the upper one.

To define the problem being solved the following must be provided by the user:

1. A calling program which makes calls to subroutine DRIVE and must set the initial values, method parameters, and output values of t. DRIVE in turn calls other routines for the solution of the problem.
2. Subroutine DIFFUN which defines the problem and is called by STIFF and also by PSET. It computes a vector $y' = f(y,t)$ of length N for given values of $T = t$ and the vector $Y = y$ of length N.

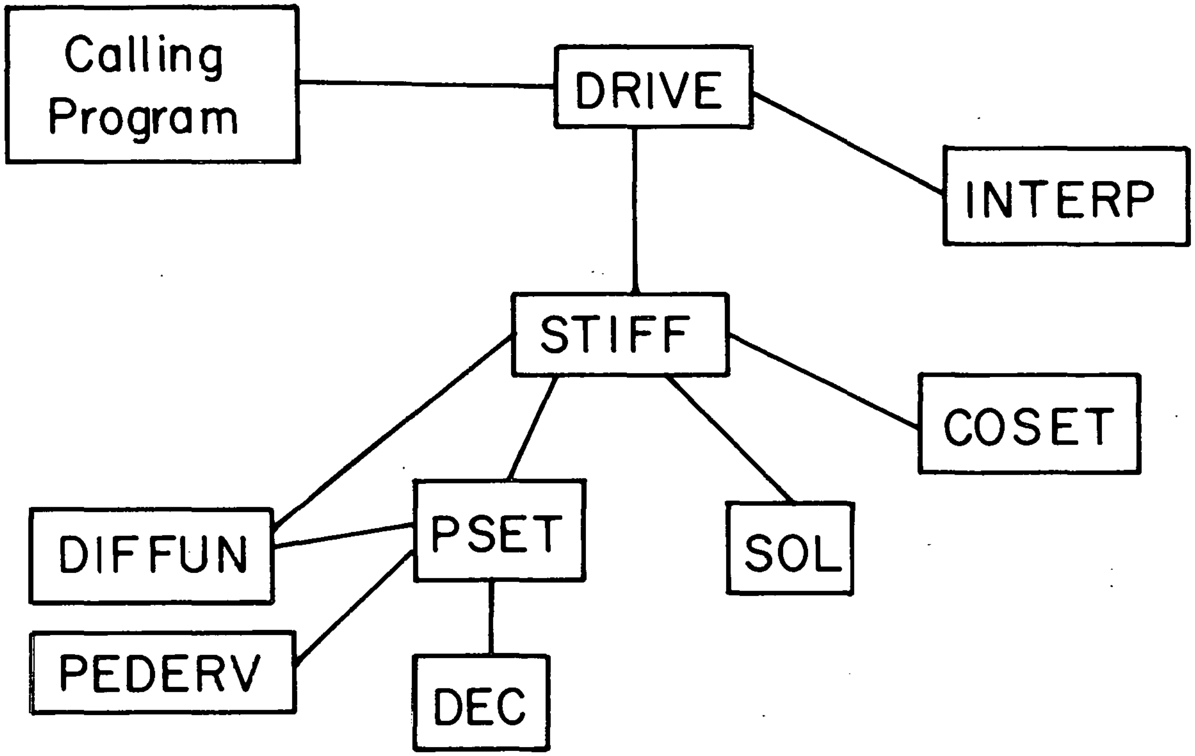

Figure 19. Structure of the GEAR package

3. Subroutine PEDERV which is called by PSET, supplies the partial derivatives of f(y,t) with respect to y (i.e., the Jacobian matrix), at T = t and Y = y. It must form a two dimensional array PD, stored as an $N_0 \times N_0$ array, according to:

$$PD(i,j) = df_i/dy_j \qquad 1 \leq i,\ j \leq N$$

If MITER is never 1, one may simply have for subroutine PEDERV:

```
SUBROUTINE PEDERV (N, T, Y, PD, N0)
RETURN
END
```

If MITER is equal 1, one must supply all partial derivatives f(y,t) with respect to y.

Possible Modifications for the Gear Package

Special situations may require that the user make some modifications to the Gear package before it can be used effectively for his particular problem. For the most part these involve changes only in DRIVE. The other routines of the package can be regarded as "black boxes"; and modifications to them are discouraged. The details have been discussed and listed in the package (18). The DRIVE routine, as written, will handle a maximum of 20 first-order ordinary differential equations. If this number is to be changed to a number N_{MAX}, then only the following statements in DRIVE must be included,

COMMON/GEAR 2/$Y_{MAX}(N_{MAX})$
COMMON/GEAR 3/ERROR(N_{MAX})
COMMON/GEAR 4/SAVE 1 (N_{MAX})
COMMON/GEAR 5/SAVE 2(N_{MAX})
COMMON/GEAR 6/PW(N_{MAX}**2)
COMMON/GEAR 7/IPIV(N_{MAX})

- - - - - - - - - - - - - - -

DIMENSION Y(N_{MAX},13)

The other subroutines do not change, because the length of the common blocks containing arrays in those subroutines is only 1, as these blocks are assumed to be loaded according to their declared lengths in DRIVE.

CONCLUSIONS

A general theoretical treatment based on the proposed models permits evaluation of the overall behavior of two-phase continuous flow operations by taking into consideration the effect of longitudinal dispersion of both fluids. Although extraction columns may be described by either a differential or stagewise model the differential model has been most widely applied to columns in common use where a linear equilibrium relation can be used. From the comparison of the models it can be determined that the two models approach each other as the number of stage becomes large.

Backmixing has an extremely undesirable effect on the extent of mass transfer in solvent extraction systems. It reduces the concentration driving force, the extraction efficiency, the number of theoretical stages, and the number of transfer units. Also, it increases the column height needed to obtain a given separation. Because of the importance of backmixing on column performance, it should always be taken into consideration.

In order to include the effect of backmixing in extraction column design and simulation the true number of transfer units, as defined by Colburn, and the backmixing coefficients must be known. This permits the separate evaluation of mass transfer and backmixing effects on column efficiency. The true number of transfer units and the extraction efficiency can be evaluated experimentally by using concentration profiles. This method, however, is not usually economically attractive because of the time and cost involved in carrying out the work. Several attempts have been made to develop a simple and rapid theoretical method for estimating the true number of transfer units and extraction efficiency.

By comparing the results obtained from these methods, the relation of Watson and Cochran, which is the only method not based on column length, is the simplest and most accurate method for design purpose, insofar as could be determined from the experimental data employed in this investigation. However, this relation may not be useful over a very wide range of variables because it may predict a negative length for some combinations of the variables. Its range of accuracy should be investigated further before the technique can be employed with confidence.

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APPENDIX A: SAMPLE CALCULATION

Calculation of column efficiency by Method 3:

From Table 2, the data for run No. 2 are:

$L = 1.96$ Ft.

$U_x = 27.0$ Ft./Hr.

$U_y = 42.0$ Ft./Hr.

$E_x = 7.27$ Sq.Ft./Hr.

$E_y = 1.20$ Sq.Ft./Hr.

$(NTU_{ox})_p = 2.84$

$(NTU_{ox})_T = 5.42$

Then the Peclet numbers are:

$P_x = HU_x/E_x = (1.96)(27)/(7.27) = 7.3$

$P_y = HU_y/E_y = (1.96)(42)/(1.20) = 68.6$

For MIBK - HAC - H_2O system, at 30°C $m = 0.52$ and the extraction factor becomes,

$F = U_x/mU_y = (27)/(0.52)(42) = 1.236$

From Equations 94 and 95 the weighting factors are:

$$f_x = \frac{(NTU_{ox})_T + k'(NTU_{ox})_T^{2\alpha}F^{-.5-\alpha}}{(NTU_{ox})_T + k'(NTU_{ox})_T^{2\alpha}F^{-1.5-\alpha}}$$

$$f_y = \frac{(NTU_{ox})_T + k'(NTU_{ox})_T^{2\alpha}F^{-.5-\alpha}}{(NTU_{ox})_T + k'(NTU_{ox})_T^{2\alpha}F^{+.5-\alpha}}$$

With $\alpha=0$ and $k' = 6.8$ the weighting factors f_x and f_y become:

$$f_x = \frac{(NTU_{ox})_T + 6.1}{(NTU_{ox})_T + 4.9} \quad \text{and} \quad f_y = \frac{(NTU_{ox})_T + 6.1}{(NTU_{ox})_T + 7.6}$$

From Equation 93 the overall Peclet group is,

$$(PB)_y = \left(\frac{F}{f_x P_x} + \frac{1}{f_y P_y}\right)^{-1}$$

and

$$(PB)_y = \frac{500.8(NTU_{ox})_T + 3054.8}{92.4(NTU_{ox})_T + 472.3}$$

Using Equation 92 the "number of overall dispersion units" is,

$$(NTU_{ox})_D = \frac{\ln F}{F-1}\,\Phi + (PB)_y$$

By setting $\Phi=1$ the result is accurate enough and it yields,

$$(NTU_{ox})_D = 0.896 + \frac{500.8(NTU_{ox})_T + 3054.8}{92.4(NTU_{ox})_T + 472.3}$$

$$= \frac{583.6(NTU_{ox})_T + 3478.1}{92.4(NTU_{ox})_T + 472.3}$$

Then Equation 91 is,

$$\frac{1}{(NTU_{ox})_p} = \frac{1}{(NTU_{ox})_T} + \frac{1}{(NTU_{ox})_D}$$

Substitute for $(NTU_{ox})_p$ and $(NTU_{ox})_D$ to obtain,

$$113.1(NTU_{ox})_T^2 + 168.8(NTU_{ox})_T - 3478.1 = 0$$

The solution of this equation gives,

$$(NTU_{ox})_T = 4.85$$

and then the column efficiency is,

$$\eta = \frac{(NTU_{ox})_p}{(NTU_{ox})_T} = \frac{2.84}{4.85} = 0.585$$

<u>Calculation of column efficiency by Method 5</u>:

In this calculation the data for run No. 2 of Table 2 is used. From Equation 104 the column efficiency is,

$$\eta = 1 - \frac{1}{NP_x + 1-F + \frac{1}{(NTU_{ox})_p}} - \frac{F}{NP_y - 1+F + \frac{1}{(NTU_{ox})_p}}$$

where NP_x and NP_y are:

$$NP_x = \frac{(HTU_{ox})_p U_x}{E_x} = \frac{U_x H}{E_x (NTU_{ox})_p} = \frac{(27)(1.96)}{(7.27)(2.84)} = 2.563$$

$$NP_y = \frac{(HTU_{ox})_p U_y}{E_y} = \frac{U_y H}{E_y (NTU_{ox})_p} = \frac{(42)(1.96)}{(1.20)(2.84)} = 24.15$$

Then the column efficiency becomes,

$$\eta = 0.577$$

and,

$$(NTU_{ox})_T = \frac{(NTU_{ox})_P}{\eta} = 4.92$$

By using the mathematical model the experimental true number of transfer units is determined and from Table 2 its value is,

$$(NTU_{ox})_T = 5.42$$

Then experimental column efficiency becomes,

$$\eta = \frac{(NTU_{ox})_P}{(NTU_{ox})_T} = \frac{2.84}{5.42} = .524$$

APPENDIX B: COMPUTER PROGRAM LISTINGS

List of symbols:

CY	Concentration of light phase
DY	Derivative of Y with respect to time, DY = dy/dt
EG	Backflow ratio for light phase
EL	Backflow ratio for heavy phase
EPS	Relative error bound (used only on the first call)
ERROR	Error, an array of N elements
G	Light phase flow rate
H	Height of a stage
HG	Holdup fraction of light phase
HL	Holdup fraction of heavy phase
HMAX,HMIN	Maximum and minimum absolute value of the step size
HO	Step size (used for input only on the first call)
HUSED	Step size h last used
INDEX	Integer used as input to indicate the type of call and for output to indicate the results of the last call
IPIV	An integer array of length N
JSTART	An integer used on input and output
KA	Mass transfer coefficient - interfacial area product

KFLAG	A completion code with special values and meanings
L	Heavy phase flow rate
LOUT	Logical unit number for the output of messages during the integration
METH	Method indicator - METH = 1, means the Adams integration method, METH = 2, means the stiff integration methods of Gear (the backward differentiation formulas)
MF	Method flag (used only on first call). Allowed values are 10, 11, 12, 13, 20, 21, 22, 23. MF has two decimal digits, METH and MITER (MF = 10*Meth + Miter)
MITER	Iteration method indicator. MITER = 1, means chord method with analytic Jacobian. For this the user should supply subroutine PEDERV. MITER = 2, means chord method with Jacobian calculated internally by finite difference
N	Number of first-order differential equations
NFE	Cumulative number of f evaluations (DIFFUN calls)
NJE	Cumulative number of Jacobian evaluations
NO	Constant integer,.GE.N, used for dimensioning purposes
NQUSED	The order last used
NSTEP	Cumulative number of steps taken
PD	Partial derivative
PW	A block of locations used to store partial derivatives
S	Distribution coefficient

SAVE 1 SAVE 2	Two arrays of working storage each of length N
T	Time, independent variable, sec
TO	Initial value of time, sec
TOUT	Output value of time, sec
TSEC	Time, sec
UROUND	Unit round off of the machine, i.e., the smallest positive U such that 1.+U.NE.1. on the machine
X	Concentration of heavy phase
XI	Concentration of heavy phase at inlet
Y	Concentration of light phase, a vector of length N
YI	Concentration of light phase at inlet
YO	A vector of length N containing the initial of Y (used for input only on first call)

```
CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC
C                                                                         C
C      SIMULATICN PROGRAM FCR COMPUTING UNSTEADY STATE CONCENTRATION     C
C      PROFILES IN BACKMIXING STAGEWISE COLUMN BY GEAR'S METHOD.          C
C      GEAR IS A PACKAGE FOR THE SOLUTICN OF THE INITIAL VALUE PROB-     C
C      LEM FOR SYSTEMS OF ORDINARY DIFFERENTIAL EQUATIONS, DY/DT=F(Y     C
C      ,T), Y=( Y(1), Y(2), ....Y(N) ).
C      THE DATA USED IN SUBROUTINE DIFFUN HAS BEEN PERFORMED BY MCD-     C
C      CNALD AND WILKINSCN.                                               C
C                                                                         C
CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC
C
C
C                    CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC
C                    C                               C
C                    C      THE 7 STAGE COLUMN       C
C                    C                               C
C                    CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC
C
C
CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC
C                                                                         C
C      MAIN PROGRAM MUST SET THE INITIAL VALUES, METHCD PARAMETERS,       C
C      AND OUTPUT VALUES OF T, AND MAKE CALLS TO DRIVE. DRIVE IN TU-     C
C     -RN CALLS OTHER ROUTINES FOR THE SOLUTICN OF THE PROBLEM.           C
C                                                                         C
CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC
C
C
      IMPLICIT REAL*8(A-H,O-Z)
      DIMENSICN Y0(14),TSEC(14),CY1(14),CY2(14),CY3(14),CY4(14),CY5(14)
      COMMON/GEAR9/HUSED,NQUSED,NSTEP,NFE,NJE
      N=14
      MF=22
      T0=0.D0
```

```
      H0=.00001D0
      EPS=.00001D0
      DO 5 I=1,14
5     Y0(I)=0.D0
      II=1
      TOUT=100.D0
      INDEX=1
10    CALL DRIVE(N,T0,H0,Y0,TOUT,EPS,MF,INDEX)
      WRITE (8,200) TOUT
      WRITE (8,201)
      DO 25 I=1,7
      J=I+7
25    WRITE (8,202) Y0(I),Y0(J)
      CY1(II)=Y0(2)
      CY2(II)=Y0(3)
      CY3(II)=Y0(4)
      CY4(II)=Y0(5)
      CY5(II)=Y0(6)
      TSEC(II)=TOUT
      IF(INDEX.EQ.0) GO TO 40
      WRITE (8,204) INDEX
      GO TO 50
40    TOUT=TOUT+100.D0
      II=II+1
      IF(TOUT.LE.1400.D0) GO TO 10
50    WRITE (8,203) NSTEP
      CALL GRAPH (-14,TSEC,CY1,1,101,6.,6.,0.,0.,0.,0.,'TSEC-TIME;',
     1      'CY-CONCENTRATION;','SAMPLE GRAPH;','N=2;')
      CALL GRAPHS(-14,TSEC,CY2,2,101,'N=3;')
      CALL GRAPHS(-14,TSEC,CY3,3,101,'N=4;')
      CALL GRAPHS(-14,TSEC,CY4,4,101,'N=5;')
      CALL GRAPHS(-14,TSEC,CY5,6,101,'N=6;')
      STOP
200   FORMAT(/11X,'AT TIME=',D22.11)
201   FORMAT(/18X,'Y',24X,'X')
```

```
  202 FORMAT(7(' ',6X,2D22.11))
  203 FORMAT (/4X,'NSTEP=',I5)
  204 FORMAT (/4X,'INDEX=',I3)
      END
CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC
C                                                                      C
C     SUBROUTINE DIFFUN IS CALLED BY STIFF, AND ALSO BY PSET IF MI-     C
C     TER=2. IT IS TO COMPUTE THE VECTOR DY=Y'=F(Y, T) OF LENGTH N      C
C     FOR GIVEN VALUES OF T=T1 AND THE VECTOR Y=Y1 OF LENGTH N. IT      C
C     IS REQUIRED REGARDLESS OF THE VALUE OF MF CHOSEN.                C
C                                                                      C
CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC
C
C
      SUBROUTINE DIFFUN (N,T,Y,DY)
      IMPLICIT REAL*8(A-H,O-Z)
      DIMENSION Y(14),DY(14)
      REAL*8 L,KA
      YI=.0005D0
      XI=.0693D0
      KA=.025D0
      H=7.45D0
      EG=.01D0
      G=.187D0
      HG=.123D0
      S=.73D0
      HL=.877D0
      EL=.32D0
      L=.203D0
      A=L/(H*HL)
      B=G/(H*HG)
      M=13
      N1=6
      NP1=N1+1
      MP1=M+1
```

```
      DY(1)=B*((1.D0+EG)*Y(2)-(1.D0+EG)*Y(1))
      DY(8)=A*(XI-(1.D0+EL)*Y(8)+EL*Y(9))
      DO 10 I=2,N1
      DY(I+7)=A*((1.D0+EL)*Y(I+6)-(1.D0+2.D0*EL)*Y(I+7)+EL*Y(I+8))
     1   -KA/(HL)*(Y(I+7)-Y(I)/S)
   10 DY(I)=B*((1.D0+EG)*Y(I+1)-(1.D0+2.D0*EG)*Y(I)+EG*Y(I-1))+KA/(HG)*
     1     (Y(I+7)-Y(I)/S)
      DY(NP1)=B*(YI-(1.D0+EG)*Y(NP1)+EG*Y(N1))
      DY(MP1)=A*((1.D0+EL)*Y(M)-(1.D0+EL)*Y(MP1))
      RETURN
      END
C
C
CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC
C                                                                      C
C      SUBROUTINE PEDERV IS CALLED BY PSET IF MITER=1. IT IS TO SUP-   C
C      PLY THE PARTIAL DERIVATIVES OF F(Y,T) WITH RESPECT TO Y (I.E.   C
C      , THE JACOBIAN MATRIX), EVALUATED AT T=T1 AND Y=Y1.             C
C                                                                      C
CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC
C
C
      SUBROUTINE PEDERV (N,T,Y,PD,N0)
      IMPLICIT REAL*8(A-H,O-Z)
      RETURN
      END
```

```
AT TIME=      0.10000000000D 03

        Y                           X
 0.24251894367D-01       0.60480345013D-01
 0.25149678509D-01       0.44491245858D-01
 0.16104404131D-01       0.29720373218D-01
 0.93361710388D-02       0.17976556754D-01
 0.48843450162D-02       0.98662195962D-02
 0.22064178056D-02       0.49648608379D-02
 0.51453886781D-03       0.27912926078D-02

AT TIME=      0.20000000000D 03

        Y                           X
 0.35265793726D-01       0.65650798315D-01
 0.35562806853D-01       0.56405089437D-01
 0.28265832424D-01       0.46335518846D-01
 0.21047230985D-01       0.36097211706D-01
 0.14199380617D-01       0.26343388815D-01
 0.76783959784D-02       0.17888840840D-01
 0.56879932312D-03       0.14967054257D-01

AT TIME=      0.30000000000D 03

        Y                           X
 0.39157643932D-01       0.66900212047D-01
 0.39270930998D-01       0.60103611392D-01
 0.33159891757D-01       0.52334781474D-01
 0.26430504047D-01       0.43726902547D-01
 0.19111062284D-01       0.34510131782D-01
 0.10976393044D-01       0.25580855386D-01
 0.60264137108D-03       0.24058421737D-01
```

```
AT TIME=      0.40000000000D 03

         Y                             X
 0.40676835024D-01       0.67344305043D-01
 0.40722276141D-01       0.61504401929D-01
 0.35125048661D-01       0.54681017621D-01
 0.28655202310D-01       0.46811037359D-01
 0.21205743772D-01       0.37937190758D-01
 0.12430537913D-01       0.28963997004D-01
 0.61766595504D-03       0.28307325491D-01

AT TIME=      0.50000000000D 03

         Y                             X
 0.41290508775D-01       0.67520083495D-01
 0.41308918373D-01       0.62066568615D-01
 0.35923697743D-01       0.55628963462D-01
 0.29564992962D-01       0.48065961763D-01
 0.22068399403D-01       0.39343267294D-01
 0.13034010961D-01       0.30367261812D-01
 0.62391041234D-03       0.30094950660D-01

AT TIME=      0.60000000000D 03

         Y                             X
 0.41542895930D-01       0.67591974439D-01
 0.41550230797D-01       0.62297360887D-01
 0.36252702302D-01       0.56018845654D-01
 0.29940418372D-01       0.48583094922D-01
 0.22425054006D-01       0.39923996879D-01
 0.13284029280D-01       0.30948551639D-01
 0.62649851813D-03       0.30838314652D-01
```

```
AT TIME=      0.70000000000D 03

        Y                          X
 0.41642950553D-01       0.67620294501D-01
 0.41645914357D-01       0.62388669835D-01
 0.36383374675D-01       0.56173415092D-01
 0.30089814949D-01       0.48788560417D-01
 0.22567288813D-01       0.40155322746D-01
 0.13383974070D-01       0.31180884387D-01
 0.62753357592D-03       0.31136730432D-01

AT TIME=      0.80000000000D 03

        Y                          X
 0.41684787385D-01       0.67632171438D-01
 0.41685919820D-01       0.62426885617D-01
 0.36437966946D-01       0.56238044898D-01
 0.30152175154D-01       0.48874385019D-01
 0.22626602009D-01       0.40251837558D-01
 0.13425608585D-01       0.31277675383D-01
 0.62796466922D-03       0.31260818115D-01

AT TIME=      0.90000000000D 03

        Y                          X
 0.41702841874D-01       0.67637323632D-01
 0.41703181307D-01       0.62443404485D-01
 0.36461490733D-01       0.56265933911D-01
 0.30179005525D-01       0.48911355554D-01
 0.22652078931D-01       0.40293330439D-01
 0.13443460078D-01       0.31319181252D-01
 0.62814944439D-03       0.31313857508D-01
```

```
AT TIME=      0.10000000000D 04

          Y                          X
 0.41708974301D-01       0.67639050567D-01
 0.41709046832D-01       0.62448991690D-01
 0.36469512027D-01       0.56275407764D-01
 0.30188190860D-01       0.48923971456D-01
 0.22660839973D-01       0.40307564827D-01
 0.13449628789D-01       0.31333519156D-01
 0.62821338367D-03       0.31332343863D-01

AT TIME=      0.11000000000D 04

          Y                          X
 0.41710221927D-01       0.67639392664D-01
 0.41710241153D-01       0.62450118899D-01
 0.36471156488D-01       0.56277335557D-01
 0.30190088682D-01       0.48926561577D-01
 0.22662665912D-01       0.40310517630D-01
 0.13450926588D-01       0.31336533723D-01
 0.62822682279D-03       0.31336297728D-01

AT TIME=      0.12000000000D 04

          Y                          X
 0.41710503942D-01       0.67639476889D-01
 0.41710510397D-01       0.62450380735D-01
 0.36471518946D-01       0.56277770980D-01
 0.30190496299D-01       0.48927129649D-01
 0.22663046871D-01       0.40311143356D-01
 0.13451188936D-01       0.31337144436D-01
 0.62822952912D-03       0.31337053406D-01
```

```
AT TIME=      0.13000000000D 04

         Y                          X
 0.41711417241D-01      0.67639755343D-01
 0.41711381695D-01      0.62451234596D-01
 0.36472684884D-01      0.56279180954D-01
 0.30191797985D-01      0.48928954727D-01
 0.22664252891D-01      0.40313133782D-01
 0.13452011079D-01      0.31339059617D-01
 0.62823799365D-03      0.31339375433D-01

AT TIME=      0.14000000000D 04

         Y                          X
 0.41711845113D-01      0.67639873654D-01
 0.41711791132D-01      0.62451622294D-01
 0.36473247249D-01      0.56279842207D-01
 0.30192444919D-01      0.48929840231D-01
 0.22664872795D-01      0.40314138676D-01
 0.13452449489D-01      0.31340078275D-01
 0.62824253979D-03      0.31340698012D-01
```

```
                    CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC
                    C                               C
                    C      THE 27 STAGE COLUMN      C
                    C                               C
                    CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC
C
C
      IMPLICIT REAL*8(A-H,O-Z)
      DIMENSION Y0(54),TSEC(54),CY1(54),CY2(54),CY3(54),CY4(54),CY5(54),
     1   CY6(54)
      COMMON/GEAR9/HUSED,NQUSED,NSTEP,NFE,NJE
      N=54
      MF=22
      T0=0.D0
      H0=.00001D0
      EPS=.00001D0
      DO 5 I=1,54
  5   Y0(I)=0.D0
      II=1
      TOUT=100.D0
      INDEX=1
  10  CALL DRIVE(N,T0,H0,Y0,TOUT,EPS,MF,INDEX)
      WRITE (8,200) TOUT
      WRITE (8,201)
      DO 25 I=1,27
      J=I+27
  25  WRITE (8,202) Y0(I),Y0(J)
      CY1(II)=Y0(2)
      CY2(II)=Y0(6)
      CY3(II)=Y0(11)
      CY4(II)=Y0(16)
      CY5(II)=Y0(21)
      CY6(II)=Y0(26)
      TSEC(II)=TOUT
      IF(INDEX.EQ.0) GO TO 40
```

```
    WRITE (8,204) INDEX
    GO TO 50
40  TOUT=TOUT+100.D0
    II=II+1
    IF(TOUT.LE.5000.D0) GO TO 10
50  WRITE (8,203) NSTEP
    CALL GRAPH (-50,TSEC,CY1,1,101,16.,9.,0.,0.,0.,0.,'TSEC-TIME;',
   1     'CY-CONCENTRATION;','SAMPLE GRAPH;','N=2;')
    CALL GRAPHS(-50,TSEC,CY2,2,101,'N=6;')
    CALL GRAPHS(-50,TSEC,CY3,3,101,'N=11;')
    CALL GRAPHS(-50,TSEC,CY4,4,101,'N=16;')
    CALL GRAPHS(-50,TSEC,CY5,5,101,'N=21;')
    CALL GRAPHS(-50,TSEC,CY6,6,101,'N=26;')
    STOP
200 FORMAT(/11X,'AT TIME=',D22.11)
201 FORMAT(/18X,'Y',24X,'X')
202 FORMAT(27(' ',6X,2D22.11))
203 FORMAT (/4X,'NSTEP=',I5)
204 FORMAT (/4X,'INDEX=',I3)
    END
    SUBROUTINE DIFFUN (N,T,Y,DY)
    IMPLICIT REAL*8(A-H,O-Z)
    DIMENSION Y(54),DY(54)
    REAL*8 L,KA
    YI=.0005D0
    XI=.0693D0
    KA=.025D0
    H=7.45D0
    EG=.01D0
    G=.187D0
    HG=.123D0
    S=.73D0
    HL=.877D0
    EL=.32D0
    L=.203D0
```

```
      A=L/(H*HL)
      B=G/(H*HG)
      M=53
      N1=26
      NP1=N1+1
      MP1=M+1
      DY(1)=B*((1.D0+EG)*Y(2)-(1.D0+EG)*Y(1))
      DY(28)=A*(XI-(1.D0+EL)*Y(28)+EL*Y(29))
      DO 10 I=2,N1
      DY(I+27)=A*((1.D0+EL)*Y(I+26)-(1.D0+2.D0*EL)*Y(I+27)+EL*Y(I+28))
     1     -KA/(HL)*(Y(I+27)-Y(I)/S)
   10 DY(I)=B*((1.D0+EG)*Y(I+1)-(1.D0+2.D0*EG)*Y(I)+EG*Y(I-1))+KA/(HG)*
     1      (Y(I+27)-Y(I)/S)
      DY(NP1)=B*(YI-(1.D0+EG)*Y(NP1)+EG*Y(N1))
      DY(MP1)=A*((1.D0+EL)*Y(M)-(1.D0+EL)*Y(MP1))
      RETURN
      END
      SUBROUTINE PEDERV (N,T,Y,PD,N0)
      IMPLICIT REAL*8(A-H,O-Z)
      RETURN
      END
CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC
C                                                                           C
C      SUBROUTINE DRIVE IS TO BE CALLED ONCE FOR EACH OUTPUT VALUE          C
C      OF T, AND IN TURN MAKES REPEATED CALLS TO THE CORE INTEGRATOR        C
C      , STIFF.                                                             C
C                                                                           C
CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC
C
C
      SUBROUTINE DRIVE (N,T0,H0,Y0,TOUT,EPS,MF,INDEX)
      REAL*8 DSQRT
      INTEGER N,MF,INDEX
      INTEGER NC,MFC,KFLAG,JSTART,IPIV,NSQ,NQUSED,NSTEP,NFE,NJE
      INTEGER LCUT,I,N0,NHCUT,KGO
```

```
      DOUBLE PRECISION T0,H0,Y0,TOUT,EPS
      DOUBLE PRECISION T,H,HMIN,HMAX,EPSC,UROUND,YMAX,ERROR,
     1   SAVE1,SAVE2,PW,EPSJ,HUSED
      DOUBLE PRECISION Y,TOUTP,AYI,D
      COMMON /GEAR1/ T,H,HMIN,HMAX,EPSC,UROUND,NC,MFC,KFLAG,JSTART
      COMMON /GEAR2/ YMAX(54)
      COMMON /GEAR3/ ERROR(54)
      COMMON /GEAR4/ SAVE1(54)
      COMMON /GEAR5/ SAVE2(54)
      COMMON /GEAR6/ PW(2916)
      COMMON /GEAR7/ IPIV(54)
      COMMON /GEAR8/ EPSJ,NSQ
      COMMON /GEAR9/ HUSED,NQUSED,NSTEP,NFE,NJE
      DATA LOUT/6/
      DIMENSION Y0(N)
      DIMENSION Y(54,13)
      IF (INDEX .EQ. 0) GO TO 20
      IF (INDEX .EQ. 2) GO TO 25
      IF (INDEX .EQ. -1) GO TO 30
      IF (INDEX .EQ. 3) GO TO 40
      IF (INDEX .NE. 1) GO TO 430
      IF (EPS .LE. 0.D0) GO TO 400
      IF (N .LE. 0) GO TO 410
      IF ((T0-TOUT)*H0 .GE. 0.D0) GO TO 420
      UROUND=2.22D-16
      DO 10 I=1,N
      YMAX(I)=DABS(Y0(I))
      IF (YMAX(I) .EQ. 0.D0) YMAX(I)=1.D0
   10 Y(I,1) = Y0(I)
      NC=N
      T=T0
      H=H0
      IF ((T+H) .EQ. T) WRITE(LOUT,15)
   15 FORMAT(35H WARNING..  T + H = T ON NEXT STEP.)
      HMIN=DABS(H0)
```

```
      HMAX=DABS(T0-TOUT)*10.D0
      EPSC=EPS
      MFC=MF
      JSTART=0
      N0=N
      NSQ=N0*N0
      EPSJ=DSQRT(UROUND)
      NHCUT=0
      GO TO 50
   20 HMAX=DABS(TOUT-TOUTP)*10.D0
      GO TO 80
   25 HMAX=DABS(TOUT-TOUTP)*10.D0
      IF ((T-TOUT)*H .GE. 0.D0) GO TO 500
      GO TO 85
   30 IF ((T-TOUT)*H .GE. 0.D0) GO TO 440
      JSTART =-1
      NC=N
      EPSC=EPS
      MFC=MF
   40 IF ((T+H) .EQ. T) WRITE(LOUT,15)
   50 CALL STIFF (Y,N0)
      KGO=1-KFLAG
      GO TO (60, 100, 200, 300), KGO
   60 CONTINUE
      D=0.D0
      DO 70 I=1,N
      AYI=DABS(Y(I,1))
      YMAX(I)=DMAX1(YMAX(I),AYI)
   70 D=D+(AYI/YMAX(I))**2
      D=D*(UROUND/EPS)**2
      IF (D .GT. DFLOAT(N)) GO TO 250
      IF (INDEX .EQ. 3) GO TO 500
      IF (INDEX .EQ. 2) GO TO 85
   80 IF ((T-TOUT)*H .LT. 0.D0) GO TO 40
      CALL INTERP (TOUT,Y,N0,Y0)
```

```
      GO TO 520
85    IF (((T+H)-TOUT)*H .LE. 0.D0) GO TO 40
      IF (DABS(T-TOUT) .LE. 100.D0*UROUND*HMAX) GO TO 500
      IF ((T-TOUT)*H .GE. 0.D0) GO TO 500
      H=(TOUT-T)*(1.D0-4.D0*UROUND)
      JSTART=-1
      GO TO 40
100   WRITE (LOUT,105) T
105   FORMAT(//35H KFLAG = -1 FROM INTEGRATOR AT T = ,E16.8/
     1   39H  ERROR TEST FAILED WITH DABS(H) = HMIN/)
110   IF (NHCUT .EQ. 10) GO TO 150
      NHCUT=NHCUT+1
      HMIN=HMIN*.1D0
      H=H*.1D0
      WRITE (LOUT,115) H
115   FORMAT(24H  H HAS BEEN REDUCED TO ,E16.8,
     1  26H  AND STEP WILL BE RETRIED//)
      JSTART=-1
      GO TO 40
150   WRITE (LOUT,155)
155   FORMAT(//44H PROBLEM APPEARS UNSOLVABLE WITH GIVEN INPUT//)
      GO TO 500
200   WRITE (LOUT,205) T,H
205   FORMAT(//35H KFLAG = -2 FROM INTEGRATOR AT T = ,E16.8,5H  H =,
     1 E16.8/52H  THE REQUESTED ERROE IS SMALLER THAN CAN BE HANDLED//)
      GO TO 500
250   WRITE (LOUT,255) T
255   FORMAT(//37H INTEGRATION HALTED BY DRIVER AT T = ,E16.8/
     1  56H  EPS TOO SMALL TO BE ATTAINED FOR THE MACHINE PRECISION/)
      KFLAG=-2
      GO TO 500
300   WRITE (LOUT,305) T
305   FORMAT(//35H KFLAG = -3 FROM INTEGRATOR AT T = ,E16.8/
     1  45H  CORRECTOR CONVERGENCE COULD NOT BE ACHIEVED/)
      GO TO 110
```

```
400 WRITE (LOUT,405)
405 FORMAT(//30H ILLEGAL INPUT.. EPS .LE. 0.D0//)
    INDEX=-4
    RETURN
410 WRITE (LOUT,415)
415 FORMAT(//25H ILLEGAL INPUT.. N .LE. 0//)
    INDEX=-4
    RETURN
420 WRITE (LOUT,425)
425 FORMAT(//38H ILLEGAL INPUT.. (T0-TOUT)*H .GE. 0.D0//)
    INDEX=-4
    RETURN
430 WRITE (LOUT,435) INDEX
435 FORMAT(//24H ILLEGAL INPUT.. INDEX =,I5//)
    INDEX=-4
    RETURN
440 WRITE(LOUT,445) T,TOUT,H
445 FORMAT(//46H INDEX = -1 ON INPUT WITH (T-TOUT)*H .GE. 0.D0/
   1   4H T =,E16.8,9H   TOUT =,E16.8,6H   H =,E16.8/
   1   44H INTERPOLATION WAS DONE AS ON NORMAL RETURN./
   2   41H DESIRED PARAMETER CHANGES WERE NOT MADE.)
    CALL INTERP (TOUT,Y,N0,Y0)
    INDEX=-5
    RETURN
500 TOUT=T
    DO 510 I=1,N
510 Y0(I)=Y(I,1)
520 INDEX=KFLAG
    TOUTP=TOUT
    H0=HUSED
    IF (KFLAG .NE. 0) H0=H
    RETURN
    END
```

```
AT TIME=      0.10000000000D 03                                    AT TIME=      0.30000000000D 03

          Y                          X                                  Y                            X
  0.24224923957D-01          0.60465554674D-01                  0.40240907300D-01          0.67035535169D-01
  0.25123996941D-01          0.44465837637D-01                  0.40402245594D-01          0.60825663797D-01
  0.16071528689D-01          0.29683244613D-01                  0.35156436060D-01          0.53838324040D-01
  0.93020783684D-02          0.17915916899D-01                  0.29729623379D-01          0.46363781219D-01
  0.48814797689D-02          0.97757905214D-02                  0.24399011488D-01          0.38765405277D-01
  0.23284455563D-02          0.48340096917D-02                  0.19401742864D-01          0.31411855158D-01
  0.10140286615D-02          0.21759510812D-02                  0.14927240913D-01          0.24628656757D-01
  0.40553112744D-03          0.89689576484D-03                  0.11098687857D-01          0.18659775489D-01
  0.14991843428D-03          0.34080533441D-03                  0.79671400430D-02          0.13646414040D-01
  0.51595314238D-04          0.12022717440D-03                  0.55178552394D-02          0.96253880270D-02
  0.16669086257D-04          0.39661379093D-04                  0.36855908436D-02          0.65444505320D-02
  0.51451588004D-05          0.12344035958D-04                  0.23742111050D-02          0.42884616112D-02
  0.16442113359D-05          0.37083549432D-05                  0.14759805889D-02          0.27090628282D-02
  0.77507060643D-06          0.12096689729D-05                  0.88709944469D-03          0.16514022592D-02
  0.84159788312D-06          0.67777271051D-06                  0.51777619404D-03          0.97376020194D-03
  0.14494398418D-05          0.88793241001D-06                  0.29662150887D-03          0.55868575755D-03
  0.27093113803D-05          0.16343037337D-05                  0.17192240062D-03          0.31656661021D-03
  0.50434715550D-05          0.31455810596D-05                  0.10724125177D-03          0.18387226238D-03
  0.92249676050D-05          0.59956469562D-05                  0.79878551408D-04          0.11857585382D-03
  0.16529094167D-04          0.11223013243D-04                  0.76300854928D-04          0.94788764869D-04
  0.28958541216D-04          0.20582052130D-04                  0.89329721417D-04          0.97876471830D-04
  0.49511599162D-04          0.36908843994D-04                  0.11588274861D-03          0.12061010553D-03
  0.82430524270D-04          0.64554305523D-04                  0.15541414493D-03          0.16040474308D-03
  0.13332496821D-03          0.10961666424D-03                  0.20891491186D-03          0.21734332278D-03
  0.20920176172D-03          0.17827667998D-03                  0.27846016932D-03          0.29180824177D-03
  0.32014569937D-03          0.26169541615D-03                  0.36844414614D-03          0.37411205316D-03
  0.49819241820D-03          0.22055753541D-03                  0.49869178924D-03          0.36655513852D-03
```

```
AT TIME=      0.50000000000D 03                          AT TIME=      0.70000000000D 03

        Y                         X                           Y                         X
 0.44434041033D-01         0.68032433792D-01         0.46396215094D-01         0.68455570296D-01
 0.44499002600D-01         0.64369920795D-01         0.46431313641D-01         0.65969969301D-01
 0.41198412134D-01         0.60155616219D-01         0.44133686100D-01         0.63086927728D-01
 0.37593990509D-01         0.55453303991D-01         0.41570608907D-01         0.59818662769D-01
 0.33787111304D-01         0.50369729882D-01         0.38785024349D-01         0.56201537425D-01
 0.29879240307D-01         0.45036352482D-01         0.35821127209D-01         0.52287161179D-01
 0.25977168898D-01         0.39600193357D-01         0.32731056050D-01         0.48140525164D-01
 0.22185195935D-01         0.34212916920D-01         0.29572465565D-01         0.43837135979D-01
 0.18597602744D-01         0.29019421877D-01         0.26405625931D-01         0.39459311774D-01
 0.15292364522D-01         0.24147351566D-01         0.23290321792D-01         0.35091934160D-01
 0.12326781570D-01         0.19698762778D-01         0.20282810956D-01         0.30818012685D-01
 0.97354061486D-02         0.15744825111D-01         0.17433095254D-01         0.26714439535D-01
 0.75302968480D-02         0.12323937631D-01         0.14782719342D-01         0.22848268194D-01
 0.57033155117D-02         0.94431432865D-02         0.12363253152D-01         0.19273945199D-01
 0.42299442426D-02         0.70822862412D-02         0.10195538792D-01         0.16031268796D-01
 0.30739722570D-02         0.52000614234D-02         0.82897032400D-02         0.13144856205D-01
 0.21923894273D-02         0.37409797734D-02         0.66458638503D-02         0.10624387114D-01
 0.15399086123D-02         0.26423096690D-02         0.52553929227D-02         0.84659087972D-02
 0.10726929475D-02         0.18402219180D-02         0.41025656661D-02         0.66538490380D-02
 0.75105233592D-03         0.12746167619D-02         0.31663951478D-02         0.51634933883D-02
 0.54105989819D-03         0.89239458347D-03         0.24224565540D-02         0.39636446678D-02
 0.41519280133D-03         0.64919411676D-03         0.18445167620D-02         0.30191910849D-02
 0.35220256836D-03         0.50981157731D-03         0.14058069290D-02         0.22933403013D-02
 0.33647110830D-03         0.44754634006D-03         0.10797942127D-02         0.17493536230D-02
 0.35720123891D-03         0.44211704698D-03         0.84027336477D-03         0.13520878947D-02
 0.40860617602D-03         0.47083025925D-03         0.66003903238D-03         0.10742463025D-02
 0.49907363835D-03         0.44908385570D-03         0.50147877213D-03         0.95826148988D-03
```

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AT TIME=      0.90000000000D 03                           AT TIME=      0.11000000000D 04

        Y                            X                            Y                            X
 0.47534164188D-01          0.68691994946D-01          0.48270418073D-01          0.68841959671D-01
 0.47555971566D-01          0.66884817679D-01          0.48285113004D-01          0.67472207374D-01
 0.45862247130D-01          0.64779866002D-01          0.46990030144D-01          0.65872565169D-01
 0.43951014481D-01          0.62373462585D-01          0.45517967391D-01          0.64034120834D-01
 0.41841635619D-01          0.59676745970D-01          0.43877431921D-01          0.61957679985D-01
 0.39553626883D-01          0.56709981013D-01          0.42076313641D-01          0.59649655269D-01
 0.37112486158D-01          0.53502351550D-01          0.40126633888D-01          0.57122264011D-01
 0.34548986229D-01          0.50091289975D-01          0.38044411042D-01          0.54393507880D-01
 0.31898133347D-01          0.46521332275D-01          0.35849324286D-01          0.51486898920D-01
 0.29197871710D-01          0.42842550042D-01          0.33564201730D-01          0.48430929782D-01
 0.26487609923D-01          0.39108646374D-01          0.31214349902D-01          0.45258301349D-01
 0.23806660045D-01          0.35374830877D-01          0.28826750629D-01          0.42004935588D-01
 0.21192666312D-01          0.31695607241D-01          0.26429158142D-01          0.38708813917D-01
 0.18680258133D-01          0.28122612900D-01          0.24049132950D-01          0.35408690305D-01
 0.16299590463D-01          0.24702643250D-01          0.21713048849D-01          0.32142732555D-01
 0.14075535154D-01          0.21475973362D-01          0.19445104964D-01          0.28947143808D-01
 0.12026860939D-01          0.18475059733D-01          0.17266365662D-01          0.25854808825D-01
 0.10165829342D-01          0.15723666041D-01          0.15193837417D-01          0.22893995609D-01
 0.84980409459D-02          0.13236412987D-01          0.13239573407D-01          0.20087122595D-01
 0.70224929073D-02          0.11018706208D-01          0.11409773692D-01          0.17449575220D-01
 0.57317552526D-02          0.90669507185D-02          0.97038212921D-02          0.14988524709D-01
 0.46121403184D-02          0.73689211558D-02          0.81131602587D-02          0.12701678454D-01
 0.36436992798D-02          0.59041630508D-02          0.66198647264D-02          0.10575975380D-01
 0.27997788945D-02          0.46446890278D-02          0.51945301361D-02          0.85872830199D-02
 0.20452473053D-02          0.35599720844D-02          0.37915725943D-02          0.67113812442D-02
 0.13273200214D-02          0.26632575486D-02          0.23272510161D-02          0.50351634392D-02
 0.50798474236D-03          0.24244050936D-02          0.51782892676D-03          0.47233297320D-02
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AT TIME=      0.13000000000D 04                  AT TIME=      0.15000000000D 04

        Y                       X                        Y                       X
 0.48779923922D-01      0.68944471617D-01        0.49148762021D-01      0.69018081177D-01
 0.48790355623D-01      0.67876759752D-01        0.49156428625D-01      0.68168695591D-01
 0.47774588173D-01      0.66627571325D-01        0.48344523631D-01      0.67173560434D-01
 0.46614105030D-01      0.65186575350D-01        0.47413316410D-01      0.66022382248D-01
 0.45311982813D-01      0.63550117035D-01        0.46363004247D-01      0.64709598512D-01
 0.43870266558D-01      0.61718056043D-01        0.45192554278D-01      0.63231855285D-01
 0.42293790458D-01      0.59694031872D-01        0.43902779853D-01      0.61588243135D-01
 0.40590228976D-01      0.57485623394D-01        0.42496435163D-01      0.59780478916D-01
 0.38770024705D-01      0.55104368999D-01        0.40978229058D-01      0.57813005150D-01
 0.36846201426D-01      0.52565633534D-01        0.39354759630D-01      0.55692991398D-01
 0.34834059571D-01      0.49888313980D-01        0.37634359832D-01      0.53430223331D-01
 0.32750755058D-01      0.47094381723D-01        0.35826845151D-01      0.51036866643D-01
 0.30614765576D-01      0.44208264733D-01        0.33943154760D-01      0.48527094144D-01
 0.28445250163D-01      0.41256077169D-01        0.31994877313D-01      0.45916564995D-01
 0.26261307980D-01      0.38264706274D-01        0.29993651214D-01      0.43221744650D-01
 0.24081139834D-01      0.35260766081D-01        0.27950426500D-01      0.40459052107D-01
 0.21921110902D-01      0.32269423698D-01        0.25874570948D-01      0.37643817098D-01
 0.19794704799D-01      0.29313096276D-01        0.23772796336D-01      0.34789023284D-01
 0.17711347173D-01      0.26410004467D-01        0.21647871591D-01      0.31903803884D-01
 0.15675061133D-01      0.23572551217D-01        0.19497077310D-01      0.28991643478D-01
 0.13682896227D-01      0.20805475117D-01        0.17310340118D-01      0.26048227007D-01
 0.11723043798D-01      0.18103725770D-01        0.15067960017D-01      0.23058894186D-01
 0.97724853476D-02      0.15450199544D-01        0.12737767607D-01      0.19995954650D-01
 0.77936760942D-02      0.12815321507D-01        0.10271074835D-01      0.16818774291D-01
 0.57271283894D-02      0.10176203455D-01        0.75930452780D-02      0.13501787761D-01
 0.34549838037D-02      0.77050106257D-02        0.45523291255D-02      0.10300252323D-01
 0.52898553319D-03      0.73780800414D-02        0.53986940427D-03      0.99940431850D-02
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AT TIME=      0.17000000000D 04                        AT TIME=      0.19000000000D 04

        Y                         X                         Y                         X
 0.49424375671D-01        0.69072785482D-01        0.49633382068D-01        0.69114082536D-01
 0.49430139219D-01        0.68386379108D-01        0.49637803682D-01        0.68551166150D-01
 0.48771410118D-01        0.67581260291D-01        0.49095754315D-01        0.67890252157D-01
 0.48013414390D-01        0.66647701790D-01        0.48470280401D-01        0.67122376846D-01
 0.47154742415D-01        0.65579389253D-01        0.47759090337D-01        0.66241073257D-01
 0.46192669619D-01        0.64371358637D-01        0.46958551290D-01        0.65240645344D-01
 0.45125644618D-01        0.63020177524D-01        0.46065710991D-01        0.64116286898D-01
 0.43953374344D-01        0.61524096022D-01        0.45078349369D-01        0.62864178933D-01
 0.42676850821D-01        0.59883143432D-01        0.43994983435D-01        0.61481545582D-01
 0.41298317873D-01        0.58099155390D-01        0.42814822429D-01        0.59966654675D-01
 0.39821165483D-01        0.56175715416D-01        0.41537660737D-01        0.58318747470D-01
 0.38249738749D-01        0.54117993978D-01        0.40163694431D-01        0.56537880085D-01
 0.36589047295D-01        0.51932467142D-01        0.38693245399D-01        0.54624656967D-01
 0.34844359487D-01        0.49626495527D-01        0.37126374672D-01        0.52579834122D-01
 0.33020663594D-01        0.47207742146D-01        0.35462363680D-01        0.50403766566D-01
 0.31121974851D-01        0.44683404627D-01        0.33699038493D-01        0.48095670438D-01
 0.29150462925D-01        0.42059232785D-01        0.31831907498D-01        0.45652665048D-01
 0.27105368278D-01        0.39338296185D-01        0.29853077160D-01        0.43068553649D-01
 0.24981668051D-01        0.36519457836D-01        0.27749903287D-01        0.40332293650D-01
 0.22768441865D-01        0.33595499643D-01        0.25503326179D-01        0.37426097616D-01
 0.20446874416D-01        0.30550836944D-01        0.23085826006D-01        0.34323101143D-01
 0.17987808092D-01        0.27358791778D-01        0.20458911712D-01        0.30984578207D-01
 0.15348671287D-01        0.23978786807D-01        0.17569958487D-01        0.27357158733D-01
 0.12469014573D-01        0.20357212412D-01        0.14347509367D-01        0.23374532003D-01
 0.92591402891D-02        0.16463877574D-01        0.10688530766D-01        0.19001406492D-01
 0.55373209457D-02        0.12628442851D-01        0.63849927836D-02        0.14631382117D-01
 0.54965290372D-03        0.12358811588D-01        0.55807952514D-03        0.14402306942D-01
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```
AT TIME=      0.21000000000D 04                      AT TIME=      0.23000000000D 04

        Y                          X                          Y                          X
 0.49794458692D-01      0.69145813368D-01      0.49920364279D-01      0.69170574486D-01
 0.49797898626D-01      0.68678015018D-01      0.49923059946D-01      0.68777101964D-01
 0.49346041388D-01      0.68128292159D-01      0.49541819004D-01      0.68314315256D-01
 0.48823305304D-01      0.67488442302D-01      0.49099653403D-01      0.67774682284D-01
 0.48226896046D-01      0.66752098145D-01      0.48593455339D-01      0.67152009482D-01
 0.47552680237D-01      0.65913256477D-01      0.48018791583D-01      0.66440168781D-01
 0.46796838331D-01      0.64966339698D-01      0.47371264628D-01      0.65633111393D-01
 0.45955877552D-01      0.63906237840D-01      0.46646490388D-01      0.64724861582D-01
 0.45026603727D-01      0.62728314047D-01      0.45840037401D-01      0.63709475332D-01
 0.44006048461D-01      0.61428361063D-01      0.44947323552D-01      0.62580952416D-01
 0.42891339662D-01      0.60002494285D-01      0.43963458811D-01      0.61333088229D-01
 0.41679501412D-01      0.58446964529D-01      0.42883020435D-01      0.59959249261D-01
 0.40367166878D-01      0.56757870939D-01      0.41699744582D-01      0.58452053141D-01
 0.38950185179D-01      0.54930751213D-01      0.40406115458D-01      0.56802930802D-01
 0.37423099867D-01      0.52960022480D-01      0.38992829664D-01      0.55001544229D-01
 0.35778472709D-01      0.50838241576D-01      0.37448109467D-01      0.53035028561D-01
 0.34006021722D-01      0.48555147908D-01      0.35756833927D-01      0.50887021650D-01
 0.32091536700D-01      0.46096445474D-01      0.33899451226D-01      0.48536437576D-01
 0.30015528570D-01      0.43442272671D-01      0.31850628902D-01      0.45955932871D-01
 0.27751560533D-01      0.40565299878D-01      0.29577590645D-01      0.43110006037D-01
 0.25264197755D-01      0.37428391528D-01      0.27038077573D-01      0.39952669070D-01
 0.22506489252D-01      0.33981823657D-01      0.24177848333D-01      0.36424691629D-01
 0.19416787638D-01      0.30160590323D-01      0.20927515870D-01      0.32451016723D-01
 0.15913922649D-01      0.25886898448D-01      0.17197653729D-01      0.27943955681D-01
 0.11883376086D-01      0.21120554438D-01      0.12864122801D-01      0.22858932670D-01
 0.70949812134D-02      0.16308632969D-01      0.76784903513D-02      0.17686905322D-01
 0.56514123593D-03      0.16118419045D-01      0.57094693848D-03      0.17531214619D-01
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AT TIME=      0.25000000000D 04                          AT TIME=      0.27000000000D 04

        Y                          X                             Y                          X
 0.50019575709D-01         0.69190067715D-01          0.50097943314D-01         0.69205450849D-01
 0.50021699533D-01         0.68855154318D-01          0.50099615621D-01         0.68916782012D-01
 0.49696159389D-01         0.68460885250D-01          0.49818107209D-01         0.68576638089D-01
 0.49317606919D-01         0.68000291442D-01          0.49489882691D-01         0.68178518661D-01
 0.48882724415D-01         0.67467360591D-01          0.49111483347D-01         0.67716584828D-01
 0.48386885472D-01         0.66855919994D-01          0.48678158322D-01         0.67184664581D-01
 0.47825284913D-01         0.66159611717D-01          0.48184810708D-01         0.66576196318D-01
 0.47192886603D-01         0.65371846353D-01          0.47625920082D-01         0.65884149208D-01
 0.46484333957D-01         0.64485721690D-01          0.46995428200D-01         0.65100907814D-01
 0.45693818693D-01         0.63493895372D-01          0.46286583088D-01         0.64218110498D-01
 0.44814896800D-01         0.62388398483D-01          0.45491730866D-01         0.63226429054D-01
 0.43840238525D-01         0.61160374493D-01          0.44602042560D-01         0.62115274527D-01
 0.42761296802D-01         0.59799725070D-01          0.43607160772D-01         0.60872411320D-01
 0.41567875644D-01         0.58294640866D-01          0.42494748279D-01         0.59483458318D-01
 0.40247576716D-01         0.56630991363D-01          0.41249917353D-01         0.57931251885D-01
 0.38785098326D-01         0.54791543215D-01          0.39854514785D-01         0.56195040979D-01
 0.37161356466D-01         0.52754970951D-01          0.38286233049D-01         0.54249479271D-01
 0.35352392066D-01         0.50494617496D-01          0.36517512747D-01         0.52063372858D-01
 0.33328022194D-01         0.47976954394D-01          0.34514195208D-01         0.49598134863D-01
 0.31050185117D-01         0.45159683871D-01          0.32233876485D-01         0.46805890720D-01
 0.28470918634D-01         0.41989424043D-01          0.29623903592D-01         0.43627177988D-01
 0.25529886928D-01         0.38398986524D-01          0.26618929120D-01         0.39988257243D-01
 0.22151247443D-01         0.34304899120D-01          0.23137810633D-01         0.35798730512D-01
 0.18238722586D-01         0.29611195374D-01          0.19078664424D-01         0.30955824024D-01
 0.13660258710D-01         0.24269551869D-01          0.14302995692D-01         0.25408093824D-01
 0.81525409564D-02         0.18806536141D-01          0.85354493323D-02         0.19710853597D-01
 0.57566458128D-03         0.18680218901D-01          0.57947572593D-03         0.19608951336D-01
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AT TIME=      0.29000000000D 04                      AT TIME=      0.31000000000D 04

         Y                       X                            Y                       X
 0.50159796463D-01      0.69217581076D-01          0.50208752278D-01      0.69227175864D-01
 0.50161121928D-01      0.68965407066D-01          0.50209806564D-01      0.69003883576D-01
 0.49914401142D-01      0.68667991589D-01          0.49990636802D-01      0.68740290544D-01
 0.49625974835D-01      0.68319225242D-01          0.49733748734D-01      0.68430607843D-01
 0.49292294162D-01      0.67913432322D-01          0.49435533446D-01      0.68069302767D-01
 0.48908533533D-01      0.67444472134D-01          0.49091118884D-01      0.67650275760D-01
 0.48469390287D-01      0.66905656145D-01          0.48695053033D-01      0.67166756115D-01
 0.47968985606D-01      0.66289640066D-01          0.48241186883D-01      0.66611170749D-01
 0.47400728613D-01      0.65588279120D-01          0.47722520388D-01      0.65974975017D-01
 0.46757138748D-01      0.64792436508D-01          0.47131006421D-01      0.65248435937D-01
 0.46029616167D-01      0.63891733016D-01          0.46457302836D-01      0.64420356251D-01
 0.45208147883D-01      0.62874223325D-01          0.45690460811D-01      0.63477725403D-01
 0.44280935029D-01      0.61725981757D-01          0.44817535322D-01      0.62405280792D-01
 0.43233923875D-01      0.60430576921D-01          0.43823100936D-01      0.61184959459D-01
 0.42050220017D-01      0.58968410866D-01          0.42688652927D-01      0.59795216557D-01
 0.40709361392D-01      0.57315893861D-01          0.41391870012D-01      0.58210182563D-01
 0.39186421331D-01      0.55444420634D-01          0.39905710632D-01      0.56398625957D-01
 0.37450907662D-01      0.53319107733D-01          0.38197309561D-01      0.54322681999D-01
 0.35465417707D-01      0.50897244504D-01          0.36226635509D-01      0.51936301203D-01
 0.33184001548D-01      0.48126402961D-01          0.33944863053D-01      0.49183363970D-01
 0.30550175560D-01      0.44942152437D-01          0.31292401839D-01      0.45995409026D-01
 0.27494503113D-01      0.41265401536D-01          0.28196500519D-01      0.42289002940D-01
 0.23931524654D-01      0.37000099140D-01          0.24568204291D-01      0.37963510832D-01
 0.19754802175D-01      0.32037921470D-01          0.20297395078D-01      0.32906112418D-01
 0.14820628588D-01      0.26324863033D-01          0.15236166223D-01      0.27060716243D-01
 0.88439422548D-02      0.20439394241D-01          0.90916577695D-02      0.21024384846D-01
 0.58254650978D-03      0.20357556504D-01          0.58501248870D-03      0.20958892822D-01
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AT TIME=      0.33000000000D 04                        AT TIME=      0.35000000000D 04

          Y                        X                           Y                        X
 0.50247652849D-01        0.69234798501D-01          0.50278667411D-01        0.69240876055D-01
 0.50248492501D-01        0.69034454947D-01          0.50279335870D-01        0.69058829093D-01
 0.50051219179D-01        0.68797738204D-01          0.50099519668D-01        0.68843540073D-01
 0.49819401246D-01        0.68519116724D-01          0.49887688728D-01        0.68589682378D-01
 0.49549385140D-01        0.68193174987D-01          0.49640153804D-01        0.68291933664D-01
 0.49236265606D-01        0.67813850585D-01          0.49351983230D-01        0.67944261000D-01
 0.48874476256D-01        0.67374312888D-01          0.49017519718D-01        0.67539786065D-01
 0.48457658149D-01        0.66866813222D-01          0.48630237553D-01        0.67070620638D-01
 0.47978491113D-01        0.66282496068D-01          0.48182562295D-01        0.66527662266D-01
 0.47428482713D-01        0.65611161900D-01          0.47665647825D-01        0.65900340926D-01
 0.46797705285D-01        0.64840970429D-01          0.47069101335D-01        0.65176305690D-01
 0.46074469520D-01        0.63958070751D-01          0.46380645047D-01        0.64341038188D-01
 0.45244920896D-01        0.62946142259D-01          0.45585701249D-01        0.63377377119D-01
 0.44292542591D-01        0.61785827036D-01          0.44666884658D-01        0.62264934958D-01
 0.43197545407D-01        0.60454030765D-01          0.43603383100D-01        0.60979384448D-01
 0.41936121611D-01        0.58923064832D-01          0.42370203870D-01        0.59491588161D-01
 0.40479535233D-01        0.57159597193D-01          0.40937258907D-01        0.57766539388D-01
 0.38793016332D-01        0.55123373519D-01          0.39268256873D-01        0.55762076683D-01
 0.36834420656D-01        0.52765663226D-01          0.37319354244D-01        0.53427327491D-01
 0.34552608828D-01        0.50027377933D-01          0.35037590256D-01        0.50700829408D-01
 0.31885488858D-01        0.46836811516D-01          0.32358840180D-01        0.47508279453D-01
 0.28757639903D-01        0.43107032861D-01          0.29205555323D-01        0.43759945687D-01
 0.25077293448D-01        0.38733714254D-01          0.25483713715D-01        0.39348542275D-01
 0.20731372127D-01        0.33600413311D-01          0.21077868709D-01        0.34154724802D-01
 0.15568598805D-01        0.27649350292D-01          0.15834046918D-01        0.28119357071D-01
 0.92898690639D-02        0.21492459685D-01          0.94481545899D-02        0.21866246690D-01
 0.58698575885D-03        0.21440178028D-01          0.58856158825D-03        0.21824562718D-01
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AT TIME=     0.37000000000D 04                           AT TIME=     0.39000000000D 04

       Y                          X                             Y                          X
 0.50303425535D-01         0.69245727816D-01          0.50323208894D-01         0.69249604956D-01
 0.50303957227D-01         0.69078286661D-01          0.50323631149D-01         0.69093834948D-01
 0.50138076030D-01         0.68880102716D-01          0.50168884162D-01         0.68909318926D-01
 0.49942198933D-01         0.68646012593D-01          0.49985753486D-01         0.68691023440D-01
 0.49712607863D-01         0.68370767881D-01          0.49770497477D-01         0.68433758522D-01
 0.49444349704D-01         0.68048358678D-01          0.49518145258D-01         0.68131531893D-01
 0.49131694258D-01         0.67671868067D-01          0.49222907679D-01         0.67777394894D-01
 0.48767982382D-01         0.67233295932D-01          0.48878018258D-01         0.67363257000D-01
 0.48345436465D-01         0.66723342288D-01          0.48475536339D-01         0.66879659349D-01
 0.47854927998D-01         0.66131141096D-01          0.48006107156D-01         0.66315498373D-01
 0.47285693000D-01         0.65443933763D-01          0.47458665703D-01         0.65657688873D-01
 0.46624984285D-01         0.64646669345D-01          0.46820101545D-01         0.64890753760D-01
 0.45857647418D-01         0.63721515997D-01          0.46074787605D-01         0.63996325202D-01
 0.44965604647D-01         0.62647265181D-01          0.45204097458D-01         0.62952538980D-01
 0.43927228158D-01         0.61398606619D-01          0.44185752709D-01         0.61733300340D-01
 0.42716580407D-01         0.59945247774D-01          0.42993062554D-01         0.60307395520D-01
 0.41302495109D-01         0.58250846686D-01          0.41594001427D-01         0.58637418174D-01
 0.39647467475D-01         0.56271721091D-01          0.39950097722D-01         0.56678474173D-01
 0.37706316349D-01         0.53955289996D-01          0.38015096685D-01         0.54376621451D-01
 0.35424573657D-01         0.51238197021D-01          0.35723353353D-01         0.51666994883D-01
 0.32736546243D-01         0.48044066923D-01          0.33037901088D-01         0.48471568441D-01
 0.29562968828D-01         0.44280932209D-01          0.29848114726D-01         0.44696593561D-01
 0.25808020338D-01         0.39839145477D-01          0.26066739266D-01         0.40230541045D-01
 0.21354362466D-01         0.34597045147D-01          0.21574928269D-01         0.34949902518D-01
 0.16045869300D-01         0.28494411127D-01          0.16214839144D-01         0.28793594204D-01
 0.95744649067D-02         0.22164524718D-01          0.96752193642D-02         0.22402454063D-01
 0.58981908902D-03         0.22131303835D-01          0.59082215730D-03         0.22375974891D-01
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AT TIME=      0.41000000000D 04                    AT TIME=      0.43000000000D 04

        Y                          X                        Y                          X
 0.50338921812D-01         0.69252683685D-01         0.50351467547D-01         0.69255141735D-01
 0.50339257505D-01         0.69106183112D-01         0.50351734185D-01         0.69116042139D-01
 0.50193355731D-01         0.68932523241D-01         0.50212895037D-01         0.68951050264D-01
 0.50020353066D-01         0.68726775024D-01         0.50047979599D-01         0.68755320611D-01
 0.49816490291D-01         0.68483796383D-01         0.49853214794D-01         0.68523749576D-01
 0.49576783641D-01         0.68197610704D-01         0.49623606748D-01         0.68250373311D-01
 0.49295398346D-01         0.67861245874D-01         0.49353284431D-01         0.67928201237D-01
 0.48965483733D-01         0.67466541262D-01         0.49035330077D-01         0.67549016978D-01
 0.48578970454D-01         0.67003913293D-01         0.48661571653D-01         0.67103137558D-01
 0.48126324463D-01         0.66462070815D-01         0.48222331956D-01         0.66579122130D-01
 0.47596248771D-01         0.65827669720D-01         0.47706125471D-01         0.65963419823D-01
 0.46975322254D-01         0.65084894217D-01         0.47099292374D-01         0.65239944231D-01
 0.46247562687D-01         0.64214949691D-01         0.46385556981D-01         0.64389559642D-01
 0.45393898749D-01         0.63195449160D-01         0.45545495540D-01         0.63389461202D-01
 0.44391532773D-01         0.61999671906D-01         0.44555895311D-01         0.62212427799D-01
 0.43213172578D-01         0.60595668728D-01         0.43388933454D-01         0.60825922351D-01
 0.41826106559D-01         0.58945183410D-01         0.42011500125D-01         0.59191009357D-01
 0.40191091339D-01         0.57002354217D-01         0.40383585307D-01         0.57261053841D-01
 0.38261015383D-01         0.54712152574D-01         0.38457443046D-01         0.54980159136D-01
 0.35979294832D-01         0.52008509342D-01         0.36175739624D-01         0.52281294349D-01
 0.33277947466D-01         0.48812081611D-01         0.33469681865D-01         0.49084064881D-01
 0.30075264037D-01         0.45027700563D-01         0.30256694984D-01         0.45292167890D-01
 0.26272846804D-01         0.40542336972D-01         0.26437468962D-01         0.40791376604D-01
 0.21750647811D-01         0.35231010825D-01         0.21890996646D-01         0.35455536263D-01
 0.16349457086D-01         0.29031950454D-01         0.16456976355D-01         0.29222326428D-01
 0.97554917927D-02         0.22592015154D-01         0.98196046118D-02         0.22743415957D-01
 0.59162131943D-03         0.22570911806D-01         0.59225960064D-03         0.22726603442D-01
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AT TIME=      0.45000000000D 04                AT TIME=      0.47000000000D 04

        Y                       X                      Y                       X
  0.50361391129D-01      0.69257085487D-01      0.50369283625D-01      0.69258631368D-01
  0.50361603445D-01      0.69123839704D-01      0.50369452763D-01      0.69130041259D-01
  0.50228352327D-01      0.68965704463D-01      0.50240646078D-01      0.68977359306D-01
  0.50069837299D-01      0.68777901347D-01      0.50087221754D-01      0.68795860519D-01
  0.49882275346D-01      0.68555358428D-01      0.49905388972D-01      0.68580498275D-01
  0.49660665751D-01      0.68292123441D-01      0.49690141707D-01      0.68325329666D-01
  0.49399110032D-01      0.67981192863D-01      0.49435559811D-01      0.68023341067D-01
  0.49090638587D-01      0.67614307988D-01      0.49134632659D-01      0.67666240353D-01
  0.48726999291D-01      0.67181708964D-01      0.48779044669D-01      0.67244206828D-01
  0.48298402627D-01      0.66671838127D-01      0.48358917251D-01      0.66745590265D-01
  0.47793214537D-01      0.66070982320D-01      0.47862498463D-01      0.66156548813D-01
  0.47197586477D-01      0.65362841826D-01      0.47275789900D-01      0.65460613477D-01
  0.46495010118D-01      0.64528011159D-01      0.46582098366D-01      0.64638164541D-01
  0.45665781677D-01      0.63543354059D-01      0.45761497415D-01      0.63665802399D-01
  0.44686358003D-01      0.62381251662D-01      0.44790181002D-01      0.62515591904D-01
  0.43528583077D-01      0.61008698740D-01      0.43639688040D-01      0.61154155320D-01
  0.42158759523D-01      0.59386218089D-01      0.42275972597D-01      0.59541584118D-01
  0.40536534824D-01      0.57466557438D-01      0.40658289611D-01      0.57630134221D-01
  0.38613566152D-01      0.55193126618D-01      0.38737860162D-01      0.55362662624D-01
  0.36331920534D-01      0.52498126098D-01      0.36456273247D-01      0.52670756792D-01
  0.33622156785D-01      0.49300320698D-01      0.33743570645D-01      0.49472510918D-01
  0.30401008752D-01      0.45502501332D-01      0.30515934521D-01      0.45669992756D-01
  0.26568438154D-01      0.40989484610D-01      0.26672745511D-01      0.41147255486D-01
  0.22002672765D-01      0.35634177809D-01      0.22091621102D-01      0.35776457841D-01
  0.16542541119D-01      0.29373821704D-01      0.16610696368D-01      0.29494489946D-01
  0.98706314292D-02      0.22863913145D-01      0.99112780871D-02      0.22959897604D-01
  0.59276761707D-03      0.22850533499D-01      0.59317229546D-03      0.22949259766D-01
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AT TIME=      0.49000000000D 04                      AT TIME=      0.50000000000D 04

        Y                        X                           Y                        X
 0.50375559094D-01      0.69259860528D-01       0.50378197397D-01      0.69260377346D-01
 0.50375693904D-01      0.69134972228D-01       0.50378317743D-01      0.69137045375D-01
 0.50250421080D-01      0.68986626277D-01       0.50254530443D-01      0.68990522311D-01
 0.50101044505D-01      0.68810140178D-01       0.50106855230D-01      0.68816143413D-01
 0.49923767186D-01      0.68600487445D-01       0.49931492414D-01      0.68608890531D-01
 0.49713578939D-01      0.68351732660D-01       0.49723429941D-01      0.68362831236D-01
 0.49464542481D-01      0.68056854249D-01       0.49476723207D-01      0.68070940448D-01
 0.49169614702D-01      0.67707533651D-01       0.49184315331D-01      0.67724888321D-01
 0.48820429737D-01      0.67293901992D-01       0.48837819213D-01      0.67314785563D-01
 0.48407038395D-01      0.66804235710D-01       0.48427255913D-01      0.66828877652D-01
 0.47917595241D-01      0.66224590946D-01       0.47940740672D-01      0.66253177759D-01
 0.47337982964D-01      0.65538364474D-01       0.47364106220D-01      0.65571026201D-01
 0.46651361600D-01      0.64725766603D-01       0.46680450988D-01      0.64762561891D-01
 0.45837627816D-01      0.63763188656D-01       0.45869597446D-01      0.63804088410D-01
 0.44872766573D-01      0.62622444224D-01       0.44907442936D-01      0.62667313970D-01
 0.43728074096D-01      0.61269859420D-01       0.43765181966D-01      0.61318440544D-01
 0.42369226978D-01      0.59665182558D-01       0.42408374851D-01      0.59717072637D-01
 0.40755167453D-01      0.57760277993D-01       0.40795832785D-01      0.57814910524D-01
 0.38836769013D-01      0.55497562272D-01       0.38878283589D-01      0.55541861193D-01
 0.36555239460D-01      0.52808134183D-01       0.36596775281D-01      0.52865793631D-01
 0.33840208137D-01      0.49609553059D-01       0.33880754282D-01      0.49667067973D-01
 0.30607417065D-01      0.45803309705D-01       0.30645808029D-01      0.45859258117D-01
 0.26755783291D-01      0.41272848131D-01       0.26790629099D-01      0.41325552591D-01
 0.22162437548D-01      0.35889729739D-01       0.22192153987D-01      0.35937262206D-01
 0.16664962135D-01      0.29590564357D-01       0.16687733009D-01      0.29630879169D-01
 0.99436431611D-02      0.23036325166D-01       0.99572239226D-02      0.23068395111D-01
 0.59349452735D-03      0.23027877174D-01       0.59362973907D-03      0.23060865438D-01

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