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SIMULATION OF NONISOTHERMAL ABSORBER-REACTORS FOR MULTICOMPONENT SYSTEMS

by

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ABSTRACT

There are various models available for calculations involving one transferring component with chemical reaction for isothermal conditions using linear equilibrium data. However, the differential equations for multicomponent mass and energy transfer with chemical reaction have not been developed or implemented. This work demonstrates the development of a reliable model describing multicomponent mass and energy transfer in a continuous two phase absorber-reactor for nonisothermal conditions and demonstrates the feasibility of solving the differential equations numerically. The numerical solution, using nonlinear equilibrium data, is used to obtain the absorber-reactor column specifications.

PROBLEM STATEMENT

Although an abundant amount of literature is available on mass transfer, which includes chemical reaction in a continuous contactor, most of what has been written is primarily concerned with local mass transfer rates at specific points within the column, and relatively few attempts have been made to integrate the rate equations over the column length in order to determine the two-phase absorber-reactor height for nonisothermal conditions. With the increasing use of absorber-reactors in air pollution control, it is important that an accurate method be developed for determining their height.

MASS TRANSFER

In the development of the model, steady-state mass balance equations are considered first, because the energy balance equations are dependent on the mass balance equations. Figure 1 depicts the generalized continuous countercurrent absorber-reactor considered in this study. Axial mixing effects are assumed to be negligible, and the steady-state film concept is used.

The most simple case of mass transfer is a system in which only <u>one</u> component transfers from the noncondensing gas phase to the nonvolatile liquid with no chemical reaction. These equations are:

$$\frac{dy}{dz} = \frac{(1-y)^2}{V'} k_y a \ (y-y^i) \tag{1a}$$

$$\frac{dx}{dz} = \frac{(1-x)^2}{L'} k_x a \ (x^i-x) \tag{1b}$$

A full development of Equation 1 is presented in Appendix A.

If the flow rates L and V are assumed to be constant throughout the entire length of the tower as the result of dilute solute concentrations, Equation 1 reduces to:

$$\frac{dy}{dz} = \frac{k_y a}{V'} (y-y^i) \tag{2a}$$

$$\frac{dx}{dz} = \frac{k_x a}{L'} (x^i-x) \tag{2b}$$

Equations 1 and 2 are normally presented in chemical engineering texts on mass transfer, and they may be solved either graphically, analytically, or numerically. However, many industrial applications are not confined to a system with one transferring component. There may be two, three, or even more undesirable components (e.g., in a stack gas) which require removal by absorption.

The steady-state mass balance equation for N transferring components in the vapor phase (assuming the carrier gas is noncondensable) is:

$$\frac{dy_k}{dz} = \frac{(1-\sum_{j=1}^{N} y_j)}{V'} [(1-y_k)\ (k_y a)_k\ (y_k - y_k^i) - \sum_{\substack{j=1 \\ j\neq k}}^{N} y_k\ (k_y a)_k\ (y_j - y_j^i)] \qquad k=1,2,\ldots,N \qquad (3a)$$

and the equation for the liquid phase (assuming the carrier liquid is nonvolatile) is:

$$\frac{dx_k}{dz} = \frac{(1-\sum_{j=1}^{N} x_j)}{L'} [(1-x_k)\ (k_x a)_k\ (x_k^i - x_k) - \sum_{\substack{j=1 \\ j\neq k}}^{N} x_k\ (k_x a)_k\ (x_j^i - x_j)]. \qquad k=1,2,\ldots,N \qquad (3b)$$

For two transferring components, Equation 3 becomes:

$$\frac{dy_1}{dz} = \frac{(1-y_1-y_2)}{V'} [(1-y_1)\ (k_y a)_1\ (y_1 - y_1^i) - y_1\ (k_y a)_2\ (y_2 - y_2^i)], \qquad (4a)$$

$$\frac{dy_2}{dz} = \frac{(1-y_1-y_2)}{V'} [(1-y_2) \ (k_ya)_1 \ (y_2-y_2^i)$$

$$- y_2 \ (k_ya)_2 \ (y_1-y_1^i), \tag{4b}$$

$$\frac{dx_1}{dz} = \frac{(1-x_1-x_2)}{L'} [(1-k_1) \ (k_xa)_1 \ (x_1^i-x_1)$$

$$- x_1 \ (k_xa)_2 \ (x_2^i-x_2)], \tag{4c}$$

and

$$\frac{dx_2}{dz} = \frac{(1-x_1-x_2)}{L'} [(1-x_2) \ (k_xa)_2 \ (x_2^i-x_2)$$

$$- x_2 \ (k_xa)_1 \ (x_1^i-x_1)]. \tag{4d}$$

Equation 3 describes the change in composition of the vapor and liquid phases with respect to height for countercurrent flow and steady-state mass transfer with N transferring components. This equation can be solved for the liquid and vapor compositions as a function of tower height only by numerical methods. For a volatile carrier liquid, the liquid phase equations are altered slightly, and the vapor equations are unchanged. They are:

$$\frac{dy_k}{dz} = \frac{(1-\sum_{j=1}^{N} y_j)}{V'} [(1-y_k) \ (k_ya)_k \ (y_k-y_k^i)$$

$$- \sum_{\substack{j=1 \\ j\neq k}}^{N} y_k \ (k_ya)_k \ (y_j-y_j^i)], \qquad k=1,2,\ldots,N \tag{5a}$$

$$\frac{dx_k}{dz} = \frac{(1-\sum_{j=1}^{N-1} x_j)}{L'} [(1-x_k)\ (k_x a)_k\ (x_k^i - x_k)$$

$$- \sum_{\substack{j=1\\ j\neq k}}^{N-1} x_k\ (k_x a)_j\ (x_j^i - x_j)], \qquad (5b)$$

$$k=1,2,\ldots,N-1$$

and

$$\frac{dL'}{dz} = (k_x a)_N\ (x_N^i - x_N). \qquad (5c)$$

The volatile carrier liquid increases the total number of components, N, by one.

Equation 5 is applicable to all cases where the solvent is vaporizing. This equation also must be solved numerically.

Even though the development of the above equations is accomplished on the premise of a gas-liquid system, the equations can be applied with no modification to a steady-state countercurrent, liquid-liquid system. If the system were to be cocurrent, -V' or -L' would be substituted for V' or L', respectively depending on which of the flows were reversed. The above model assumes an isothermal system. Energy transfer and heat effects are considered in a later section.

MASS TRANSFER WITH CHEMICAL REACTION

The chemical industry's concern over meeting exhaust gas emission standards has created an interest in absorption with chemical reaction primarily, because it reduces tower height through increased mass transfer rates resulting from the chemical reaction. Specifically, Levenspiel[6] demonstrates that a particular physical absorption separation, which would require a tower height of 1550 feet, could be adapted to a tower height of 16.4 feet if the transferring component chemically reacts instantaneously in the liquid phase. It is, therefore, advantageous for the design engineer to have at his disposal a method for accurately estimating the height of an absorber-reactor. Currently, a generalized technique is not available or, at least, is not in the open literature.*

Levenspiel[6] has classified mass transfer with chemical reaction into three categories: 1) reaction only in the liquid film, which includes instantaneous and fast chemical reaction rates with respect to the mass transfer rate; 2) reaction in the liquid film and liquid bulk, which could result from an intermediate chemical reaction rate

*A design engineer of a large chemical company has indicated that the absorber-reactors in his company were designed and purchased only on previous experience and on estimates from calculations of absorption without chemical reaction.

with respect to the mass transfer rate; and 3) reaction in the bulk only, which includes both slow and extremely slow reaction rates with respect to the mass transfer rate. This study is confined to the first category.

Levenspiel[6] and Danckwerts[4] have subdivided the chemical reaction in the liquid film category into four types:

1. Instantaneous interior reaction in which the reaction occurs at a plane in the liquid film where the diffusion rate of both reactants controls and results in movement of the reaction plane to a fixed position in the film. Figure 2a depicts the interfacial behavior.
2. Instantaneous interfacial reaction in which the concentration of reactant B in the liquid bulk is high enough to move the reaction plane to the gas-liquid interface. The diffusion rate of component A transferring from the gas phase is the controlling factor (Figure 2b).
3. Fast reaction, second order rate in which the reaction rate is slow enough to cause the reaction plane to become a zone but fast enough to complete the reaction before A reaches the liquid bulk (Figure 2c).
4. Fast reaction, pseudo first order or first order in which the concentration of B is sufficiently high so that it is essentially undepleted by the

reaction within the film. The second order rate equation is thus reduced to first order (Figure 2d).

To understand how the foregoing applies to a continuous absorber-reactor, consider the case of an instantaneous and irreversible reaction, $A+bB \rightarrow pP$. Several regimes could possibly be present in the column simultaneously, depending on the column operating condition. The reaction may occur at the gas-liquid interface, or in the film, or not at all, if the liquid reactant concentration has been totally consumed.

REPRESENTATIVE TYPES OF REACTION

Because the chemical reaction rates of many of the industrially important reactions are instantaneous, this work will be confined to instantaneous reactions occurring in the liquid phase film. The stoichiometric equation, which we use in this study, has the form: $A+bB \rightarrow pP$. After the reaction occurs in the liquid phase, it is assumed that the products of this form remain in the liquid and do not transfer to the vapor phase. The carrier gas is considered to be noncondensable and the overall process is considered to be steady-state.

In order to develop the mathematical models, the same differential element of the column can still be considered as in Figure 1. Because the reaction takes place in the liquid film, the equation for the vapor phase mass transfer with a chemical reaction remains unchanged from Equation 3a.

In developing the mathematical model to describe an absorber-reactor, it is desirable to separate the transferring components into four groups:

1. Components which transfer and react.

   These diffuse from the vapor to the liquid and chemically react instantaneously in the liquid film with another component, which diffuses from the bulk of the liquid phase into the liquid film.

2. Products of reaction.

   These result from the transfer of the vapor phase and liquid phase components. The products are assumed to remain in the liquid phase.

3. Components which transfer and do not react.

   These diffuse from the vapor to the liquid but remain unreacted in the liquid phase.

4. Liquid phase reactants.

These are contained in the incoming liquid and react with components transferring from the vapor phase.

Each of these groups must be considered when the differential mass balance equations for the liquid phase components are developed.

The general form of the steady-state mass balance, which includes chemical reaction, is:

$$\frac{d(Lx_k)}{dz} = E_k \ (k_x a)_k \ (x_k^i - x_k) - r_k, \qquad k=1,2,\ldots,N_r \quad (6)$$

where E_k is the liquid film enhancement factor and r_k is the reaction rate in the liquid bulk. This equation describes all the components in Group 1. Components which are products of the reaction $A+bB \rightarrow pP$ (Group 2) are described by:

$$\frac{d(Lx_k)}{dz} = p_{k-N_x} \ r_{k-N_x}. \qquad k=N_x+1,\ldots,N_r+N_x \quad (7)$$

For unreactive components, $r_k = 0$ and $E_k = 1$, mass transfer is described by:

$$\frac{d(Lx_k)}{dz} = (k_x a)_k \ (x_k^i - x_k). \qquad k=N_r+1,\ldots,N_x \quad (8)$$

This equation depicts all components in Group 3. Components which are in the liquid phase as reactants (Group 4) are described by:

$$\frac{d(Lx_k)}{dz} = - \sum_{j=1}^{N_r} b_j \, r_j . \qquad k=N_r+N_x+1 \quad (9)$$

Equations 6 through 9 are solved for dx_1/dz, dx_2/dz, ..., dx_N/dz to give:

$$\frac{dx_k}{dz} = (1-x_k) \; (1-\sum_{j=1}^{N} x_j) \; R_k \; - \; \sum_{\substack{j=1 \\ j\neq k}}^{N} x_k$$

$$(1-\sum_{j=1}^{N} x_j) \; R_j \qquad k=1,2,\ldots,N \quad (10a)$$

in which

$$R_m = \frac{E_m (k_x a)_m}{L'} \, (x_m^i - x_m^i) - \frac{r_m}{L'} \qquad \text{for } m=1,2,\ldots,N_r \quad (10b)$$

$$R_m = \frac{p_{m-N_x} r_{m-N_x}}{L'} \qquad \text{for } m=N_x+1,\ldots,N_r+N_x \quad (10c)$$

$$R_m = \frac{(k_x a)_m}{L'} \, (x_m^i - x_m) \qquad \text{for } m=N_r+1,\ldots,N_x \quad (10d)$$

$$R_m = - \sum_{j=1}^{N_r} \frac{b_m r_m}{L'} \qquad \text{for } m=N_x+N_r+1,\ldots,N \quad (10e)$$

Equations 3a and 10 produce 2N simultaneous differential equations which must be solved numerically for the vapor and liquid compositions as a function of column height.

For an instantaneous and irreversible chemical reaction, in which the reactants from the vapor phase are completely consumed by the reaction in the liquid film, Equations 6 through 9 become:

$$\frac{d(Lx_k)}{dz} = 0 \qquad k=1,2,\ldots,N_r \quad (11a)$$

$$\frac{d(Lx_k)}{dz} = p_{k-N_x} E_{k-N_x} (k_xa)_{k-N_x} x^i_{k-N_x} \qquad k=N_x+1,\ldots,N_r+N_x \qquad (11b)$$

$$\frac{d(Lx_k)}{dz} = (k_xa)_k (x^i_k - x_k) \qquad k=N_r+1,\ldots,N_x \qquad (11c)$$

$$\frac{d(Lx_k)}{dz} = - \sum_{j=1}^{N_r} b_j E_j (k_xa)_j x^i_j \qquad k=N_x+N_r+1,\ldots,N \qquad (11d)$$

ENHANCEMENT FACTOR

A method for calculating the enhancement factor, E, must be developed before the above equations can be solved. The enhancement factor is the ratio of the rate of mass transfer with chemical reaction to the rate of mass transfer if no chemical reaction occurs.

For the reactions

$$A_1 + b_1B_r \rightarrow p_1P_1 \qquad (12a)$$

and

$$A_2 + b_2B_r \rightarrow p_2P_2, \qquad (12b)$$

the chemical reaction rate equations are assumed to be

$$r_1 = (k_{rx})_1 x_1^m x_r^n \qquad (13a)$$

and

$$r_2 = (k_{rx})_2 x_2^m x_r^n. \qquad (13b)$$

For a second order reaction, for example, m=n=1, the equation for the enhancement factor is given by Danckwerts[4] as

$$E_k = \frac{\sqrt{M_k \frac{(E_i)_k - E_k}{(E_i)_k - 1}}}{\tanh \sqrt{M_k \frac{(E_i)_k - E_k}{(E_i)_k - 1}}}, \qquad k=1,2,\ldots,N_r \qquad (14)$$

which is implicit in E_k and must be solved by an iterative technique after calculating $(E_i)_k$ and M_k. The equation for E_k must be solved for each of the transferring reacting components. The instantaneous enhancement factor, $(E_i)_k$, is given by Roper et al[9] as

$$(E_i)_k = \sqrt{\frac{D_k}{D_r}} \left[\frac{1}{1 + \sum_{j=1}^{N_r} \frac{b_j \, x_j^i \, D_j}{x_r D_r}} \right] . \qquad k=1,2,\ldots,N_r \qquad (15)$$

Danckwerts[4] gives the value of M_k as

$$M_k = \frac{1}{[(k_x)_k]^2} \left[\frac{2D_k (k_{rx})_k (x_k^i)^{m-1} (x_N)^{n-\bar{\rho}}}{m+1} \right] \qquad k=1,2,\ldots,N_r \qquad (16)$$

and he notes two limiting cases for Equation 14. If $M_k > 10(E_i)_k$, the reaction is instantaneous, and $E_k = (E_i)_k$. If $M_k < 0.5(E_i)_k$, the reaction is pseudo first order, i.e., the liquid phase reactant concentration remains constant in the film and, therefore,

$$(E)_k = \frac{\sqrt{M_k}}{\tanh \sqrt{M_k}} \qquad (17)$$

in which $M_k = [\bar{\rho}\ D_k\ (k_{rx})_k\ x_n]/(k_L)_k^2$. However, if $M_k > 3$, then E_k may be further approximated by the following expression:

$$(E)_k = M_k. \tag{18}$$

For a first order reaction, the enhancement factor can be calculated from Equation 17 in which $M_k = \bar{\rho}\ D_k\ (k_{rx})_k/(k_L)_k^2$. The limiting case is the instantaneous reaction in which

$$(E)_k = (E_i)_k. \tag{19}$$

The term E_i is given by Equation 15 and M_k is given by Equation 16.

ENERGY TRANSFER

There are many industrial problems for which a differential mass balance is sufficient to describe the physical phenomenon of a continuous contactor. However, there are some problems, particularly those with large heats of solution or vaporization and those with large heats of reaction which require an energy balance to completely describe the behavior in the adiabatic absorber-reactor for nonisothermal conditions.

The differential energy balance equations are developed in a manner similar to that for the mass balance equations. There are N total components with N_r transferring-reacting and N_x-N_r transferring-nonreacting components.

The adiabatic steady-state energy equations for the gas phase are

$$\frac{V'}{1-\sum\limits_{j=1}^{N} y_j} \frac{d(H_V)_{N+1}}{dz} + \sum_{j=1}^{N} V' \frac{d\left[\frac{y_j}{1-\sum\limits_{j=1}^{N} y_j} (H_V)_j\right]}{dz} =$$

$$h_V a \ (t_V - t^i) + \sum_{j=1}^{N} \frac{V'}{(1-\sum\limits_{j=1}^{N} y_j)} \frac{dy_j}{dz} (H_V)_j \qquad (20a)$$

assuming a noncondensing carrier gas, and for the liquid phase:

$$\frac{L'}{(1-\sum\limits_{j=1}^{N} y_j)} \frac{d(H_L)_{N+1}}{dz} + \sum_{j=1}^{N} L' \frac{d\left[\frac{x_j}{(1-\sum\limits_{j=1}^{N} x_j)} (H_L)_j\right]}{dz} = h_L a \ (t^i - t_L) +$$

$$\sum_{j=1}^{N} \frac{L'}{(1-\sum\limits_{j=1}^{N} x_j)} \frac{dx_j}{dz} (H_L)_j + \sum_{j=1}^{N_r} \frac{L'}{(1-\sum\limits_{j=1}^{N} x_j)} \frac{dx_j}{dz} (\Delta H_{rx})_j + \sum_{j=1}^{N_r}$$

$$\frac{L'}{(1-\sum\limits_{j=1}^{N} x_j)} \left[\frac{dx_{j+N_r}}{dz} p_j \ (Cp_L)_{j+N_r} - \frac{dx_j}{dz} (Cp_V)_j\right] (t^i - 77) \qquad (20b)$$

if the carrier liquid is assumed to be nonvolatile. If it is assumed that the reference state (at temperature, t_R) is the gaseous state for the carrier gas and the liquid state for all others, Equation 20a and 20b respectively become after rearranging

$$
\begin{aligned}
\frac{dt_V}{dz} = \Bigg[& h_V a \; (t_V - t^i) + \sum_{j=1}^{N} \frac{V'}{(1-\sum\limits_{j=1}^{N} y_j)} \frac{dy_j}{dz} \Big\{ (Cp_L)_j \; (t^i - t_R) + \\
& (Q_V)_j + (Cp_V)_j \; (t_V - t^i) \Big\} - \Big\{ V' \; (t_V - t_R) \frac{d(Cp_V)_{N+1}}{dz} \Big\} - \\
& \sum_{j=1}^{N} V' \; (t^i - t_R) \frac{y_j}{(1-\sum\limits_{j=1}^{N} y_j)} \frac{d(Cp_L)_j}{dz} - \sum_{j=1}^{N} V' \; (t_V - t^i) \frac{y_j}{(1-\sum\limits_{j=1}^{N} y_j)} \\
& \frac{d(Cp_V)_j}{dz} - \sum_{j=1}^{N} V' \; \Big\{ (Cp_L)_j \; (t^i - t_L) + (Q_V)_j + (Cp_V)_j \; (t_V - \\
& t^i) \Big\} \; \Bigg\{ \frac{1-(\sum\limits_{j=1}^{N} y_j)+y_j}{(1-\sum\limits_{j=1}^{N} y_j)^2} \frac{dy_j}{dz} + \sum_{\substack{k=1 \\ k \neq j}}^{N} \frac{y_j}{(1-\sum\limits_{j=1}^{N} y_j)^2} \frac{dy_k}{dz} \Bigg\} \Bigg] \Bigg/ \Bigg[V' \; (Cp_V)_{N+1} + \\
& V' \sum_{j=1}^{N} (Cp_V)_j \frac{y_j}{(1-\sum\limits_{j=1}^{N} y_j)} \Bigg] \qquad (21a)
\end{aligned}
$$

and

$$
\begin{aligned}
\frac{dt_L}{dz} = \Bigg[& h_L a \ (t^i - t_L) + \sum_{j=1}^{N} \frac{L'}{(1-\sum\limits_{j=1}^{N} x_j)} \frac{dx_j}{dz} \Big\{ (Cp_L)_j \ (t^i - t_R) + \\
& (Q_s)_j + (Q_v)_j + (Cp_V)_j \ (t_V - t^i) \Big\} + \sum_{j=1}^{N_r} \frac{L'}{(1-\sum\limits_{j=1}^{N} x_j)} \frac{dx_j}{dz} \ (\Delta H_{rx})_j \\
& + \sum_{j=1}^{N_r} \frac{L'}{(1-\sum\limits_{j=1}^{N} x_j)} \left\{ \frac{dx_{j+N_x}}{dz} \ p_j \ (Cp_L)_{j+N_x} - \frac{dx_j}{dz} \ (Cp_V)_j \right\} \ (t^i - 77) - \\
& \sum_{j=1}^{N} L' \ (t_L - t_R) \ \frac{x_j}{(1-\sum\limits_{j=1}^{N} x_j)} \frac{d(Cp_L)_j}{dz} - L' \ (t_L - t_R) \ \frac{d(Cp_L)_{N+1}}{dz} - \\
& \sum_{j=1}^{N} \frac{L'}{(1-\sum\limits_{j=1}^{N} x_j)} \ (Cp_L)_j \ (t^i - t_R) \left\{ \frac{1 - (\sum\limits_{j=1}^{N} x_j) + x_j}{(1-\sum\limits_{j=1}^{N} x_j)^2} \frac{dx_j}{dz} + \sum_{\substack{k=1 \\ k \neq j}}^{N} \frac{x_j}{(1-\sum\limits_{j=1}^{N} x_j)^2} \right. \\
& \left. \frac{dx_k}{dz} \right\} \Bigg] \Bigg/ \left[L' \ (Cp_L)_{N+1} + \sum_{j=1}^{N} L' \ \frac{x_j}{(1-\sum\limits_{j=1}^{N} x_j)} \ (Cp_L)_j \right] . \qquad (21b)
\end{aligned}
$$

Equations 3a, 10, 21a, and 21b can be solved simultaneously by a numerical method (Runge-Kutta, Euler's, or Predictor-Corrector) for the compositions and temperatures of the vapor and liquid phases as a function of tower height.

For one component transfer with negligibly small heats of reaction, solution, and vaporization, Equations 21a and 21b reduce to

$$\frac{dt_V}{dz} = \frac{h_V a\ (t_V - t^i)}{(Cp)_V\ V'} \tag{22a}$$

and

$$\frac{dt_L}{dz} = \frac{h_L a\ (t^i - t_L)}{(Cp)_L\ L'}\ . \tag{22b}$$

These are the equations which normally appear in texts on the subject.[1,5]

To summarize the development, the nonisothermal absorber-reactor is described by the differential equations 3a, 10, 21a, and 21b, which can be represented in the form of

$$\frac{dx_k}{dz} = e_k\ (\underline{x},\ \underline{y},\ t_L,\ t_V,\ \underline{x}^i,\ \underline{y}^i,\ t^i), \qquad k=1,2,\ldots,N \tag{23a}$$

$$\frac{dy_k}{dz} = f_k\ (\underline{x},\ \underline{y},\ t_L,\ t_V,\ \underline{x}^i,\ \underline{y}^i,\ t^i), \qquad k=1,2,\ldots,N \tag{23b}$$

$$\frac{dt_L}{dz} = g\ (\underline{x},\ \underline{y},\ t_L,\ t_V,\ \underline{x}^i,\ \underline{y}^i,\ t^i), \tag{23c}$$

and

$$\frac{dt_V}{dz} = h\ (\underline{x},\ \underline{y},\ t_L,\ t_V,\ \underline{x}^i,\ \underline{y}^i,\ t^i). \tag{23d}$$

These equations can be solved with a numerical integration technique, such as Runge-Kutta, Euler, or Taylor, or by means of analog computer techniques. For this work, a fourth order Runge-Kutta numerical method was used because it is stable, accurate, and has been previously used by the authors with excellent results. However, before Equation 23 can be solved, the interfacial composition, $\underline{x}^i$, and temperature, t^i, must be obtained at each axial position in the contactor at which the differential numerical procedure is applied. For example, Equation 2 describes mass transfer in a continuous contactor for one transferring component. The overall material balance is

$$V \frac{dy}{dz} - L \frac{dx}{dz} = 0. \tag{24}$$

The substitution of Equation 2a into Equation 2b yields

$$k_y a \ (y-y^i) - k_x a \ (x^i-x) = 0. \tag{25}$$

If the equilibrium data are of the form

$$y^i = mx^i, \tag{26}$$

then Equation 26 can be easily solved for either x^i or y^i:

$$x^i = \frac{k_x a \ x + k_y a \ y}{k_x a \ + k_y a \ m} . \tag{27}$$

However, if the equilibrium data are nonlinear, for example of the form

$$y^i = a + bx^i + c(x^i)^2 + \ldots, \tag{28}$$

Equation 25 must be solved with Equation 28 for x^i using an iterative procedure. The authors were successful in using Newton's iterative method, which is

$$x^i_{k+1} = x^i_k - \frac{ff(x^i_k)}{\frac{d[ff(x^i_k)]}{dz}} \tag{29}$$

in which $ff(x^i) = k_y a \ (y-y^i) - k_x a \ (x^i-x)$. The iterative scheme is used until $ff(x^i)$ is very nearly zero.

For a one component system with chemical reaction, Equation 24 is

$$k_y a \ (y-y^i) - [E \ (k_x a) \ (x^i-x) - r] = 0. \qquad (30)$$

If more than one chemical reaction occurs, then the insertion of Equations 10 and 3a into Equation 24 gives

$$(1-y_k) \ (k_y a)_k \ (y_k-y_k^i) - \sum_{\substack{j=1 \\ j \neq k}}^{N} y_k \ (k_y a)_j \ (y_j-y_j^i) -$$

$$[(1-x_k) \ R_k - \sum_{\substack{j=1 \\ j \neq k}}^{N} x_k \ R_j] = 0 \qquad k=1,2,\ldots,N_r \qquad (31)$$

in which R is defined by Equation 10.

To use Newton's method, it is necessary to evaluate the enhancement factor, E, at every iteration, because E_i, which is used to calculate E, is a function of the interfacial compositions. To determine the interfacial temperature, t^i, the overall energy balance is needed:

$$V \frac{dH_V}{dz} - L \frac{dH_L}{dz} = 0. \qquad (32)$$

The insertion of Equation 20 into Equation 32 for a one-transferring-component system gives

$$h_V a\ (t_V - t^i) + \frac{V'}{(1-\sum_{j=1}^{N} y_j)} \frac{dy_1}{dz} (H_V)_1 - \Big[h_L a\ (t^i - t_L) +$$

$$\frac{L'}{(1-\sum_{j=1}^{N} x_j)} \frac{dx_1}{dz} (H_L)_1 + \frac{L'}{(1-\sum_{j=1}^{N} x_j)} \frac{dx_1}{dz} (\Delta H_{rx})_1 + \frac{L'}{(1-\sum_{j=1}^{N} x_j)} \Big\{ \frac{dx_2}{dz} p_1$$

$$(Cp_L)_2 - \frac{dx_1}{dz} (Cp_V)_1 \Big\} (t^i - 77) \Big] = 0. \qquad (33)$$

The addition of the energy balance complicates the necessary representation of the equilibrium data. In fact, Equation 28 is not a sufficient representation for the equilibrium data for nonisothermal conditions, because it does not include the effect of changes in temperature on the equilibrium data. For example, for the air-carbon dioxide-water system, it is necessary to represent the equilibrium data by an expression similar to the following:

$$y^i = a_0 + [a_1 + b_1 t^i + c_1 (t^i)^2]\ x^i + [a_2 + b_2 t^i + c_2 (t^i)^2 + \ldots]\ (x^i)^2 + \ldots \qquad (34)$$

The air-ammonia-water system can be represented by the more complex Stern[3] equation:

$$y^i = 10^{\{7.6657 + \frac{1222.2}{t+230} - \log[(\frac{1000}{c} - 1.6)(0.7574 + \frac{62.51}{t+230})]\}} / 760 \qquad (35)$$

in which $c = (17/0.018)\ x^i/(1-x^i)$.

Because H_L is a function of t_L and H_V is a function of

t_V, Equations 30 and 34 must be solved simultaneously with the equilibrium equation by using Newton's method for systems of nonlinear equations. The authors recommend Newton's method which is given as follows:

$$\sum_{n=1}^{N} \Delta\varepsilon_n \frac{\partial F_k}{\partial \varepsilon_n} = -F_k \qquad k=1,2,\ldots,N \qquad (36)$$

in which ε represents the independent variable, either x^i or t^i. It is helpful to illustrate the application of Equation 35 for a two component nonisothermal system as follows:

$$[(x_1^i)_{k+1} - (x_1^i)_k] \frac{\partial F_1}{\partial x_1^i} + [(x_2^i)_{k+1} - (x_2^i)_k] \frac{\partial F_1}{\partial x_2^i} +$$

$$[(t^i)_{k+1} - (t^i)_k] \frac{\partial F_1}{\partial t^i} = -F_1 \qquad (37\,a)$$

$$[(x_1^i)_{k+1} - (x_1^i)_k] \frac{\partial F_2}{\partial x_1^i} + [(x_2^i)_{k+1} - (x_2^i)_k] \frac{\partial F_2}{\partial x_2^i} +$$

$$[(t^i)_{k+1} - (t^i)_k] \frac{\partial F_2}{\partial t^i} = -F_2 \qquad (37b)$$

$$[(x_1^i)_{k+1} - (x_1^i)_k] \frac{\partial F_3}{\partial x_1^i} + [(x_2^i)_{k+1} - (x_2^i)_k] \frac{\partial F_3}{\partial x_2^i} +$$

$$[(t^i)_{k+1} - (t^i)_k] \frac{\partial F_3}{\partial t^i} = -F_3 \qquad (37c)$$

in which

$$F_1 = \frac{V'}{(1-\sum_{j=1}^{N} y_j)} \frac{dy_1}{dz} - \frac{L'}{(1-\sum_{j=1}^{N} x_j)} \frac{dx_1}{dz}$$

$$F_2 = \frac{V'}{(1-\sum_{j=1}^{N} y_j)} \frac{dy_2}{dz} - \frac{L'}{(1-\sum_{j=1}^{N} x_j)} \frac{dx_2}{dz}$$

$$F_3 = \frac{V'}{(1-\sum_{j=1}^{N} y_j)} \frac{dH_V}{dz} - \frac{L'}{(1-\sum_{j=1}^{N} x_j)} \frac{dH_L}{dz}$$

Application of the Runge-Kutta numerical integration technique and Newton's method for solving the sets of nonlinear equations allows the equations for the model to be programmed for solution on a digital computer (Figure 3).

RESULTS

Because only the simplest of systems can be studied by using either a graphical or analytical solution, the numerical solution of Equations 3a, 10, 21a, and 21b is obviously the most desirable. The equations were programmed in Fortran for an IBM 370/165 computer. In order to demonstrate the accuracy and versatility of the model, a broad range of contactor problems was chosen. These problems included nonisothermal conditions, fast chemical reaction in the liquid phase, and multicomponent transfer.

The system first selected for study was gaseous ammonia absorption by liquid water initially investigated by Sherwood and Pigford[10]. The heats of vaporization of ammonia and water were sufficiently large $[(Q_V)_{\text{ammonia}} =$

15380 BTU/lb mole and $(Q_v)_{water}$ = 19250 BTU/lb mole] to insure nonisothermal conditions and require an energy balance calculation. The data used in the computation of the composition and temperature profiles are presented in Table 1. Sherwood and Pigford[10] made some additional assumptions which include: dilute solutions, all resistance to mass transfer is in the vapor phase, and the interfacial temperature is the same as the bulk liquid temperature. The equilibrium equation used in this work for ammonia is the Stern[3] equation and the equilibrium equation used for water is the result of a least squares curve fit of the water vapor pressure data in Perry[8]. Sherwood and Pigford[10] do not state the source of their equilibrium data for either ammonia or water.

In addition, Sherwood and Pigford[10] do not report in their work the flow rates per square foot of cross sectional tower area and the type of packing which they used in their calculations. Therefore, it was necessary in this work to calculate the flow rates and transfer coefficients assuming the tower was operating at 50 percent of the flooding velocity and was packed with one inch Raschig rings. As in all the examples used in this work, the heat transfer coefficients and the physical mass transfer coefficients, $k_x a$, were assumed constant throughout the column and were usually evaluated at an average of the inlet and outlet conditions. These data were used to generate the concentration and temperature profiles which appear in Figure 4 (Cases C and D) with the results given graphically by Sherwood and Pigford[10] (Case A). Two solutions for the above data were obtained using the model developed in this work. First, the profiles were calculated using the data as it appears in Table 1 [i.e., all resistances to mass and heat transfer were finite (Case D)]. Then, all the resistance to mass and heat transfer was assumed to be in the vapor phase (i.e., liquid mass and heat transfer coefficients were infinite) and the profiles were recalculated (Case C). The deviation between the calculated profiles (Cases C and D) and the reported results (Case A) indicates that, in addition to the differences in the equilibrium data used in both works, the authors' assumption (i.e., the column was operating at 50 percent of the flooding velocity and was packed with one inch Raschig rings) was not the same as that of Sherwood and Pigford[10]. In fact, the equations used by Sherwood and Pigford[10] do not require individual values of the flow rates or transfer coefficients and these values may never have been calculated.

The column heat and mass transfer equations given by Sherwood and Pigford[10] were also solved numerically with the equilibrium equations for ammonia and water used in this work (Figure 4, Case B) and compared with the results given graphically by Sherwood and Pigford[10] (Figure 4, Case A). The greatest deviation between the concentration and temperature profiles was ten percent and six percent, respectively, approximately in the center of the column. At most axial positions, the differences between curves A and B were less than five percent. Since the results are very sensitive to the equilibrium data used, the differences between curves A and B are possibly a result of the variation between equilibrium data used in this investigation and that used by Sherwood and Pigford[10].

As mentioned above, the accuracy of the model is dependent on the accuracy of the data supplied to the model, particularly the exact representation of the equilibrium data. The sensitivity of the computations to the equilibrium data can be illustrated by using data from Othmer and Scheibel[7] which was later used by Sherwood and Pigford[10] in the following nonisothermal absorption. Absorption from air of acetone and water vapor in liquid water was studied in a sixteen foot column packed with one inch Raschig rings. The heat of vaporization of both acetone and water is sufficiently large [$(Q_v)_{acetone}$ = 18000 BTU/lb mole and $(Q_v)_{water}$ = 19323 BTU/lb mole] to require energy balance calculations. Sherwood and Pigford[10] also made the additional assumptions outlined previously (i.e., dilute solutions, all resistance to mass transfer is in the vapor phase, and the interfacial temperature is the same as the bulk liquid). In this work, mass and heat transfer coefficients were calculated for both the vapor and liquid phases by a procedure outlined by Treybal[12]. The data used in the computation of the profiles are presented in Table 2.

Equilibrium data were not available in any of the literature surveyed for this study. An attempt was made to develop an equation to represent the equilibrium data from the heat of vaporization and activity coefficients as suggested by Sherwood and Pigford[10]. Since this method is, at best, an estimation, accurate results could not be expected. The model was not capable of reproducing the profiles estimated by Sherwood and Pigford[10] (Figure 5) probably due to the inaccuracy of the equilibrium data. This problem demonstrates the necessity of having an accurate representation of the equilibrium data if a model is used.

If the equilibrium data are accurately represented, the model is capable of predicting column heights and output compositions for absorber-reactors. A total of nine systems involving mass transfer with chemical reaction was used to test the mass and heat balance equations and their solutions. A summary of these systems is presented in Table 3. In addition, a comparison of the column height reported by the various investigators and the column heights predicted by the model is presented. The difference between the reported and predicted column height in most of the systems studied was six percent or under; and in over half of the systems studied, the difference was less than three percent.

A typical mass transfer problem with chemical reaction system is that of Tepe and Dodge[11]. In the 7.7 foot absorber-reactor filled with one-half inch Raschig rings, carbon dioxide is transferring from air and reacting instantaneously with sodium hydroxide in the aqueous phase and is the only transferring component. The heats of reaction and vaporization are sufficiently large to require both mass and energy balance calculations. The concentration and temperature profiles calculated in this work are presented in Figure 6. The data for this system are presented in Table 4. The difference between the column height used by Tepe and Dodge[11] and that predicted by the model is six percent.

All compositions and temperatures were checked at the opposite end of the column from which the integration procedure was started. The vapor phase compositions at the opposite end of the column are used as the stopping criteria for the numerical integration. The reported and predicted liquid phase compositions and vapor and liquid temperatures [i.e., $\underline{y}_{in}$, $\underline{x}_{out}$, $(t_L)_{out}$, $(t_V)_{in}$] differ by no more than ten percent and two percent, respectively. In most cases, the terminal conditions (i.e., at the opposite end of the column from which the numerical integration procedure was started) reported by the original investigators do not differ from the calculated terminal conditions by more than ten percent.

As a final demonstration of the versatility of the model and resulting computer program, a problem which would incorporate all the features of the model (energy balance, chemical reaction, and multicomponent transfer) was desired; however, no such problem was available in the open literature. Therefore, a three component test problem was proposed and then simulated. Two of the components (y_1 and y_2) transfer from the vapor to the liquid phase and react instantaneously in the liquid film. The other transferring component (y_3) transfers from the vapor to the liquid phase and does not react. The heats of vaporization and reaction were chosen to necessitate using the energy balance calculations. A summary of the data is presented in Table 5. The resulting concentration and temperature profiles, which appear to represent the typical behavior of three component nonisothermal absorption with chemical reaction, are shown in Figure 7.

The authors await experimental data to appear in the open literature on multicomponent absorption with chemical reaction to further test the model presented in this work. This work, however, does demonstrate the development of a reliable model describing multicomponent mass and energy transfer in a continuous two phase absorber-reactor for nonisothermal conditions which has not previously appeared in the literature and demonstrates the feasibility of solving the differential equations numerically. The numerical solution, using nonlinear equilibrium data, is used to obtain the absorber-reactor column specifications.

COMPUTER USAGE

The amount of computer time consumed by the program on the IBM 370/165 is quite reasonable. For an increment size of $\Delta z = z/200$, systems with one transferring component and chemical reaction average 12 seconds. The two component absorption problems with chemical reaction require 25 seconds. The one component absorption problems with chemical reaction and energy calculations use 38 seconds. From the above data, the following formulas can be developed for estimating the computer time required to execute the program:

1. Absorption without energy calculations

$$\text{Time (sec)} \cong (10)(N)$$

2. Absorption with energy calculations

   Time (sec) $\cong$ (20)(N)

3. Absorption with chemical reaction and without energy calculations

   Time (sec) $\cong$ (10)(N)

4. Absorption with chemical reaction and energy calculations

   Time (sec) $\cong$ (30)(N)

where N is the total number of components in the system.

CONCLUSIONS

1. The computer solution of the equations for mass and energy transfer is a reliable method for simulating a continuous contactor in which an instantaneous chemical reaction is occurring.
2. Equilibrium data are extremely important in the simulation. Much care is required to assure that accurate equilibrium data are obtained for the operating conditions of the absorber-reactor.

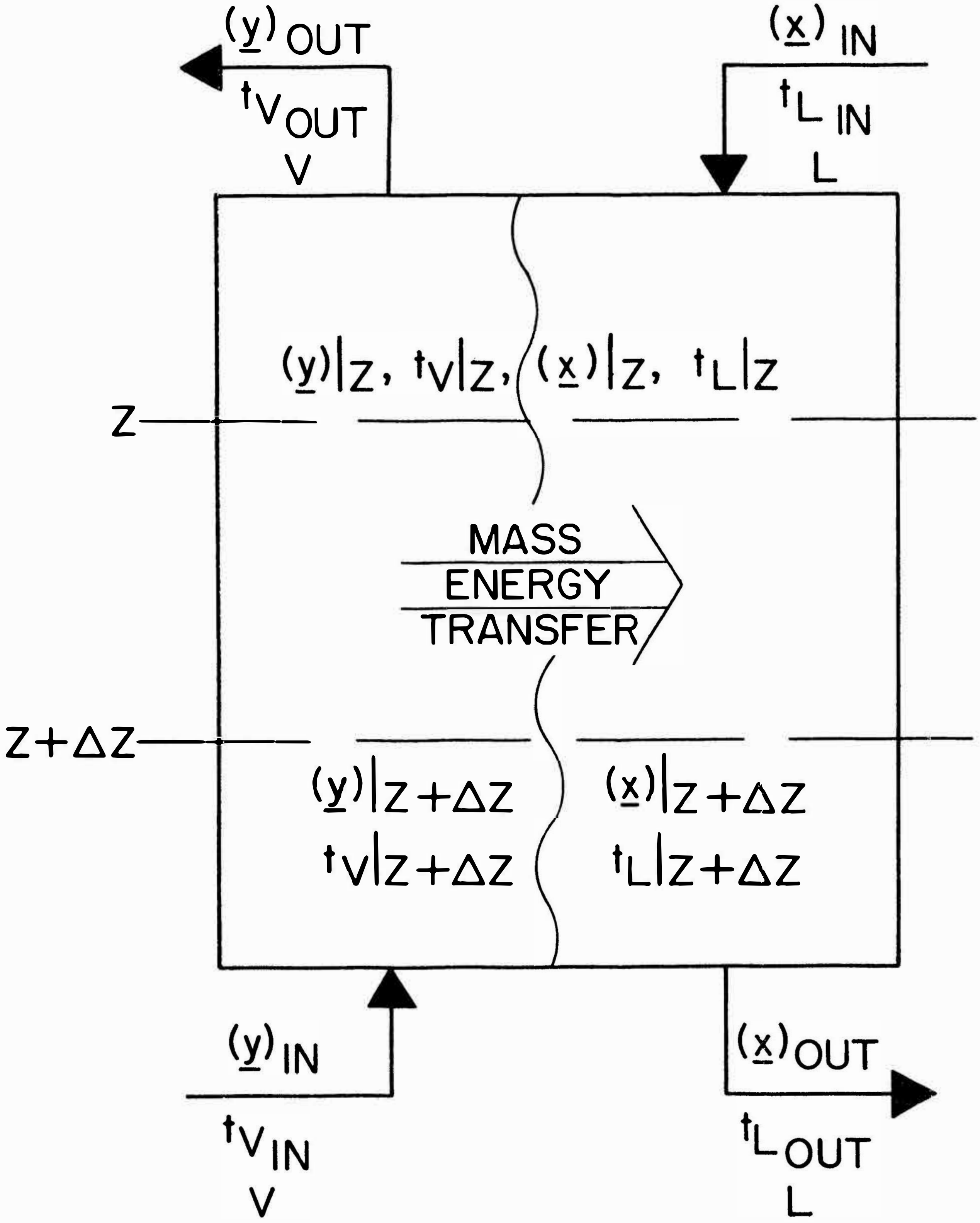

Figure 1. A Model of a Continuous Absorber-Reactor

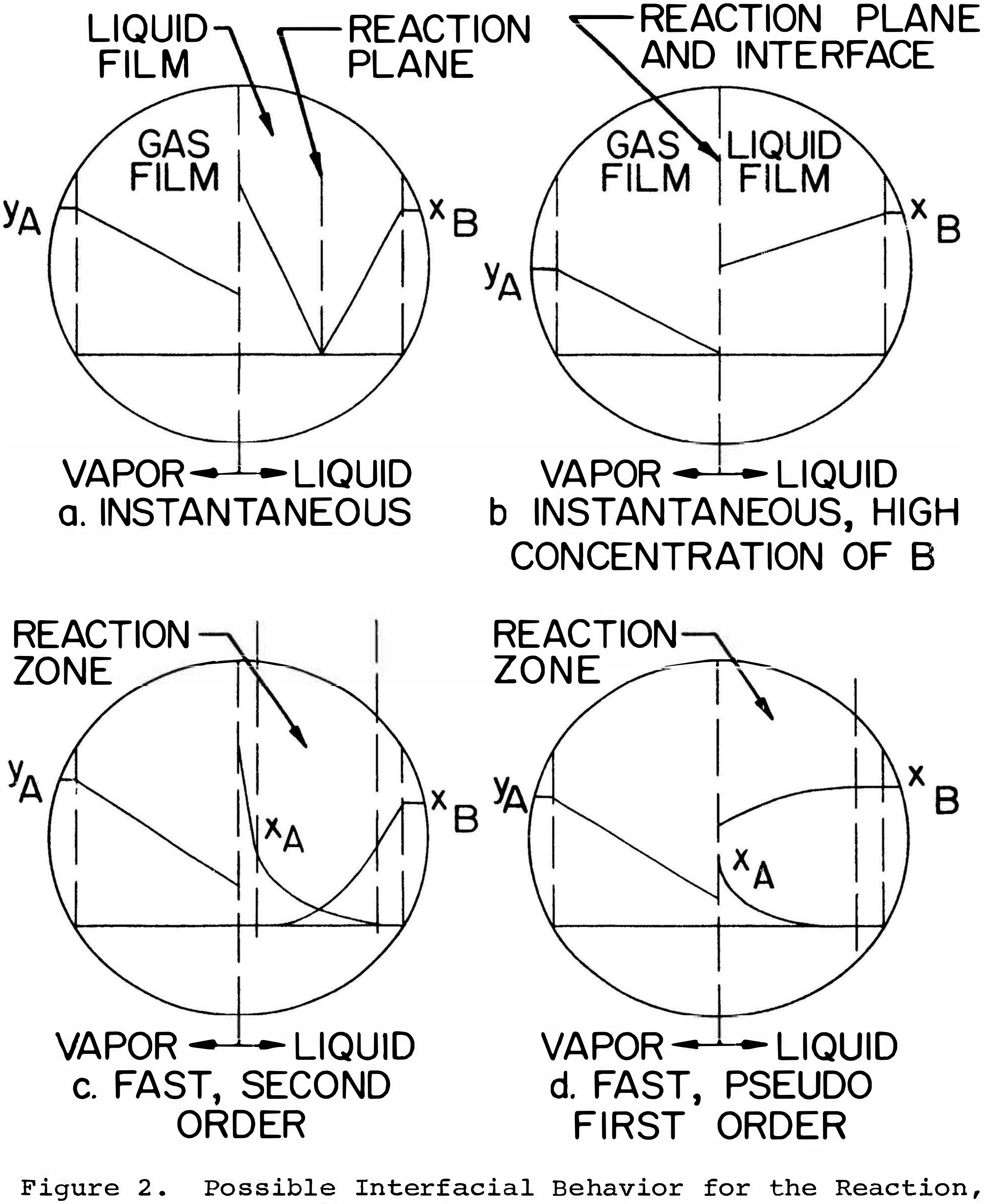

Figure 2. Possible Interfacial Behavior for the Reaction, $A+bB \rightarrow pP$[6]

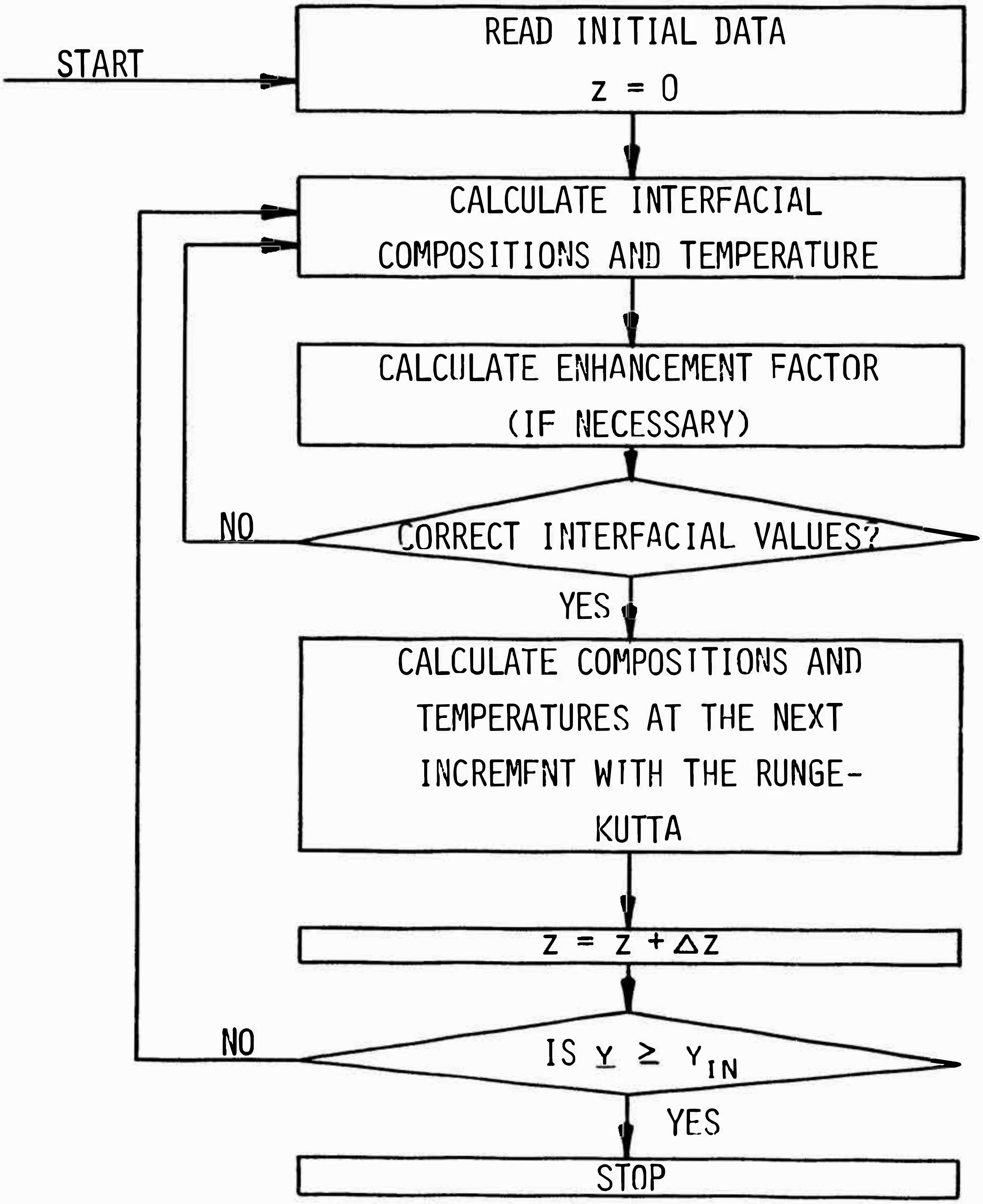

Figure 3. Flow Diagram for the Numerical Solution of the Mass and Energy Balance Equations

TABLE 1

PHYSICAL DATA -- AMMONIA-WATER ABSORPTION

Carrier Liquid: Water

Carrier Gas: Air

Components: 1 = Ammonia, 2 = Water

Reaction: None

Compositions: $(y_{in})_1 = 0.0049$ $(y_{out})_1 = 0.0881$
$(y_{in})_2 = 0.025$ $(y_{out})_2 = 0.0305$
$(x_{in})_1 = 0.0$ $(x_{out})_1 = 0.0302$
$(x_{in})_2 = 1.0$ $(x_{out})_2 = 0.9698$

Temperature: $(t_L)_{in} = 61.3°F$ $(t_L)_{out} = 92.1°F$
$(t_V)_{in} = 77°F$ $(t_V)_{out} = 68.3°F$

Flow Rates: $L' = 65.1$ lb moles/hr ft^2
$V' = 24.6$ lb moles/hr ft^2

Packing: 1" Raschig rings

Transfer Coefficients[12] (at 77°F, assumed constant):

$(k_xa)_1 = 126.0$ $(k_ya)_1 = 23.1$
$(k_xa)_2 = 143.7$ $(k_ya)_2 = 26.5$
$h_La = 12600$ $h_Va = 23.2$

Equilibrium Data:

$$y_1^i = [10^{(7.6657+\frac{1222.2}{t+230})} - \log\{(\frac{1000}{c} - 1.6)(0.7574+\frac{62.51}{t+230})\}]$$

$$/760$$

$$y_2^i = [0.027721 - 0.000733\ t^i + 0.0000112819\ (t^i)^2][1-\sum_{j=1}^{N} x_j]$$

Reference: 10

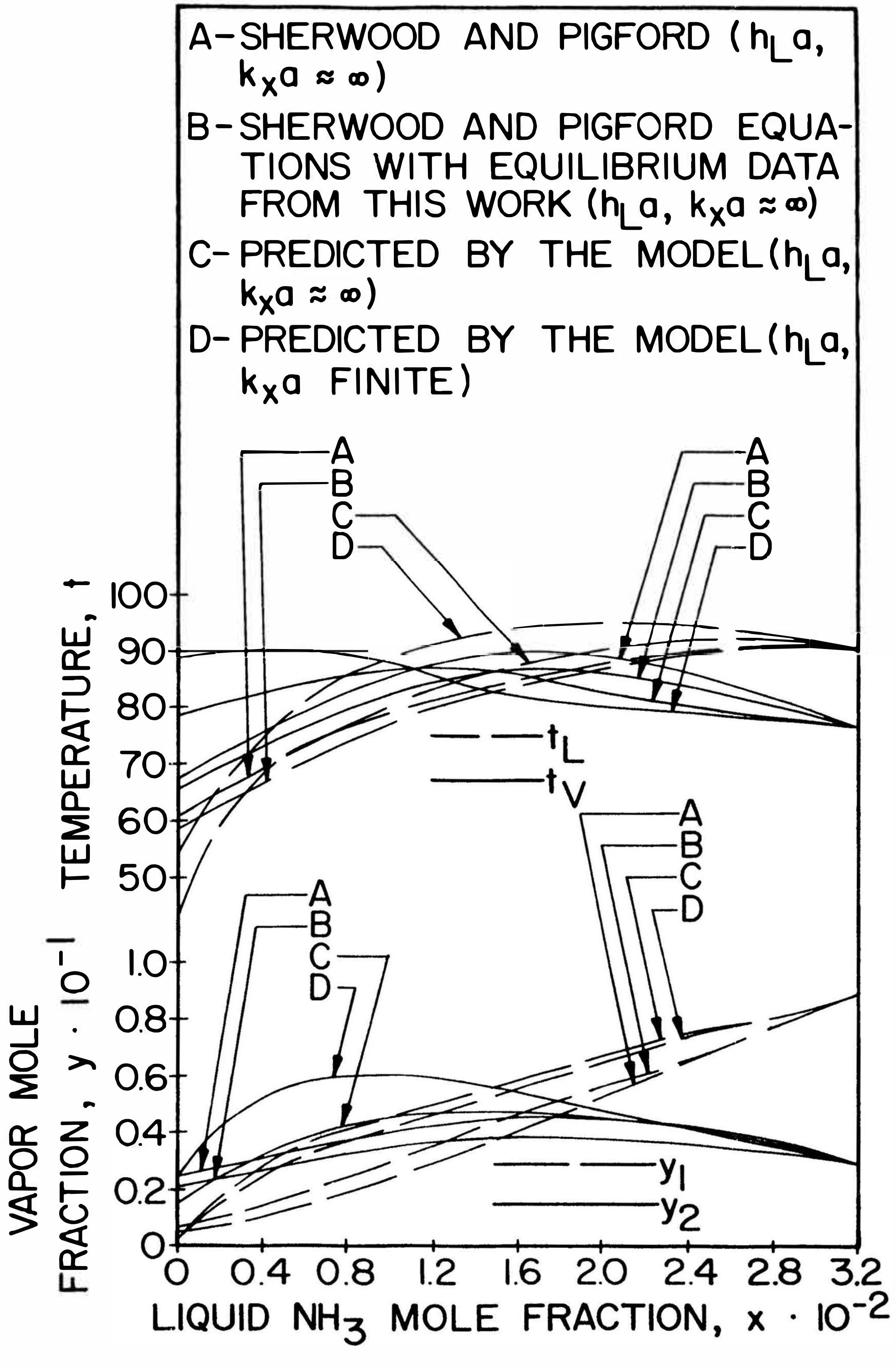

Figure 4. Concentration and Temperature Profiles for an Adiabatic Absorption of Ammonia in Water[10]

TABLE 2

PHYSICAL DATA -- ACETONE-WATER ABSORPTION

Carrier Liquid: Water

Carrier Gas: Air

Components: 1 = Acetone, 2 = Water

Reaction: None

Compositions: $(y_{in})_1 = 0.0309$ $(y_{out})_1 = 0.00231$

$(y_{in})_2 = 0.0116$ $(y_{out})_2 = 0.0265$

$(x_{in})_1 = 0.0114$ $(x_{out})_1 = 0.0114$

$(x_{in})_2 = 0.9886$ $(x_{out})_2 = 0.9886$

$(\hat{y}_{out})_1 = 0.00227$ $(\hat{x}_{in})_1 = 0.0$

$(\hat{y}_{out})_2 = 0.0186$ $(\hat{x}_{in})_2 = 1.0$

Temperature: $(t_L)_{in} = 54.5°F$ $(t_L)_{out} = 69.3°F$

$(t_V)_{in} = 58.8°F$ $(t_V)_{out} = 72°F$

$(\hat{t}_L)_{in} = 56.8°F$

$(\hat{t}_V)_{out} = 58°F$

Flow Rates: $L' = 38.33$ lb moles/hr ft^2

$V' = 15.24$ lb moles/hr ft^2

Packing: 1" Ceramic rings

Mass Transfer Coefficients[12] (at 65°F, assumed constant):

$(k_x a)_1 = 21.65$ lb moles/hr ft^3 mole fraction

$(k_x a)_2 = 39.4$ lb moles/hr ft^3 mole fraction

$(k_y a)_1 = 4.36$ lb moles/hr ft^3 mole fraction

$(k_y a)_2 = 7.93$ lb moles/hr ft^3 mole fraction

$h_L a = 120.0$ BTU/hr ft^3 °F

$h_V a = 6.93$ BTU/hr ft^3 °F

TABLE 2 (continued)

Equilibrium Data:

$$y_1^i = \gamma_1 P^o x_1^i / P$$

$$y_2^i = [0.027721 - 0.000733\, t^i + 0.0000112819\, (t^i)^2][1 - \sum_{j=1}^{N} x_j]$$

Reference: 10

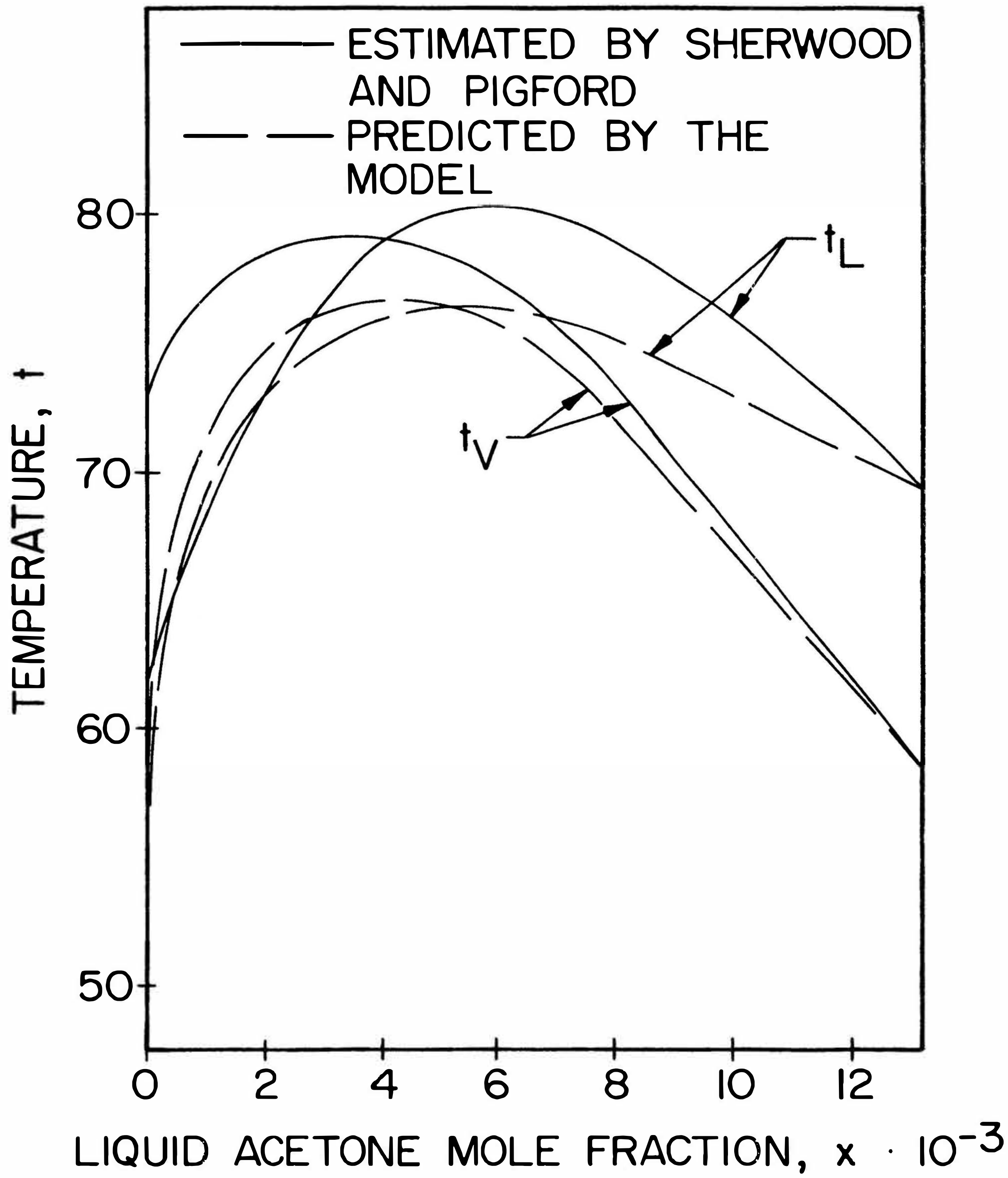

Figure 5. Vapor and Liquid Temperature Profiles for an Adiabatic Absorption of Acetone in Water[10]

TABLE 3

THE REACTION SYSTEMS STUDIED WITH REPORTED AND CALCULATED COLUMN HEIGHTS

System	Reaction	Carrier Liquid	Carrier Gas	Transferring Component	Heat Effects	Reported Column Height (Ft)	Program Predicted Height (Ft)	% Error	Reference
1	None	H_2O	Air	A	Isothermal	1550*	1465	5.5	6
2	A+B→C	H_2O	Air	A	Isothermal	16.4*	16.55	0.9	6
3	A+B→C	H_2O	Air	A	Isothermal	80.0*	81.0	1.2	6
4	A+B→C	H_2O	Air	A	Isothermal	23.0*	25.4	9.4	6
5	$CO_2+K_2CO_3+H_2O \rightarrow 2KHCO_3$	H_2O	N_2	CO_2	Isothermal	22.9*	22.5	1.7	4
6	$CO_2+K_2CO_3+H_2O \rightarrow 2KHCO_3$	H_2O	N_2	CO_2	Isothermal	22.9*	22.8	0.4	4
7	$CO_2+2RNH_3 \rightarrow RNH_2COO^- + RNH_2$	H_2O	N_2	CO_2	Isothermal	10.5*	9.8	6.7	4

TABLE 3 (continued)

System	Reaction	Carrier Liquid	Carrier Gas	Transferring Component	Heat Effects	Reported Column Height (Ft)	Program Predicted Height (Ft)	% Error	Reference
8	$CO_2+2NaOH \rightarrow Na_2CO_3+H_2O$	H_2O	Air	CO_2	Isothermal	3.0+	3.08	2.7	11
9	$CO_2+2NaOH \rightarrow Na_2CO_3+H_2O$	H_2O	Air	CO_2	Adiabatic	7.7+	8.2	6.1	11
10	$A_1+2B \rightarrow P_1$ $A_2+B \rightarrow P_2$	H_2O	Air	A	Adiabatic	---	3.1	---	---

* - Calculated column height

\+ - Experimental column height

TABLE 4

PHYSICAL DATA -- CARBON DIOXIDE ABSORPTION WITH CHEMICAL REACTION

Carrier Liquid: Water

Carrier Gas: Air

Column Height: 7.7 ft

Components: $1 = CO_2$, $2 = Na_2CO_3$, $3 = NaOH$

Reaction: $CO_2 + 2NaOH \rightarrow Na_2CO_3 + H_2O$

Compositions: $(y_{in})_1 = 0.0472$ $(y_{out})_1 = 0.0099$
$(y_{in})_2 = 0.0$ $(y_{out})_2 = 0.0$
$(y_{in})_3 = 0.0$ $(y_{out})_3 = 0.0$
$(x_{in})_1 = 0.0$ $(x_{out})_1 = 0.0$
$(x_{in})_2 = 0.000427$ $(x_{out})_2 = 0.00685$
$(x_{in})_3 = 0.01883$ $(x_{out})_3 = 0.00539$
$(\hat{y}_{in})_1 = 0.0472$ $(\hat{x}_{out})_1 = 0.0$
$(\hat{y}_{in})_2 = 0.0$ $(\hat{x}_{out})_2 = 0.00619$
$(\hat{y}_{in})_3 = 0.0$ $(\hat{x}_{out})_3 = 0.00741$

Temperature: $(t_L)_{in} = 63°F$ $(t_L)_{out} = 80°F$
$(t_V)_{in} = 80°F$ $(t_V)_{out} = 69°F$
$(\hat{t}_L)_{out} = 79.0°F$
$(\hat{t}_V)_{in} = 80.1°F$

Flow Rates: $L' = 40.1$ lb moles/hr ft^2
$V' = 6.15$ lb moles/hr ft^2

Packing: 1/2" Raschig rings

TABLE 4 (continued)

Transfer Coefficients[12] (assumed constant):

$(k_x a)_1$ = 52.5 lb moles/hr ft^3 mole fraction

$(k_y a)_1$ = 2.99 lb moles/hr ft^3 mole fraction

$h_L a$ = 8758 BTU/hr ft^3 °F

$h_V a$ = 24.6 BTU/hr ft^3 °F

Diffusivities (at 79°F): $(D_V)_1$ = 0.6355 ft^2/hr

$(D_L)_1 = 6.85 \times 10^{-5}$ ft^2/hr

$(D_L)_3 = 5.85 \times 10^{-5}$ ft^2/hr

Equilibrium Data:

$y_1^i = h\ (10^4)\ x_1^i$ where $h = 0.025499 + 0.00122338\ t^i + 0.0000073484\ (t^i)^2$

Program Predicted Tower Height: 8.2 ft

Reference: 11

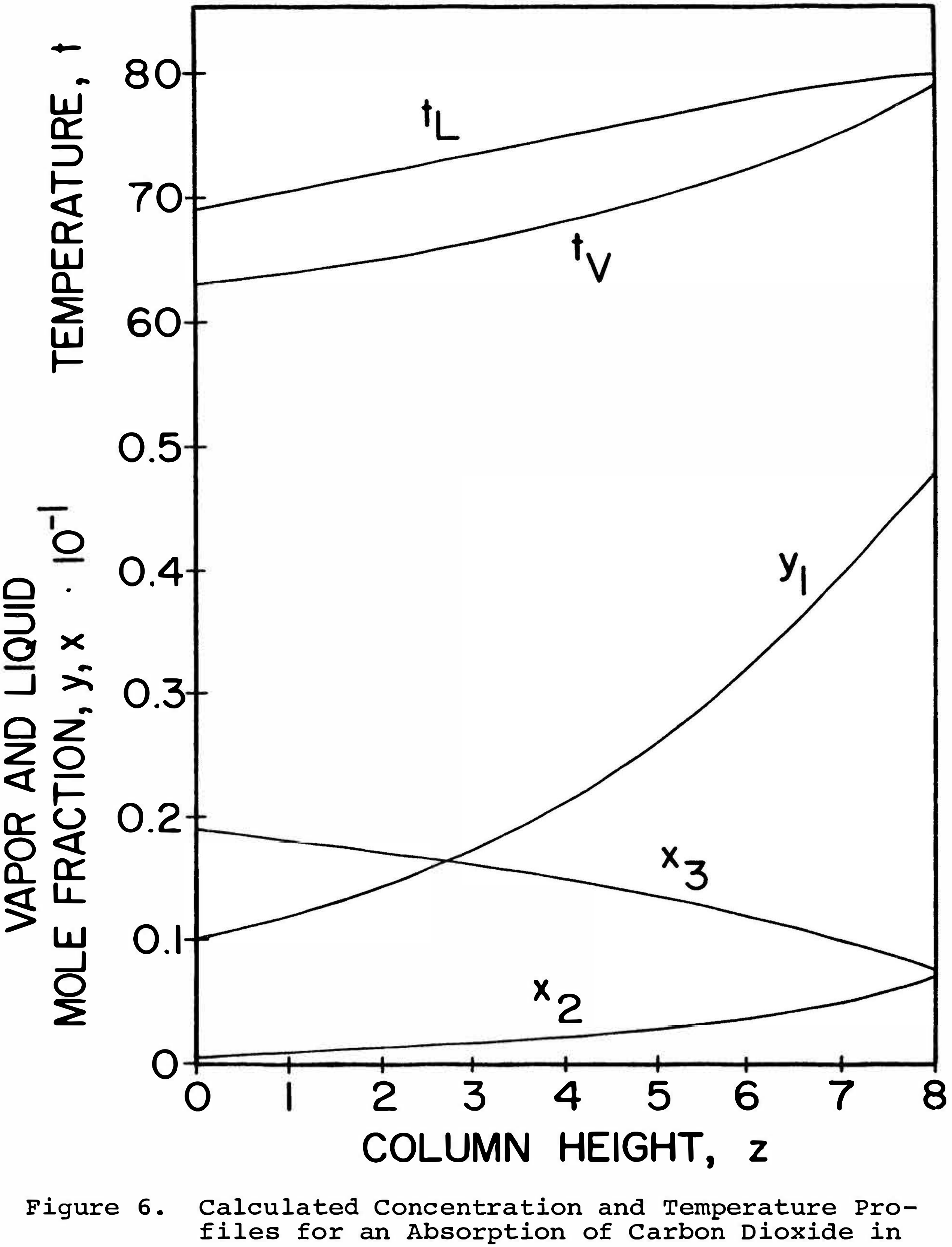

Figure 6. Calculated Concentration and Temperature Profiles for an Absorption of Carbon Dioxide in Water with a Chemical Reaction[11]

TABLE 5

PHYSICAL DATA -- THREE COMPONENTS TRANSFERRING - TWO COMPONENTS REACTING

Carrier Liquid: Water

Carrier Gas: Air

Components: 1 = A, 2 = C, 3 = D, 4 = E, 5 = F, 6 = B

Reactions: $A+2B \rightarrow E$

$C+B \rightarrow F$

Compositions:

$(y_{in})_1 = 0.05$ $(y_{out})_1 = 0.01$ $(x_{in})_1 = 0.00$
$(y_{in})_2 = 0.075$ $(y_{out})_2 = 0.02$ $(x_{in})_2 = 0.00$
$(y_{in})_3 = 0.014$ $(y_{out})_3 = 0.01$ $(x_{in})_3 = 0.00$
$(y_{in})_4 = 0.00$ $(y_{out})_4 = 0.00$ $(x_{in})_4 = 0.0001$
$(y_{in})_5 = 0.00$ $(y_{out})_5 = 0.00$ $(x_{in})_5 = 0.00015$
$(y_{in})_6 = 0.00$ $(y_{out})_6 = 0.00$ $(x_{in})_6 = 0.02$

Temperature: $(t_L)_{in} = 60°F$ $(t_V)_{in} = 65°F$
$(t_L)_{out} = 87°F$ $(t_L)_{out} = 58°F$

Flow Rates: $L' = 45$ lb moles/hr ft^2
$V' = 5$ lb moles/hr ft^2

Packing: 1" Raschig rings

Transfer Coefficients (at 79°F, assumed constant):

$(k_x a)_1 = 50$ lb moles/hr ft^3 mole fraction
$(k_y a)_1 = 3$ lb moles/hr ft^3 mole fraction
$(k_x a)_2 = 45$ lb moles/hr ft^3 mole fraction
$(k_y a)_2 = 2.5$ lb moles/hr ft^3 mole fraction

TABLE 5 (continued)

Transfer Coefficients (continued):

$(k_x a)_3$ = 332 lb moles/hr ft^3 mole fraction

$(k_y a)_3$ = 14 lb moles/hr ft^3 mole fraction

$h_L a$ = 9000 BTU/hr ft^3 °F

$h_V a$ = 10 BTU/hr ft^3 °F

Diffusivities: $(D_V)_1 = 0.64$ ft^2/hr

$(D_L)_1 = 7.0 \times 10^{-5}$ ft^2/hr

$(D_V)_2 = 0.70$ ft^2/hr

$(D_L)_2 = 7.5 \times 10^{-5}$ ft^2/hr

$(D_L)_6 = 6.0 \times 10^{-5}$ ft^2/hr

Equilibrium Data:

$$y_1^i = [0.025 + 0.0012\, t^i + 0.000007\, (t^i)^2]\, 10^4\, x_1^i$$

$$y_2^i = [0.030 + 0.020\, t^i + 0.00010\, (t^i)^2]\, 10^4\, x_2^i$$

$$y_3^i = 29\, x_3^i$$

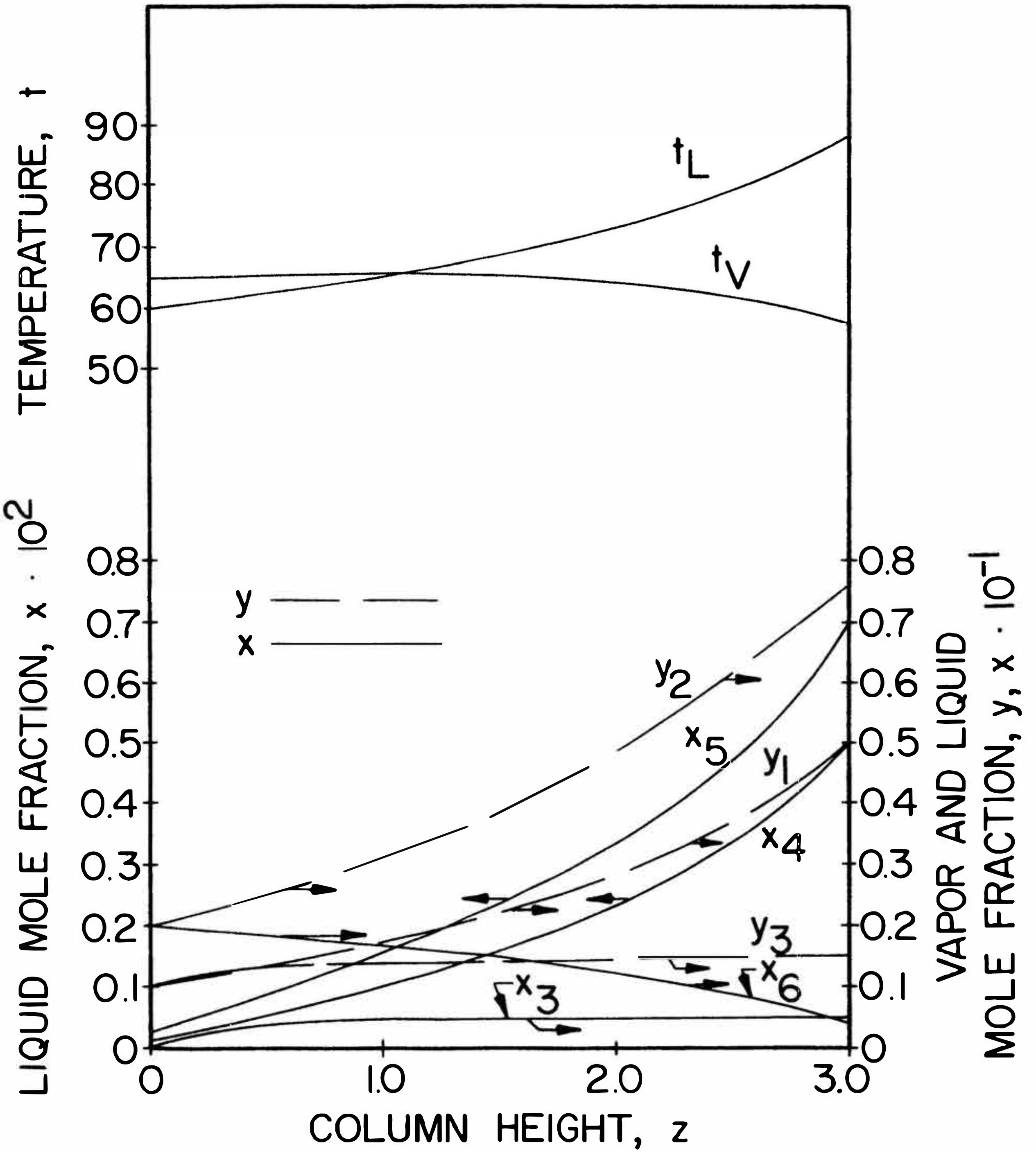

Figure 7. Calculated Concentration and Temperature Profiles -- Three Components Transferring - Two Components Reacting

NOMENCLATURE

a	Interfacial area cubic foot of contactor volume, ft^2/ft^3
a,b,c	Curve fitting parameters for equilibrium data
a,b,p	Stoichiometric coefficients of the reactants and product
A	A transferring-reacting component from the vapor phase
A_c	Cross-sectional area of the column, ft^2
B	The reacting component in the liquid phase
Cp	Heat capacity, BTU/lb mole
c	Concentration of ammonia, lb moles NH_3/1000 lb H_2O
D	Diffusivity, ft^2/hr
E	Enhancement factor
E_i	Instantaneous enhancement factor
e,f,g,h	Indicators of functions
F	Defined by Equation 36
ff	Defined by Equation 29
h_La	Liquid heat transfer coefficient, BTU/hr ft^3 °F
h_Va	Vapor heat transfer coefficient, BTU/hr ft^3 °F
H_G	Height of a transfer unit, ft
H_{rx}	Heat of reaction, BTU/lb mole

H	Enthalpy, BTU/lb mole
k	Iteration counter
$k_x a$	Liquid mass transfer coefficient, lb moles/hr ft^3 mole fraction
$k_y a$	Vapor mass transfer coefficient, lb moles/hr ft^3 mole fraction
k_{rx}	Reaction rate constant, lb moles/hr ft^3
L	Total liquid flow rate, lb moles/hr ft^2
L'	Flow rate of the solvent liquid, lb moles/hr ft^2
M	Defined by Equation 16
m	Equilibrium constant
m,n	Reaction order
N	Total number of components
N_r	Number of transferring-reacting components
N_x	Number of transferring-reacting and transferring-nonreacting components
N_G	Number of transfer units
P	Reaction product
P	Total pressure, atm
P^o	Vapor pressure, atm
Q_s	Heat of solution, BTU/lb mole
Q_v	Heat of vaporization, BTU/lb mole
r	Rate of reaction, lb moles of A/hr ft^3
R	Defined by Equation 10
t	Temperature, °F

T	Temperature, °K
V	Total vapor flow rate, lb moles/hr ft^2
V'	Flow rate of the noncondensing carrier gas, lb moles/hr ft^2
x	Component concentration in the liquid phase, mole fraction
$\underline{x}$	A vector representing all liquid phase compositions
y	Component concentration in the vapor phase, mole fraction
$\underline{y}$	A vector representing all vapor phase compositions
z	Column height, ft
$\bar{\rho}$	Molar density

Subscripts

L	Liquid phase
$N+1$	Component number of the carrier gas and carrier liquid
r	Component number of the liquid phase reactant
R	Reference
V	Vapor phase
ε	Defined by Equation 36
$1,2,\ldots,N$	Component numbers

Superscripts

i	Interface
$\hat{}$	Values calculated by the model

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VITA

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APPENDIX A

MASS AND ENERGY TRANSFER EQUATIONS

The great abundance of literature available on mass transfer with chemical reaction in a continuous contactor has been concerned with local concentrations at specific points within the column. Relatively few attempts have been made to integrate the rate equations over the column length to determine the two phase absorber-reactor height.

Almost every mass transfer text presents the differential equations which describe one component mass and energy transfer in a continuous contactor. Sherwood and Pigford[24] have developed the simplified equations for two component mass and energy transfers in a continuous contactor. However, the assumptions used to develop their equations (i.e., dilute solutions, $h_L a$ and $(k_x a)_k \simeq \infty$) make them difficult to apply in the general case. Toor[26] has developed some general equations for multicomponent mass transfer, although he was not particularly concerned with obtaining column height.

Astarita and Giora[2], Roper, Hatch, and Pigford[22], Goettler and Pigford[13], and many others have done work with the simultaneous absorption and reaction of two gases. Secor and Southworth[23] have demonstrated that for an instantaneous reaction more than one region can exist in an absorber-reactor simultaneously. Levenspiel[16] has expanded the work of Secor and Southworth[23] to include fast and slow chemical reactions.

It is now appropriate to develop the differential equations for mass and energy transfer in a continuous absorber-reactor and solve the equations numerically. The numerical solution can be used to obtain column height, output compositions, flow rates, or overall mass transfer coefficients.

In Appendix A, the equations for mass and heat transfer are developed for the simple case of one component mass transfer and for multicomponent mass transfer with chemical reaction (see Figure 1).

ONE COMPONENT MASS TRANSFER

If the carrier gas is assumed to be noncondensing, the steady-state mass balance on the transferring component of the differential element in the vapor phase is:

[lb moles]$_{in}$ - [lb moles]$_{out}$ - [lb moles transferring across the interface] = 0

$$-Vy|_z + [Vy|_{z+\Delta z} A_c] - k_y a\ (y-y^i)\ A_c \Delta z|_{z+\frac{\Delta z}{2}} = 0. \qquad \text{(A-1)}$$

Dividing through by $A_c\Delta z$ gives:

$$\frac{-Vy|_z + Vy|_{z+\Delta z}}{\Delta z} - k_y a\ (y-y^i) = 0, \qquad \text{(A-2)}$$

and taking limits as $\Delta z \rightarrow 0$ gives:

$$\frac{d(Vy)}{dz} = k_y a\ (y-y^i). \tag{A-3}$$

The total flow rate may be represented in terms of the flow rate of the carrier gas by:

$$V = \frac{V'}{1-y}. \tag{A-4}$$

Substitution of Equation A-4 into Equation A-3 yields:

$$V' \frac{d\left(\frac{y}{1-y}\right)}{dz} = k_y a\ (y-y^i). \tag{A-5}$$

Performing the indicated differentiation

$$V' \left[\frac{(1-y)\ (1) - y\ (-1)}{(1-y)^2}\right] \frac{dy}{dz} = k_y a\ (y-y^i), \tag{A-6}$$

then Equation A-6 reduces to:

$$\frac{dy}{dz} = \frac{(1-y)^2}{V'} k_y a\ (y-y^i). \tag{A-7}$$

A similar balance can be performed on the liquid phase. If the carrier liquid is assumed to be non-volatile, the steady-state mass balance is:

$$[\text{lb moles}]_{in} - [\text{lb moles}]_{out} - [\text{lb moles transferring across the interface}] = 0$$

$$Lx|_z A_c - [Lx|_{z+\Delta z} A_c] + k_x a\ (x^i-x)|_{z+\frac{\Delta z}{2}} A_c \Delta z = 0. \tag{A-8}$$

Dividing through by $A_c \Delta z$ gives:

$$-\left[\frac{Lx|_{z+\Delta z} - Lx|_z}{\Delta z}\right] = -\ k_x a\ (x^i-x), \tag{A-9}$$

and taking limits as $\Delta z \to 0$ gives:

$$\frac{d(Lx)}{dz} = k_xa\ (x^i - x). \tag{A-10}$$

The total flow rate in the liquid phase may be represented in terms of the carrier liquid flow rate:

$$L = L'/(1-x). \tag{A-11}$$

Substituting Equation A-11 into Equation A-10 yields:

$$L' \frac{d\ (\frac{x}{1-x})}{dz} = k_xa\ (x^i - x). \tag{A-12}$$

Performing the indicated differentiation

$$L'\ [\frac{(1-x)\ (1)\ -\ x\ (-1)}{(1-x)^2}]\ \frac{dx}{dz} = k_xa\ (x^i - x), \tag{A-13}$$

then Equation A-13 reduces to:

$$\frac{dx}{dz} = \frac{(1-x)^2}{L'}\ k_xa\ (x^i - x). \tag{A-14}$$

In summary, the equations that describe one component mass transfer in a continuous contactor are:

$$\frac{dy}{dz} = \frac{(1-y)^2}{V'}\ k_ya\ (y - y^i) \tag{A-15a}$$

$$\frac{dx}{dz} = \frac{(1-x)^2}{L'}\ k_xa\ (x^i - x). \tag{A-15b}$$

If the liquid and vapor flow rates are assumed to be constant throughout the entire length of the column as the result of dilute solution concentrations, Equation A- 15reduces to:

$$\frac{dy}{dz} = \frac{k_ya}{V'}\ (y - y^i) \tag{A-16a}$$

$$\frac{dx}{dz} = \frac{k_x a}{L'} (x^i - x). \qquad \text{(A-16b)}$$

Equation 16 is normally presented in chemical engineering texts on mass transfer[3,12,23] and may be solved either graphically, analytically, or numerically.

MULTICOMPONENT MASS TRANSFER

However, many industrial applications are not confined to a system with one transferring component. There may be two, three, or even more undesirable components (e.g., in a stack gas) which require removal by absorption. In a two transferring component absorption, a mass balance is required on each transferring component before the system is completely described.

The steady-state mass balance for component one in the vapor phase (assuming the carrier gas is non-condensable) is:

$$[\text{lb moles}]_{\text{in}} - [\text{lb moles}]_{\text{out}} - [\text{lb moles transferred across the interface}] = 0$$

$$-Vy_1|_z\, A_c - [-Vy_1|_{z+\Delta z}\, A_c] - [(k_y a)_1\, (y_1 - y_1^i)|_{z+\frac{\Delta z}{2}}\, A_c \Delta z] = 0. \qquad \text{(A-17)}$$

Dividing through by $A_c \Delta z$ and taking limits as $\Delta z \to 0$ yields:

$$\frac{d(Vy_1)}{dz} = (k_y a)_1\, (y_1 - y_1^i). \qquad \text{(A-18)}$$

The total flow rate may be represented in terms of the flow rate of the carrier gas by:

$$V = \frac{V'}{1-y_1-y_2} . \qquad \text{(A-19)}$$

Substitution of Equation A-19 into Equation A-18 gives:

$$V' \frac{d\left(\frac{y_1}{1-y_1-y_2}\right)}{dz} = (k_y a)_1 \ (y_1-y_1^i) . \qquad \text{(A-20)}$$

Performing the indicated differentiation gives:

$$\frac{1-y_2}{(1-y_1-y_2)^2} \frac{dy_1}{dz} + \frac{y_1}{(1-y_1-y_2)^2} \frac{dy_2}{dz} =$$

$$\frac{(k_y a)_1}{V'} \ (y_1-y_1^i) . \qquad \text{(A-21)}$$

The differential mass balance for component two is:

$$-Vy_2|_z \ A_c - [-Vy_2|_{z+\Delta z} \ A_c] -$$

$$[(k_y a)_2 \ (y_2-y_2^i)|_{z+\frac{\Delta z}{2}} \ A_c \Delta z] = 0. \qquad \text{(A-22)}$$

Dividing through by $A_c \Delta z$ and taking limits as $\Delta z \to 0$ yields:

$$\frac{d(Vy_2)}{dz} = (k_y a)_2 \ (y_2-y_2^i) . \qquad \text{(A-23)}$$

Substitution of Equation A-19 into Equation A-23 and differentiating produces:

$$\frac{y_2}{(1-y_1-y_2)^2} \frac{dy_1}{dz} + \frac{(1-y_1)}{(1-y_1-y_2)^2} \frac{dy_2}{dz} =$$

$$\frac{(k_y a)_2}{V'} \ (y_2-y_2^i) . \qquad \text{(A-24)}$$

Equations A-21 and A-24 can be written in matrix notation:

$$\begin{bmatrix} \frac{1-y_2}{(1-y_1-y_2)^2} & \frac{y_1}{(1-y_1-y_2)^2} \\ \frac{y_2}{(1-y_1-y_2)^2} & \frac{1-y_1}{(1-y_1-y_2)^2} \end{bmatrix} \begin{bmatrix} \frac{dy_1}{dz} \\ \frac{dy_2}{dz} \end{bmatrix} =$$

$$\begin{bmatrix} \frac{(k_ya)_1}{V'} \ (y_1-y_1^i) \\ \frac{(k_ya)_2}{V'} \ (y_2-y_2^i) \end{bmatrix} \tag{A-25}$$

and solved for dy_1/dz and dy_2/dz:

$$\frac{dy_1}{dz} = (1-y_1)\ (1-y_1-y_2)\ \frac{(k_ya)_1}{V'}\ (y_1-y_1^i)\ -$$

$$y_1\ (1-y_1-y_2)\ \frac{(k_ya)_2}{V'}\ (y_2-y_2^i) \tag{A-26a}$$

$$\frac{dy_2}{dz} = (1-y_2)\ (1-y_1-y_2)\ \frac{(k_ya)_2}{V'}\ (y_2-y_2^i)\ -$$

$$y_2\ (1-y_1-y_2)\ \frac{(k_ya)_1}{V'}\ (y_1-y_1^i). \tag{A-26b}$$

The differential mass balance for the liquid phase components is essentially the same as that of the vapor phase. If the carrier liquid is assumed to be non-volatile, the steady-state balance on component one is:

$$Lx_1\big|_z\ A_c - [Lx_1\big|_{z+\Delta z}\ A_c]\ +$$

$$(k_xa)_1\ (x_1^i-x_1)\big|_{z+\frac{\Delta z}{2}}\ A_c\Delta z = 0. \tag{A-27}$$

Dividing through by $A_c\Delta z$ and taking limits as $\Delta z\rightarrow 0$ gives:

$$\frac{d(Lx_1)}{dz} = (k_x a)_1 \; (x_1^i - x_1) . \tag{A-28}$$

The total liquid flow rate may be represented in terms of the flow rate of the carrier liquid:

$$L = \frac{L'}{1-x_1-x_2} . \tag{A-29}$$

Substitution of Equation A-29 into Equation A-28 gives:

$$L' \frac{d\left(\frac{x_1}{1-x_1-x_2}\right)}{dz} = (k_x a)_1 \; (x_1^i - x_1) . \tag{A-30}$$

Performing the indicated differentiation produces:

$$\frac{1-x_2}{(1-x_1-x_2)^2} \frac{dx_1}{dz} + \frac{x_1}{(1-x_1-x_2)^2} \frac{dx_2}{dz} =$$

$$\frac{(k_x a)_1}{L'} \; (x_1^i - x_1) . \tag{A-31}$$

A similar mass balance on component two will give:

$$\frac{x_2}{(1-x_1-x_2)^2} \frac{dx_1}{dz} + \frac{1-x_1}{(1-x_1-x_2)^2} \frac{dx_2}{dz} =$$

$$\frac{(k_x a)_2}{L'} \; (x_2^i - x_2) . \tag{A-32}$$

Equations A-31 and A-32 can be written in matrix notation:

$$\begin{bmatrix} \frac{1-x_2}{(1-x_1-x_2)^2} & \frac{x_1}{(1-x_1-x_2)^2} \\ \frac{x_2}{(1-x_1-x_2)^2} & \frac{1-x_1}{(1-x_1-x_2)^2} \end{bmatrix} \begin{bmatrix} \frac{dx_1}{dz} \\ \frac{dx_2}{dz} \end{bmatrix} = \begin{bmatrix} \frac{(k_x a)_1}{L'} \ (x_1^i - x_1) \\ \frac{(k_x a)_2}{L'} \ (x_2^i - x_2) \end{bmatrix} \tag{A-33}$$

and solved for dx_1/dz and dx_2/dz:

$$\frac{dx_1}{dz} = (1-x_1)\ (1-x_1-x_2)\ \frac{(k_x a)_1}{L'}\ (x_1^i - x_1)\ - \\ x_1\ (1-x_1-x_2)\ \frac{(k_x a)_2}{L'}\ (x_2^i - x_2) \tag{A-34a}$$

$$\frac{dx_2}{dz} = (1-x_2)\ (1-x_1-x_2)\ \frac{(k_x a)_2}{L'}\ (x_2^i - x_2)\ - \\ x_2\ (1-x_1-x_2)\ \frac{(k_x a)_1}{L'}\ (x_1^i - x_1). \tag{A-34b}$$

Equations A-26 and A-34 describe the change in composition of the vapor and liquid phases with respect to height for countercurrent flow and steady-state mass transfer for two components. These equations can be solved for the liquid and vapor compositions as a function of tower height only by numerical methods.

For a three transferring component system, the equations for the vapor and liquid phases are developed in the same manner. They are:

$$\frac{dy_1}{dz} = \frac{(1-\sum_{j=1}^{N} y_j)}{V'} [(1-y_1)\ (k_y a)_1\ (y_1-y_1^i) - y_1\ (k_y a)_2\ (y_2-y_2^i) - y_1\ (k_y a)_3\ (y_3-y_3^i)] \qquad \text{(A-35a)}$$

$$\frac{dy_2}{dz} = \frac{(1-\sum_{j=1}^{N} y_j)}{V'} [(1-y_2)\ (k_y a)_2\ (y_2-y_2^i) - y_2\ (k_y a)_1\ (y_1-y_1^i) - y_2\ (k_y a)_3\ (y_3-y_3^i)] \qquad \text{(A-35b)}$$

$$\frac{dy_3}{dz} = \frac{(1-\sum_{j=1}^{N} y_j)}{V'} [(1-y_3)\ (k_y a)_3\ (y_3-y_3^i) - y_3\ (k_y a)_1\ (y_1-y_1^i) - y_3\ (k_y a)_2\ (y_2-y_2^i)] \qquad \text{(A-35c)}$$

$$\frac{dx_1}{dz} = \frac{(1-\sum_{j=1}^{N} x_j)}{L'} [(1-x_1)\ (k_x a)_1\ (x_1^i-x_1) - x_1\ (k_x a)_2\ (x_2^i-x_2) - x_1\ (k_x a)_3\ (x_3^i-x_3)] \qquad \text{(A-36a)}$$

$$\frac{dx_2}{dz} = \frac{(1-\sum_{j=1}^{N} x_j)}{L'} [(1-x_2)\ (k_x a)_2\ (x_2^i-x_2) - x_2\ (k_x a)_1\ (x_1^i-x_1) - x_2\ (k_x a)_3\ (x_3^i-x_3)] \qquad \text{(A-36b)}$$

$$\frac{dx_3}{dz} = \frac{(1-\sum_{j=1}^{N} x_j)}{L'} [(1-x_3)\ (k_x a)_3\ (x_3^i-x_3) - x_3\ (k_x a)_1\ (x_1^i-x_1) - x_3\ (k_x a)_2\ (x_2^i-x_2)]. \qquad \text{(A-36c)}$$

Then for the general case of N transferring components, there are N steady-state equations for the vapor phase:

$$\frac{dy_k}{dz} = \frac{(1-\sum_{j=1}^{N} y_j)}{V'} [(1-y_k)\ (k_y a)_k\ (y_k - y_k^i) - \sum_{\substack{j=1\\ j\neq k}}^{N} y_k\ (k_y a)_j\ (y_j - y_j^i)], \qquad k=1,2,\ldots,N \tag{A-37a}$$

and N steady-state equations for the liquid phase:

$$\frac{dx_k}{dz} = \frac{(1-\sum_{j=1}^{N} x_j)}{L'} [(1-x_k)\ (k_x a)_k\ (x_k^i - x_k) - \sum_{\substack{j=1\\ j\neq k}}^{N} x_k\ (k_x a)_j\ (x_j^i - x_j)]. \qquad k=1,2,\ldots,N \tag{A-37b}$$

Equation A-37 describes the change in composition of the vapor and liquid phases with respect to height for countercurrent steady-state mass transfer with N transferring components. These equations can only be solved numerically for the liquid and vapor compositions as a function of tower height.

All the above equations were derived assuming a non-volatile carrier liquid; however, there are many systems in which the carrier liquid is volatile and not only acts as a vehicle for the other components but also as a transferring component. For a volatile carrier liquid, the liquid phase equations are altered slightly and the vapor phase equations are unchanged. They are:

$$\frac{dy_k}{dz} = \frac{(1-\sum_{j=1}^{N} y_j)}{V'} [(1-y_k)\ (k_ya)_k\ (y_k-y_k^i) - \sum_{\substack{j=1 \\ j \neq k}}^{N} y_k\ (k_ya)_j\ (y_j-y_j^i)], \qquad k=1,2,\ldots,N \tag{A-38a}$$

$$\frac{dx_k}{dz} = \frac{(1-\sum_{j=1}^{N-1} x_j)}{L'} [(1-x_k)\ (k_xa)_k\ (x_k^i-x_k) - \sum_{\substack{j=1 \\ j \neq k}}^{N-1} x_k\ (k_xa)_j\ (x_j^i-x_j)], \qquad k=1,2,\ldots,N-1 \tag{A-38b}$$

and

$$\frac{dL'}{dz} = (k_xa)_N\ (x_N^i-x_N). \tag{A-38c}$$

The volatile carrier liquid increases the total number of components, N, by one.

Equation A-38 is applicable to all cases where the solvent is vaporizing. This equation also must be solved numerically.

The carrier gas has been considered non-condensing because most of the industrial applications and experimental work in the literature use a non-condensing, inert carrier gas. However, for a condensing carrier gas, Equation A-38a would become:

$$\frac{dy_k}{dz} = \frac{(1-\sum_{j=1}^{N-1} y_j)}{V'} [(1-y_k)\ (k_y a)_k\ (y_k - y_k^i)\ - \sum_{\substack{j=1\\ j\neq k}}^{N-1} y_k\ (k_y a)_j\ (y_j - y_j^i)] \qquad \text{(A-39a)}$$

$$k=1,2,\ldots,N-1$$

$$\frac{dV'}{dz} = (k_y a)_N\ (y_N - y_N^i). \qquad \text{(A-39b)}$$

Although the development of all equations assumed a gas-liquid system, they can apply to a steady-state counter-current liquid-liquid system. If the system were co-current, -V' or -L' would be substituted for V' or L' respectively depending on which of the flows were reversed. The above model assumes an isothermal system. Energy transfer and heat effects are considered in a later section.

MASS TRANSFER WITH CHEMICAL REACTION

The chemical industry's concern over meeting exhaust gas emission standards has created an interest in absorption with chemical reaction primarily, because it reduces tower height through increased mass transfer rates resulting from the chemical reaction. Specifically, Levenspiel[16] demonstrates that a physical absorption separation which would require a tower height of 1550 feet could be adapted to a tower height of 16.4 feet if the transferring component chemically reacted through an instantaneous reaction in the liquid phase. It is then advantageous to the design engineer to have at his disposal a method for accurately estimating the height of an absorber-reactor. Currently, a generalized technique is not available, or at least is not in the open literature.

Levenspiel[16] has classified mass transfer with chemical reaction into three categories: 1) reaction only in the liquid film, which includes instantaneous and fast chemical reaction with respect to mass transfer; 2) reaction in the liquid film and liquid bulk, which could result from an intermediate reaction rate with respect to mass transfer; and 3) reaction in the bulk only, which includes both slow and extremely slow reaction rates with respect to mass transfer. Since many of the industrially important reactions are instantaneous, this work is confined to the first category.

Levenspiel[16] and Danckwerts[9] have subdivided the chemical reaction in the liquid film category into four types:

1. Instantaneous interior reaction.

   The reaction occurs at a plane in the liquid film with the diffusion rate of both reactants controlling and resulting in movement of the reaction plane. Figure 2a depicts the interfacial behavior.

2. Instantaneous interfacial reaction.

   Concentration of B is high enough to move the reaction plane to the gas-liquid interface. Diffusion rate of A is controlling (Figure 2b).

3. Fast reaction, second order rate.

   The reaction rate is slow enough to cause the reaction plane to become a zone but fast enough to complete the reaction before A reaches the liquid bulk (Figure 2c). The rate equation is $r = k_{rx}x_Ax_B$.

4. Fast reaction, pseudo first order or first order.

   The concentration of B is sufficiently high that it is essentially undepleted by the reaction. The second order rate equation is thus reduced to first order (Figure 2d). The rate equation for the pseudo first order is $r = (k_{rx}x_B)x_A$. The first order rate equation is $r = k_{rx}x_A$.

To understand how the foregoing applies to a continuous absorber-reactor, consider the case of an instantaneous reaction, $A+bB \rightarrow pP$. Several regimes could possibly be present in the column simultaneously, depending on the column operating condition. Figure A-1 represents all the possible regimes for an instantaneous reaction.

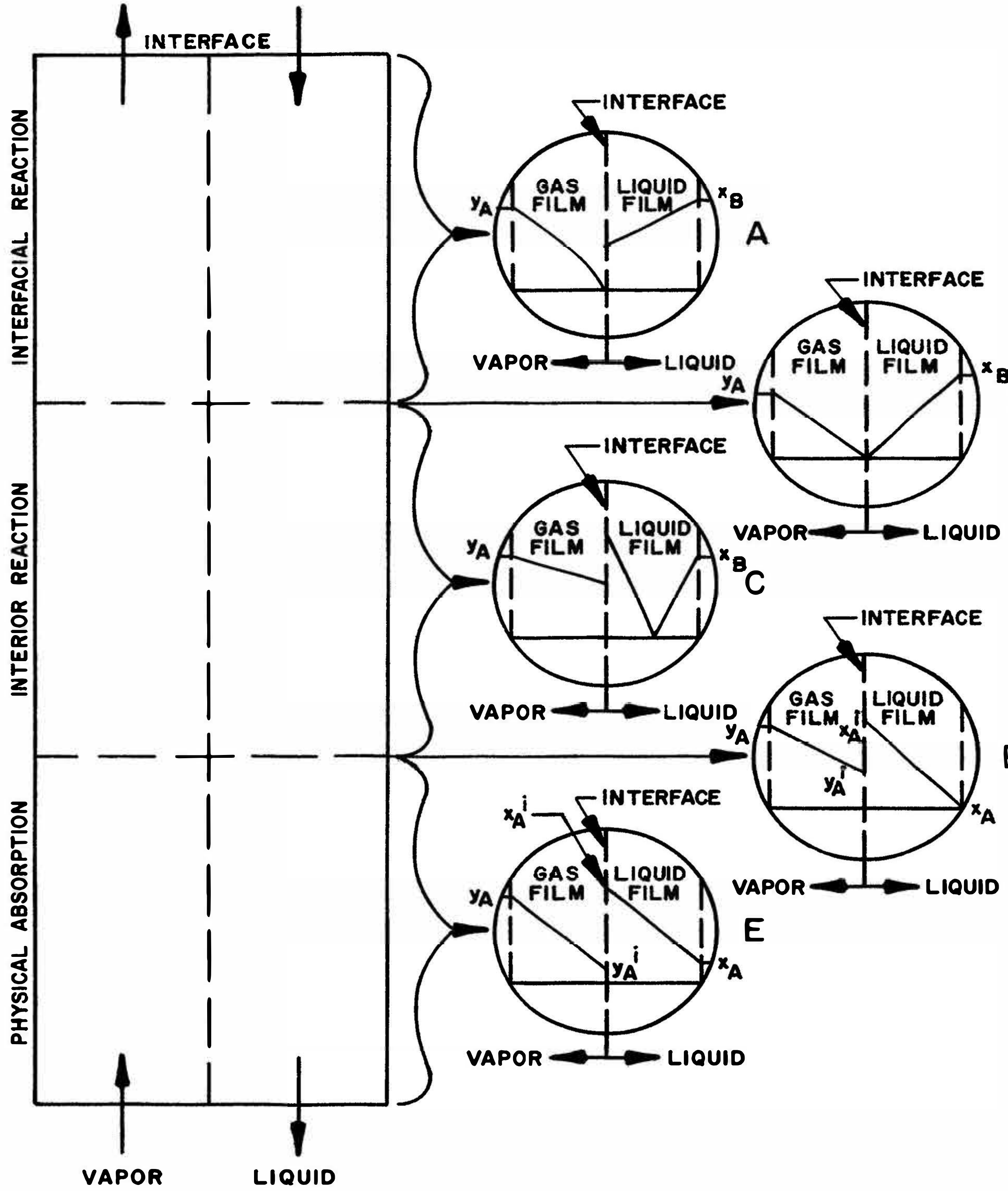

Figure A-1. Possible Interfacial Behavior in a Continuous Contactor for an Instantaneous Liquid Phase Reaction, A+bB→pP[23]

At the top of the column the concentration of B may be sufficiently high to be undepleted by a reaction with A and result in the reaction occurring at the gas-liquid interface (Figure A-1a). As the concentration of B decreases, the reaction plane would move away from the interface into the film. This is called interior reaction (Figure A-1c). If the reactant B were to be completely depleted, there would be no chemical reaction and only physical absorption occurring. Figure A-1b and Figure A-1d represent transition regions between the various regimes. It is also possible that only one regime would exist throughout the entire column. For example, if the concentration of B remained high throughout the column, then an instantaneous interfacial reaction would be occurring the entire length of the contactor. Likewise if the concentration of B was insufficient to produce an interfacial reaction but was not depleted at any column height, then an instantaneous interior reaction would exist in the entire length of the column.

The stoichiometric equation used in this study, for the reaction in the liquid film, has the form $A+bB\rightarrow pP$. The products of this reaction are non-transferring, i.e., after the reaction occurs in the liquid phase the products remain in the liquid phase and do not transfer to the vapor phase. The carrier gas is considered non-condensable and the overall process is considered steady-state.

In order to develop the mathematical model , the same differential element of the column can still be considered (Figure 1). Because the reaction takes place in the liquid film, the equation for vapor phase mass transfer (Equation A-37) remains unchanged.

In developing the mathematical models to describe an absorber-reactor, it is desirable to separate the transferring components into four groups:

1. Components which transfer and react.

    These diffuse from the vapor to the liquid and chemically react in the liquid film with another component, which diffuses from the bulk of the liquid phase into the liquid film.

2. Products of reaction.

    These result from the transfer and reaction of components from the vapor to the liquid phase. These products are assumed to remain in the liquid phase.

3. Components which transfer and do not react.

    These diffuse from the vapor to the liquid but remain unreacted in the liquid phase.

4. Liquid phase reactants.

   These are contained in the incoming liquid and react with components transferring from the vapor phase.

Each one of these groups must be considered when the differential mass balance equations for the liquid components phase are developed.

The general form of the steady-state mass balance, which includes the chemical reaction, A+bB→pP, is:

$$[\text{moles}]_{in} - [\text{moles}]_{out} + [\text{moles transferring across the interface}] - [\text{moles reacting}] = 0$$

$$Lx_k\big|_z A_c - Lx_k\big|_{z+\Delta z} A_c + E_k \, (k_x a)_k \, (x_k^i - x_k)\big|_{z+\frac{\Delta z}{2}} A_c \Delta z - r_k\big|_{z+\frac{\Delta z}{2}} A_c \Delta z = 0. \qquad k=1,2,\ldots,N_r \qquad \text{(A-40)}$$

Dividing through by $A_c \Delta z$ and taking limits as $\Delta z \to 0$ yields:

$$\frac{d(Lx_k)}{dz} = E_k \, (k_x a)_k \, (x_k^i - x_k) - r_k. \qquad k=1,2,\ldots,N_r \qquad \text{(A-41)}$$

Equation A-41 would be applied to all group 1 components.

Components which are products of the reaction (group 2), A+bB→pP, would be described by the differential equation:

$$\frac{d(Lx_k)}{dz} = p_{k-N_x} \, r_{k-N_x}. \qquad k=N_x+1,\ldots,N_r+N_x \qquad \text{(A-42)}$$

If the component is transferring but unreactive, $r_k = 0$, (group 3), mass transfer is described by:

$$\frac{d(Lx_k)}{dz} = (k_x a)_k \, (x_k^i - x_k). \qquad k=N_r+1,\ldots,N_x \qquad \text{(A-43)}$$

Components which are in the liquid phase as reactants, (group 4), are described by:

$$\frac{d(Lx_k)}{dz} = -\, b_k \, r_k. \qquad k=N_x+N_r+1,\ldots,N \qquad \text{(A-44)}$$

If only one reactant is present in the liquid phase for all N_r transferring and reacting components, Equation A-44 becomes:

$$\frac{d(Lx_k)}{dz} = -\sum_{j=1}^{N_r} b_j \, r_j. \qquad k=N_x+N_r+1 \qquad \text{(A-45)}$$

The total flow rate is related to the flow rate of the carrier liquid by:

$$L = \frac{L'}{(1-\sum_{j=1}^{N} x_j)}. \qquad \text{(A-46)}$$

For a system of N total components with N_r transferring-reacting and (N_x-N_r) transferring-nonreacting components, the steady-state differential equations describing mass transfer are:

$$\text{Group 1:} \quad \frac{(1-x_k)}{(1-\sum_{j=1}^{N} x_j)^2} \frac{dx_k}{dz} + \sum_{\substack{j=1 \\ j\neq k}}^{N} \frac{x_j}{(1-\sum_{j=1}^{N} x_j)^2} \frac{dx_j}{dz} =$$

$$\frac{E_k (k_y a)_k}{L'} (x_k^i - x_k) - \frac{r_k}{L'} \qquad k=1,2,\ldots,N_r \qquad \text{(A-47a)}$$

Group 2: $$\frac{(1-x_k)}{(1-\sum\limits_{j=1}^{N} x_j)^2} \frac{dx_k}{dz} + \sum_{\substack{j=1 \\ j\neq k}}^{N} \frac{x_j}{(1-\sum\limits_{j=1}^{N} x_j)^2} \frac{dx_j}{dz} =$$

$$\frac{p_{k-N_x} r_{k-N_x}}{L'} \qquad k=N_x+1,\ldots,N_r+N_x \qquad \text{(A-47b)}$$

Group 3: $$\frac{(1-x_k)}{(1-\sum\limits_{j=1}^{N} x_j)^2} \frac{dx_k}{dz} + \sum_{\substack{j=1 \\ j\neq k}}^{N} \frac{x_j}{(1-\sum\limits_{j=1}^{N} x_j)^2} \frac{dx_j}{dz} =$$

$$\frac{(k_x a)_k}{L'} (x_k^i - x_k) \qquad k=N_r+1,\ldots,N_x \qquad \text{(A-47c)}$$

Group 4: $$\frac{(1-x_k)}{(1-\sum\limits_{j=1}^{N} x_j)^2} \frac{dx_k}{dz} + \sum_{\substack{j=1 \\ j\neq k}}^{N} \frac{x_j}{(1-\sum\limits_{j=1}^{N} x_j)^2} \frac{dx_j}{dz} =$$

$$- \frac{b_k r_k}{L'}. \qquad k=N_x+N_r+1,\ldots,N \qquad \text{(A-47d)}$$

Equation A-47 forms a matrix and is solved as before for dx_1/dz, $dx_2/dz, \ldots,$ dx_N/dz to give:

$$\frac{dx_k}{dz} = (1-x_k) \; (1-\sum_{j=1}^{N} x_j) \; R_k - \sum_{\substack{j=1 \\ j\neq k}}^{N} x_k \; (1-\sum_{j=1}^{N} x_j) \; R_j \qquad \text{(A-48)}$$

where

$$R_m = \frac{E_m (k_x a)_m}{L'} (x_m^i - x_m) - \frac{r_m}{L'} \qquad m=1,2,\ldots,N_r$$

$$R_m = \frac{p_{m-N_x} r_{m-N_x}}{L'} \qquad m=N_x+1,\ldots,N_r+N_x$$

$$R_m = \frac{(k_x a)_m}{L'} (x_m^i - x_m) \qquad m=N_r+1,\ldots,N_x$$

$$R_m = -\frac{b_m r_m}{L'} \qquad m=N_x+N_r+1,\ldots,N$$

Equations A-37a and A-48 produce 2N simultaneous differential equations which must be solved numerically for the vapor and liquid compositions as a function of column height.

For an instantaneous and irreversible reaction, in which the reactants from the vapor phase are completely consumed by the reaction in the liquid film, Equations A-41, A-42, A-43, and A-45 respectively become:

$$\frac{d(Lx_k)}{dz} = 0 \qquad k=1,2,\ldots,N_r \qquad \text{(A-49a)}$$

$$\frac{d(Lx_k)}{dz} = p_{k-N_r}\ E_{k-N_r}\ (k_x a)_{k-N_r}\ x^i_{k-N_r} \qquad k=N_x+1,\ldots,N_r+N_x \qquad \text{(A-49b)}$$

$$\frac{d(Lx_k)}{dz} = (k_x a)_k\ (x^i_k - x_k) \qquad k=N_r+1,\ldots,N_x \qquad \text{(A-49c)}$$

$$\frac{d(Lx_k)}{dz} = -\sum_{j=1}^{N_r} b_j\ E_j\ (k_x a)_j\ x^i_j \qquad k=N_x+N_r+1,\ldots,N \qquad \text{(A-49d)}$$

ENERGY TRANSFER

There are many industrial problems for which a differential mass balance is sufficient to completely describe the physical phenomenon of a continuous contactor. However, there are some problems, particularly those with large heats of vaporization or solution, and those with large heats of reaction which require an energy balance to completely describe the behavior in the absorber-reactor.

The differential energy balance equations are developed in a manner similar to that for the mass balance equations. There are N total components with N_r transferring-reacting and (N_x-N_r) transferring-nonreactive components. The adiabatic steady-state equations for the vapor phase, assuming a noncondensing carrier gas, are:

[energy by mass flow]$_{in}$ - [energy by mass flow]$_{out}$ +

[energy transferred across interface by conduction] +

[energy transferred across interface by mass transfer] = 0

[energy by mass flow of carrier gas]$_{in}$ =

$$-V' \; (H_V)_{N+1}\big|_z \; A_c \tag{A-50a}$$

[energy by mass flow of carrier gas]$_{out}$ =

$$-V' \; (H_V)_{N+1}\big|_{z+\Delta z} \; A_c \tag{A-50b}$$

[energy by mass flow of components]$_{in}$ =

$$\sum_{j=1}^{N} - V' \; (H_V)_j\big|_z \; A_c \tag{A-50c}$$

[energy by mass flow of components]$_{out}$ =

$$\sum_{j=1}^{N} - V' \; (H_V)_j\big|_{z+\Delta z} \; A_c \tag{A-50d}$$

[energy across interface by conduction] =

$$h_V a \; (t_V-t^i)\big|_{z+\frac{\Delta z}{2}} \; A_c \Delta z \tag{A-50e}$$

[energy across interface by mass transfer] =

$$\sum_{j=1}^{N} \frac{V'}{(1-\sum\limits_{j=1}^{N} y_j)} \frac{dy_j}{dz} (Cp_V)_j \; (t_V-t_R)\Big|_{z+\frac{\Delta z}{2}} . \qquad \text{(A-50f)}$$

Combining the above yields:

$$-V' \, (H_V)_{N+1}\Big|_z A_c - \sum_{j=1}^{N} V' \frac{y_j}{(1-\sum\limits_{j=1}^{N} y_j)} (H_V)_j\Big|_z A_c -$$

$$[V' \, (H_V)_{N+1}\Big|_{z+\Delta z} A_c - \sum_{j=1}^{N} V' \frac{y_j}{(1-\sum\limits_{j=1}^{N} y_j)} (H_V)_j\Big|_{z+\Delta z} A_c] -$$

$$[h_V a \, (t_V-t^i) \, A_c \Delta z\Big|_{z+\frac{\Delta z}{2}} + \sum_{j=1}^{N} \frac{V'}{(1-\sum\limits_{j=1}^{N} y_j)} \frac{dy_j}{dz} (Cp_V)_j$$

$$(t_V-t_R)\Big|_{z+\frac{\Delta z}{2}} A_c \Delta z] = 0. \qquad \text{(A-51)}$$

Dividing through by $A_c \Delta z$ and taking limits as $\Delta z \rightarrow 0$ gives:

$$V' \frac{d(H_V)_{N+1}}{dz} + \sum_{j=1}^{N} V' \frac{d[\{\frac{y_j}{(1-\sum\limits_{j=1}^{N} y_j)}\}(H_V)_j]}{dz} = h_V a \, (t_V-t^i) +$$

$$\sum_{j=1}^{N} \frac{V'}{(1-\sum\limits_{j=1}^{N} y_j)} \frac{dy_j}{dz} (Cp_V)_j \; (t_V-t_R). \qquad \text{(A-52)}$$

Assuming the reference state for all components, except the carrier gas, is the liquid state, then:

$$\frac{d(H_V)_{N+1}}{dz} = \frac{d[(Cp_V)_{N+1}(t_V - t_R)]}{dz} = (Cp_V)_{N+1}\,\frac{dt_V}{dz} + t_V\,\frac{d(Cp_V)_{N+1}}{dz} \qquad \text{(A-53a)}$$

and

$$\frac{d\left[(H_V)_j\left\{\dfrac{y_j}{(1-\sum\limits_{j=1}^{N} y_j)}\right\}\right]}{dz} = \frac{d(H_V)_j}{dz}\,\frac{y_j}{(1-\sum\limits_{j=1}^{N} y_j)} + (H_V)_j\,\frac{d\left[\dfrac{y_j}{(1-\sum\limits_{j=1}^{N} y_j)}\right]}{dz}. \qquad \text{(A-53b)}$$

But

$$(H_V)_j = (Cp_L)_j\,(t^i - t_R) + (Q_v)_j + (Cp_V)_j\,(t_V - t^i). \qquad \text{(A-53c)}$$

Then

$$\frac{d(H_V)_j}{dz} = \frac{d(Cp_L)_j}{dz}\,(t^i - t_R) + (t_V - t^i)\,\frac{d(Cp_V)_j}{dz} + (Cp_V)_j\,\frac{dt_V}{dz} \qquad \text{(A-53d)}$$

$$d\left[\frac{y_j}{(1-\sum\limits_{j=1}^{N} y_j)}\right] = \frac{(1-\sum\limits_{j=1}^{N} y_j) + y_j}{(1-\sum\limits_{j=1}^{N} y_j)^2}\,\frac{dy_j}{dz} + \sum_{\substack{k=1\\k\neq j}}^{N} \frac{y_j}{(1-\sum\limits_{j=1}^{N} y_j)}\,\frac{dy_k}{dz}. \qquad \text{(A-53e)}$$

Combining Equations A-52 and A-53 and rearranging produces:

$$
\begin{aligned}
\frac{dt_V}{dz} = {} & [h_V a\ (t_V - t^i) + \sum_{j=1}^{N} \frac{V'}{(1-\sum_{j=1}^{N} y_j)} \frac{dy_j}{dz} \{(Cp_L)_j\ (t^i - t_R) + \\
& (Q_V)_j + (Cp_V)_j\ (t_V - t^i)\} - V'\ (t_V - t_R) \frac{d(Cp_V)_{N+1}}{dz} - \sum_{j=1}^{N} \\
& V'\ (t^i - t_R) \frac{y_j}{(1-\sum_{j=1}^{N} y_j)} \frac{d(Cp_L)_j}{dz} - \sum_{j=1}^{N} V'\ (t_V - t^i) \frac{y_j}{(1-\sum_{j=1}^{N} y_j)} \\
& \frac{d(Cp_V)_j}{dz} - \sum_{j=1}^{N} V'\ \{(Cp_L)_j\ (t^i - t_L) + (Q_V)_j + (Cp_V)_j \\
& (t_V - t^i)\}\{\frac{(1-\sum_{j=1}^{N} y_j) - y_j}{(1-\sum_{j=1}^{N} y_j)^2} \frac{dy_j}{dz} + \sum_{\substack{k=1 \\ k\neq j}}^{N} \frac{y_j}{(1-\sum_{j=1}^{N} y_j)^2} \frac{dy_k}{dz}\}] / [V' \\
& (Cp_V)_{N+1} + V' \sum_{j=1}^{N} (Cp_V)_j \frac{y_j}{(1-\sum_{j=1}^{N} y_j)}]. \qquad \text{(A-54)}
\end{aligned}
$$

The liquid phase equations are obtained in a similar manner to that of the vapor equations. The steady-state energy balance is:

$$
\begin{gathered}
[\text{energy by mass flow}]_{in} - [\text{energy by mass flow}]_{out} + \\
[\text{energy transferred across interface by conduction}] + \\
[\text{energy transferred across interface by mass transfer}] - \\
[\text{energy generated by chemical reaction}] = 0
\end{gathered}
$$

[energy by mass flow of carrier liquid]$_{in}$ =

$$L' \, (H_L)_{N+1}\big|_z \, A_c \tag{A-55a}$$

[energy by mass flow of carrier liquid]$_{out}$ =

$$L' \, (H_L)_{N+1}\big|_{z+\Delta z} \, A_c \tag{A-55b}$$

[energy by mass flow of components]$_{in}$ =

$$\sum_{j=1}^{N} L' \frac{x_j}{(1-\sum_{j=1}^{N} x_j)} (H_L)_j\big|_z \, A_c \tag{A-55c}$$

[energy by mass flow of components]$_{out}$ =

$$\sum_{j=1}^{N} L' \frac{x_j}{(1-\sum_{j=1}^{N} x_j)} (H_L)_j\big|_{z+\Delta z} \, A_c \tag{A-55d}$$

[energy transferred across interface by conduction] =

$$h_L a \, (t^i - t_L)\big|_{z+\frac{\Delta z}{2}} \, A_c \Delta z \tag{A-55e}$$

[energy transferred across interface by mass transfer] =

$$\sum_{j=1}^{N} \frac{L'}{(1-\sum_{j=1}^{N} x_j)} \frac{dx_j}{dz} (H_L)_j\big|_{z+\frac{\Delta z}{2}} \, A_c \Delta z \tag{A-55f}$$

[energy generated by chemical reaction] =

$$\sum_{j=1}^{N_r} \frac{L'}{(1-\sum_{j=1}^{N} x_j)} \frac{dx_j}{dz} (\Delta H_{rx})_j^{77°F} \tag{A-55g}$$

[compensation for temperature difference between the phase and the standard heat of reaction] =

$$\sum_{j=1}^{N_r} \frac{L'}{(1-\sum_{j=1}^{N} x_j)} \left[[\frac{dx_{j+N_x}}{dz} \, p_j \, (Cp_L)_{j+N_x} - \frac{dx_j}{dz} \, (Cp_L)_j] \; [t^i - 77°F] \Big|_{z+\frac{\Delta z}{2}} \right]. \qquad \text{(A-55h)}$$

Combining the above produces:

$$L' \, (H_L)_{N+1}\Big|_z \, A_c + \sum_{j=1}^{N} L' \, \frac{x_j}{(1-\sum_{j=1}^{N} x_j)} \, (H_L)_j \Big|_z \, A_c -$$

$$L' \, (H_L)_{N+1}\Big|_{z+\Delta z} \, A_c - \sum_{j=1}^{N} L' \, \frac{x_j}{(1-\sum_{j=1}^{N} x_j)} \, (H_L)_j \Big|_{z+\frac{\Delta z}{2}} \, A_c +$$

$$h_L a \, (t^i - t_L)\Big|_{z+\frac{\Delta z}{2}} \, A_c \Delta z + \sum_{j=1}^{N} \frac{L'}{(1-\sum_{j=1}^{N} x_j)} \, \frac{dx_j}{dz} \, (H_L)_j \Big|_{z+\frac{\Delta z}{2}} \, A_c \Delta z +$$

$$\sum_{j=1}^{N_r} \frac{L'}{(1-\sum_{j=1}^{N} x_j)} \, \frac{dx_j}{dz} \, (\Delta H_{rx})_j + \sum_{j=1}^{N_r} \frac{L'}{(1-\sum_{j=1}^{N} x_j)} \, \frac{dx_j}{dz} \, [p_j \, (Cp_L)_j -$$

$$(Cp_V)_j] \; (t^i - 77)\Big|_{z+\frac{\Delta z}{2}} = 0. \qquad \text{(A-56)}$$

Dividing through by $A_c \Delta z$ and taking limits as $\Delta z \to 0$ and rearranging gives:

$$\begin{gathered}
L' \frac{d(H_L)_{N+1}}{dz} + \sum_{j=1}^{N} L' \frac{d\left[(H_L)_j \left\{\frac{x_j}{(1-\sum_{j=1}^{N} x_j)}\right\}\right]}{dz} = h_L a \; (t^i - t_L) \; + \\
\sum_{j=1}^{N} \frac{L'}{(1-\sum_{j=1}^{N} x_j)} \frac{dx_j}{dz} (H_L)_j + \sum_{j=1}^{N_r} \frac{L'}{(1-\sum_{j=1}^{N} x_j)} \frac{dx_j}{dz} (\Delta H_{rx})_j \; + \\
\sum_{j=1}^{N_r} \frac{L'}{(1-\sum_{j=1}^{N} x_j)} \left[\frac{dx_{j+N_x}}{dz} p_j \; (Cp_L)_{j+N_x} - \frac{dx_j}{dz} (Cp_V)_j\right] \\
(t^i - 77) \qquad \text{(A-57)}
\end{gathered}$$

Assuming the reference state for all components is the liquid state, then:

$$(H_L)_j = (Cp_L)_j \; (t_L - t_R) \qquad \text{(A-58)}$$

and

$$\frac{d(H_L)_j}{dz} = \frac{d(Cp_L)_j}{dz} (t_L - t_R) + (Cp_L)_j \frac{dt_L}{dz} \qquad \text{(A-59)}$$

$$\frac{d\left[\frac{x_j}{(1-\sum_{j=1}^{N} x_j)}\right]}{dz} = \frac{(1-\sum_{j=1}^{N} x_j) - x_j}{(1-\sum_{j=1}^{N} x_j)^2} \frac{dx_j}{dz} + \sum_{\substack{k=1 \\ k \neq j}}^{N} \frac{x_j}{(1-\sum_{j=1}^{N} x_j)^2} \frac{dx_k}{dz} \; . \qquad \text{(A-60)}$$

Combining Equations A-57 - A-60 and rearranging yields:

$$\frac{dt_L}{dz} = [h_L a \; (t^i - t_L) + \sum_{j=1}^{N} \frac{L'}{(1-\sum_{j=1}^{N} x_j)} \frac{dx_j}{dz} \{(Cp_L)_j \; (t^i - t_R) +$$

$$(Q_V)_j + (Q_s)_j + (Cp_V)_j \; (t_V - t^i)\} + \sum_{j=1}^{N_r} \frac{L'}{(1-\sum_{j=1}^{N} x_j)} \frac{dx_j}{dz}$$

$$(\Delta H_{rx})_j + \sum_{j=1}^{N_r} \frac{L'}{(1-\sum_{j=1}^{N} x_j)} \{\frac{dx_{j+N_x}}{dz} \; p_j \; (Cp_L)_{j+N_x} - \frac{dx_j}{dz}$$

$$(Cp_V)_j\} \; (t^i - 77) - \sum_{j=1}^{N} L' \; (t_L - t_R) \frac{x_j}{(1-\sum_{j=1}^{N} x_j)} \frac{d(Cp_L)_j}{dz} -$$

$$L' \; (t_L - t_R) \frac{d(Cp_L)_{N+1}}{dz} - \sum_{j=1}^{N} L' \; (Cp_L)_j \; (t^i - t_R)$$

$$\{\frac{(1-\sum_{j=1}^{N} x_j) + x_j}{(1-\sum_{j=1}^{N} x_j)^2} \frac{dx_j}{dz} + \sum_{\substack{k=1 \\ k \neq j}}^{N} \frac{x_j}{(1-\sum_{j=1}^{N} x_j)^2} \frac{dx_k}{dz}\}] \; / \; [L' \; (Cp_L)_{N+1} +$$

$$\sum_{j=1}^{N} L' \frac{x_j}{(1-\sum_{j=1}^{N} x_j)} (Cp_L)_j]. \qquad \text{(A-61)}$$

Equations A-36, A-49, A-54, and A-61 can be solved simultaneously by a numerical methods technique (such as Runge-Kutta, Euler's Method, or Predictor-Corrector) for the compositions and temperatures of the vapor and liquid phases as a function of tower height.

If the flow rates are assumed to be constant throughout the entire length of the tower and if the heats of reaction, solution, and vaporization are negligibly small, Equations A-54 and A-61 reduce to:

$$\frac{dt_V}{dz} = \frac{h_V a(t_V - t^i)}{(Cp_V)_{N+1} V'} \qquad \text{(A-62a)}$$

and

$$\frac{dt_L}{dz} = \frac{h_L a(t^i - t_L)}{(Cp_L)_{N+1} L'} \ . \qquad \text{(A-62b)}$$

These are the equations which normally appear in texts on the subject[3,24].

APPENDIX B

ADAPTATION OF THE EQUATIONS FOR THE MODEL TO THE COMPUTER

Now that the equations for mass and heat transfer in a continuous contactor have been developed, it is important to detail how these equations will be solved. Particular attention is given to the method needed to solve 2N+2 simultaneous differential equations and the method required to solve for the interfacial compositions and temperature.

The differential equations developed in the previous section, 3a, 10, 23a, and 23b, can be represented in the form:

$$\frac{dx_k}{dz} = e_k\ (\underline{x},\ \underline{y},\ t_L,\ t_V,\ \underline{x}^i,\ \underline{y}^i,\ t^i) \qquad k=1,2,\ldots,N \qquad \text{(B-1a)}$$

$$\frac{dy_k}{dz} = f_k\ (\underline{x},\ \underline{y},\ t_L,\ t_V,\ \underline{x}^i,\ \underline{y}^i,\ t^i) \qquad k=1,2,\ldots,N \qquad \text{(B-1b)}$$

$$\frac{dt_L}{dz} = g\ (\underline{x},\ \underline{y},\ t_L,\ t_V,\ \underline{x}^i,\ \underline{y}^i,\ t^i) \qquad \text{(B-1c)}$$

$$\frac{dt_V}{dz} = h\ (\underline{x},\ \underline{y},\ t_L,\ t_V,\ \underline{x}^i,\ \underline{y}^i,\ t^i) \qquad \text{(B-1d)}$$

These equations can be solved with a numerical integration technique, such as the Runge-Kutta, Euler's, or Taylor's methods. For this study, a fourth order Runge-Kutta method was used because it is very stable, gives good accuracy, and has been used by the author in preliminary work with excellent results. The other methods had some disadvantages which made them unacceptable for this work. Euler's method requires a very small step size for reasonable accuracy consuming too much computer time.[7] Taylor's method requires the evaluation of higher order total derivatives.[7]

The Runge-Kutta method circumvents these problems by evaluating the functions at selected points along the subinterval. The starting values for the integration at the top of the column (Figure 1) would be $\underline{x}_0=\underline{x}_{in}$, $\underline{y}_0=\underline{y}_{out}$, $(t_L)_0=(t_L)_{in}$, and $(t_V)_0=(t_V)_{out}$. The values at the first increment are calculated from the formulas:

First Runge-Kutta Step:

$$J_{1,k} = e_k\,(\underline{x}_0, \underline{y}_0, (t_L)_0, (t_V)_0, \underline{x}^i, \underline{y}^i, t^i) \qquad k=1,2,\ldots,N \tag{B-2a}$$

$$J_{2,k} = f_k\,(\underline{x}_0, \underline{y}_0, (t_L)_0, (t_V)_0, \underline{x}^i, \underline{y}^i, t^i) \qquad k=1,2,\ldots,N \tag{B-2b}$$

$$L_1 = g\,(\underline{x}_0, \underline{y}_0, (t_L)_0, (t_V)_0, \underline{x}^i, \underline{y}^i, t^i) \tag{B-2c}$$

$$M_1 = h\,(\underline{x}_0, \underline{y}_0, (t_L)_0, (t_V)_0, \underline{x}^i, \underline{y}^i, t^i) \tag{B-2d}$$

Second Runge-Kutta Step:

$$J_{2,k} = e_k\,(\underline{x}_0 + \frac{J_1}{2}, \underline{y}_0 + \frac{K_1}{2}, (t_L)_0 + \frac{L_1}{2}, (t_V)_0 + \frac{M_1}{2}, \underline{x}^i, \underline{y}^i, t^i)\,\Delta z \qquad k=1,2,\ldots,N \tag{B-3a}$$

$$K_{2,k} = f_k\,(\underline{x}_0 + \frac{J_1}{2}, \underline{y}_0 + \frac{K_1}{2}, (t_L)_0 + \frac{L_1}{2}, (t_V)_0 + \frac{M_1}{2}, \underline{x}^i, \underline{y}^i, t^i)\,\Delta z \qquad k=1,2,\ldots,N \tag{B-3b}$$

$$\begin{aligned} L_2 = g\ (&\underline{x}_0 + \frac{\underline{J}_1}{2},\ \underline{y}_0 + \frac{\underline{K}_1}{2},\ (t_L)_0 + \frac{L_1}{2},\ (t_V)_0 + \frac{M_1}{2}, \\ &\underline{x}^i,\ \underline{y}^i,\ t^i)\ \Delta z \end{aligned} \qquad \text{(B-3c)}$$

$$\begin{aligned} M_2 = h\ (&\underline{x}_0 + \frac{\underline{J}_1}{2},\ \underline{y}_0 + \frac{\underline{K}_1}{2},\ (t_L)_0 + \frac{L_1}{2},\ (t_V)_0 + \frac{M_1}{2}, \\ &\underline{x}^i,\ \underline{y}^i,\ t^i)\ \Delta z \end{aligned} \qquad \text{(B-3d)}$$

Third Runge-Kutta Step:

$$\begin{aligned} J_{3,k} = e_k\ (&\underline{x}_0 + \frac{\underline{J}_2}{2},\ \underline{y}_0 + \frac{\underline{K}_2}{2},\ (t_L)_0 + \frac{L_2}{2},\ (t_V)_0 + \frac{M_2}{2}, \\ &\underline{x}^i,\ \underline{y}^i,\ t^i)\ \Delta z \qquad k=1,2,\ldots,N \end{aligned} \qquad \text{(B-4a)}$$

$$\begin{aligned} K_{3,k} = f_k\ (&\underline{x}_0 + \frac{\underline{J}_2}{2},\ \underline{y}_0 + \frac{\underline{K}_2}{2},\ (t_L)_0 + \frac{L_2}{2},\ (t_V)_0 + \frac{M_2}{2}, \\ &\underline{x}^i,\ \underline{y}^i,\ t^i)\ \Delta z \qquad k=1,2,\ldots,N \end{aligned} \qquad \text{(B-4b)}$$

$$\begin{aligned} L_3 = g\ (&\underline{x}_0 + \frac{\underline{J}_2}{2},\ \underline{y}_0 + \frac{\underline{K}_2}{2},\ (t_L)_0 + \frac{L_2}{2},\ (t_V)_0 + \frac{M_2}{2}, \\ &\underline{x}^i,\ \underline{y}^i,\ t^i)\ \Delta z \end{aligned} \qquad \text{(B-4c)}$$

$$\begin{aligned} M_3 = h\ (&\underline{x}_0 + \frac{\underline{J}_2}{2},\ \underline{y}_0 + \frac{\underline{K}_2}{2},\ (t_L)_0 + \frac{L_2}{2},\ (t_V)_0 + \frac{M_2}{2}, \\ &\underline{x}^i,\ \underline{y}^i,\ t^i)\ \Delta z \end{aligned} \qquad \text{(B-4d)}$$

Fourth Runge-Kutta Step:

$$\begin{aligned} J_{4,k} = e_k\ (&\underline{x}_0 + \underline{J}_3,\ \underline{y}_0 + \underline{K}_3,\ (t_L)_0 + L_3,\ (t_V)_0 + M_3, \\ &\underline{x}^i,\ \underline{y}^i,\ t^i)\ \Delta z \qquad k=1,2,\ldots,N \end{aligned} \qquad \text{(B-5a)}$$

$$\begin{aligned} K_{4,k} = f_k\ (&\underline{x}_0 + \underline{J}_3,\ \underline{y}_0 + \underline{K}_3,\ (t_L)_0 + L_3,\ (t_V)_0 + M_3, \\ &\underline{x}^i,\ \underline{y}^i,\ t^i)\ \Delta z \qquad k=1,2,\ldots,N \end{aligned} \qquad \text{(B-5b)}$$

$$\begin{aligned} L_4 = g\ (&\underline{x}_0 + \underline{J}_3,\ \underline{y}_0 + \underline{K}_3,\ (t_L)_0 + L_3,\ (t_V)_0 + M_3, \\ &\underline{x}^i,\ \underline{y}^i,\ t^i)\ \Delta z \end{aligned} \qquad \text{(B-5c)}$$

$$M_4 = h\,(\underline{x}_0 + \underline{J}_3,\ \underline{y}_0 + \underline{K}_3,\ (t_L)_0 + L_3,\ (t_V)_0 + M_3,\ \underline{x}^i,\ \underline{y}^i,\ t^i)\ \Delta z \qquad \text{(B-5d)}$$

The values at the first increment are:

$$(x_k)_1 = (x_k)_0 + (J_{1,k} + 2J_{2,k} + 2J_{3,k} + J_{4,k})/6 \qquad k=1,2,\ldots,N \qquad \text{(B-6a)}$$

$$(y_k)_1 = (x_k)_0 + (K_{1,k} + 2K_{2,k} + 2K_{3,k} + K_{4,k})/6 \qquad k=1,2,\ldots,N \qquad \text{(B-6b)}$$

$$(t_L)_1 = (t_L)_0 + (L_1 + 2L_2 + 2L_3 + L_4)/6 \qquad \text{(B-6c)}$$

$$(t_V)_1 = (t_V)_0 + (M_1 + 2M_2 + 2M_3 + M_4)/6 \qquad \text{(B-6d)}$$

and then the independent variable is calculated by:

$$z_1 = z_0 + \Delta z \qquad \text{(B-7)}$$

To calculate the values at the next increment, replace $\underline{x}_0$, $\underline{y}_0$, $(t_L)_0$, $(t_V)_0$ with $\underline{x}_1$, $\underline{y}_1$, $(t_L)_1$, $(t_V)_1$ and repeat the calculations. The procedure is continued to the bottom of the column where $\underline{y} = \underline{y}_{in}$ and the calculations would be terminated.

Before Equation B-1 can be solved, the interfacial compositions, $\underline{x}^i$, and temperature, t^i, must be obtained at each axial position in the contactor at which the differential numerical procedure is applied. For example, Equation A-16 describes mass transfer in a continuous contactor for one transferring component. The overall material balance is:

$$V \frac{dy}{dz} - L \frac{dx}{dz} = 0. \tag{B-8}$$

The substitution of Equation A-16 into Equation B-8 yields:

$$k_y a \; (y-y^i) - k_x a \; (x^i-x) = 0. \tag{B-9}$$

If the equilibrium data are of the form

$$y^i = mx^i, \tag{B-10}$$

then Equation B-8 can be easily solved for x^i (or y^i):

$$x^i = \frac{k_x a \; x_1 + k_y a \; y}{k_x a + k_y a \; m} . \tag{B-11}$$

However, if the equilibrium data are nonlinear, for example of the form

$$y^i = a + bx^i + c(x^i)^2 + \ldots, \tag{B-12}$$

then Equation B-9 must be solved with B-12 for x^i using Newton's method:

$$x^i_{k+1} = x^i_k - \frac{ff(x^i_k)}{\dfrac{d[ff(x^i_k)]}{dx^i_k}} \tag{B-13}$$

where $ff(x^i) = k_y a \; (y-y^i) - k_x a \; (x^i-x)$. For a one component system with chemical reaction, Equation B-9 is:

$$k_y a \; (y-y^i) - [E \; (k_x a) \; (x^i-x) - r] = 0. \tag{B-14}$$

If more than one chemical reaction occurs, then the insertion of Equations A-37a and A-48 into Equation B-9 gives:

$$(1-y_k)\ (k_y a)_k\ (y_k-y_k^i) - \sum_{\substack{j=1\\j\neq k}}^{N} y_k\ (k_y a)_j\ (y_j-y_j^i) -$$

$$[(1-x_k)\ R_k - \sum_{\substack{j=1\\j\neq k}}^{N} x_k\ R_j]. \qquad k=1,2,\ldots,N_r \qquad \text{(B-15)}$$

To use Newton's method, it is necessary to evaluate the enhancement factor, E, at every iteration, because E_i, which is used to calculate E, is a function of interfacial compositions. Newton's method is used until $ff(\underline{x}^i)$ is very nearly zero.

To determine the interfacial temperature, t^i, the overall energy balance is needed:

$$V\ \frac{H_V}{dz} - L\ \frac{dH_L}{dz} = 0 \qquad \text{(B-16)}$$

Insertion of Equations A-54 and A-61 into Equation B-16 for a one transferring component system with no chemical reaction gives:

$$h_V a\ (t_V-t^i) + \frac{V'}{(1-\sum_{j=1}^{N} y_j)}\ \frac{dy_1}{dz}\ (H_V)_1 - [h_L a\ (t^i-t_L) +$$

$$\frac{L'}{(1-\sum_{j=1}^{N} x_j)}\ \frac{dx_1}{dz}\ (H_L)_1] = 0. \qquad \text{(B-17)}$$

Equations B-9 and B-17 must be solved simultaneously for interfacial compositions and the interfacial temperature using Newton's method for systems. The general equations are:

$$\sum_{k=1}^{N} \Delta\varepsilon_k \frac{\partial ff_i}{\partial \varepsilon_k} = -ff_i \qquad i=1,2,\ldots,N \qquad \text{(B-18)}$$

in which ε represents the independent variable, $\underline{x}^i$ or t^i.

For the problem under consideration, Newton's would be:

$$\begin{array}{l}
\Delta x_1^i \frac{\partial F_1}{\partial x_1^i} + \Delta x_2^i \frac{\partial F_1}{\partial x_2^i} + \ldots + \Delta x_{N_x} \frac{\partial F_1}{\partial x_{N_x}^i} + \Delta t^i \frac{\partial F_1}{\partial t^i} = -F_1 \\
\Delta x_1^i \frac{\partial F_2}{\partial x_1^i} + \Delta x_2^i \frac{\partial F_2}{\partial x_2^i} + \ldots + \Delta x_{N_x} \frac{\partial F_2}{\partial x_{N_x}^i} + \Delta t^i \frac{\partial F_2}{\partial t^i} = -F_2 \\
\quad \vdots \qquad\qquad \vdots \qquad\quad \vdots \qquad\quad \vdots \qquad\qquad \vdots \qquad\quad \vdots \qquad \text{(B-19)} \\
\Delta x_1^i \frac{\partial F_N}{\partial x_1^i} + \Delta x_2^i \frac{\partial F_N}{\partial x_2^i} + \ldots + \Delta x_{N_x} \frac{\partial F_N}{\partial x_{N_x}^i} + \Delta t^i \frac{\partial F_N}{\partial t^i} = -F_N \\
\Delta x_1^i \frac{\partial M}{\partial x_1^i} + \Delta x_2^i \frac{\partial M}{\partial x_2^i} + \ldots + \Delta x_{N_x} \frac{\partial M}{\partial x_{N_x}^i} + \Delta t^i \frac{\partial M}{\partial t^i} = -M
\end{array}$$

where:

$$F_k = f_k - e_k$$

$$M = h - g$$

$$\Delta x_k^i = (x_k^i)_{n+1} - (x_k^i)_n$$

$$\Delta t^i = (t^i)_{n+1} - (t^i)_n.$$

The starting values for Newton's method to determine $\underline{x}^i$ and t^i are calculated by multiplying $\underline{x}$ and t_L by 1.1.

The recursive formulas are used until the Δx^i's and Δt^i are less than some preset value (i.e., 10^{-6}). These interfacial values are used in the Runge-Kutta equations to determine the compositions and temperatures at the next increment. For the multicomponent system with chemical reaction, Equation B-16 becomes:

$$h_V a \; (t_V - t^i) + \sum_{j=1}^{N} \frac{V'}{(1-\sum\limits_{j=1}^{N} y_j)} \frac{dy_j}{dz} (H_V)_j - \{h_L a \; (t^i - t_L) +$$

$$\sum_{j=1}^{N} \frac{L'}{(1-\sum\limits_{j=1}^{N} x_j)} \frac{dx_j}{dz} (H_L)_j + \sum_{j=1}^{N_r} \frac{L'}{(1-\sum\limits_{j=1}^{N} x_j)} \frac{dx_j}{dz} \Delta (H_{rx})_j +$$

$$\sum_{j=1}^{N_r} \frac{L'}{(1-\sum\limits_{j=1}^{N} x_j)} [\frac{dx_{j+N_x}}{dz} pj \; (Cp_L)_{j+N_x} - \frac{dx_j}{dz} (Cp_V)_j]\}$$

$$(t^i - 77) = 0 \qquad \text{(B-20)}$$

which must be solved with the multicomponent B-20 interfacial composition equation by Newton's method for systems for the interfacial compositions and temperatures.

APPENDIX C

RESULTS AND DISCUSSION

In order to demonstrate the accuracy and versatility of the model, a broad range of contactor problems is presented. These problems include nonisothermal conditions, fast chemical reaction in the liquid phase, and multi-component transfer.

One of the systems selected for study is gaseous ammonia absorption by liquid water, first investigated by Sherwood and Pigford.[24] The water, the liquid carrier, is also vaporizing making this a two component problem. The heats of vaporization of ammonia and water are sufficiently large [$(Q_v)_{\text{ammonia}}$=15380 BTU/lb mole and $(Q_v)_{\text{water}}$=19250 BTU/lb mole] to insure nonisothermal conditions and require energy balance calculations. The data for the computation of the composition and temperature profiles are presented in Table C-12. Sherwood and Pigford[24] made additional assumptions: that there are dilute solutions, that all resistance to mass transfer is in the vapor phase, and that the interfacial temperature is the same as the bulk liquid temperature. The resulting equations are:

Mass Transfer:

$$\text{Ammonia:} \quad -\frac{dy_1}{dN_M} = y_1 - y_1^i \qquad \text{(C-1a)}$$

Water: $$-\frac{dy_2}{dN_M} = \alpha\ (y_2 - y_2^i) \qquad \text{(C-1b)}$$

Heat Transfer:

Vapor: $$-\frac{dt_V}{dN_M} = \beta\ (t_V - t_L) \qquad \text{(C-1c)}$$

Liquid: $$-\frac{dt_L}{dz} = \frac{V}{LCp_L}\ [Cp_V \frac{dt}{dN_M} + (Q_V)_1 \frac{dy_1}{dN_M} + (Q_V)_2 \frac{dy_2}{dN_M}] \qquad \text{(C-1d)}$$

where

N_M - number of transfer units

α - $(k_x a)_2/(k_x a)_1$

β - $[h_V a/(VCp_V)]/[(h_x a)_1/V]$.

Sherwood and Pigford[24] do not state the source of the equilibrium data for ammonia and water. The representation of the equilibrium data used in this work for ammonia is the Stern[8] equation and the equilibrium equation used for water is the result of a least squares curve fit of the water vapor pressure data in Perry[21].

The difficulty with the data given by Sherwood and Pigford[24] is that it is incomplete. Unfortunately, the flow rates are not given per square foot of cross sectional tower area and the type of packing used is not stated. Therefore, the flow rates and mass and heat transfer coefficients are calculated assuming that the tower is operating at 50 percent of the flooding velocity and is packed with one inch Raschig rings.

The procedure for these calculations is outlined in Foust[12]. As in all the examples used in this work, the mass and heat transfer coefficients are assumed constant throughout the column and are usually evaluated at an average of the inlet and outlet conditions.

These data are used to generate the concentration and temperature profiles which appear in Figure C-12 (Cases C and D) with the results given graphically by Sherwood and Pigford[24] (Case A). Two solutions for the above data are obtained using the model developed in this work. First, the composition and temperature profiles are calculated using the data as they appear in Table C-12 [i.e., all resistances to mass and heat transfer are finite (Case D)]. Then, all the resistance to mass and heat transfer is assumed to be in the vapor phase [i.e., liquid mass and transfer coefficients are infinite] and the profiles are recalculated (Case C).

Equation C-1 is also solved numerically with the equilibrium data for ammonia and water used in this work (Figure C-12, Case B) and compared with the results given graphically by Sherwood and Pigford[24] (Figure C-12, Case A). The greatest deviation between the concentration and temperature profiles is ten percent and six percent, respectively, occurring approximately in the center of the column. At most axial positions the disagreement between curves A and B is less than five percent. Since the results are very sensitive to the equilibrium data used, the differences between curves A and B are possibly a result of variation between the equilibrium data used in this investigation and that used by Sherwood and Pigford[24].

As mentioned above, the accuracy of the model is dependent on the accuracy of the data supplied to the model, particularly the exact representation of the equilibrium data. The sensitivity of the computations to the equilibrium data can be illustrated by using data from Othmer and Scheibel[20] and later used by Sherwood and Pigford[24] in the following nonisothermal absorption. Absorption of acetone and water vapor by liquid water is studied in a sixteen foot column packed with one inch Raschig rings. The heat of vaporization of both acetone and water is sufficiently large [$(Q_v)_{acetone}$=18000 BTU/ lb mole and $(Q_v)_{water}$=19323 BTU/lb mole] to require energy balance calculations.

Sherwood and Pigford[24] also make the additional assumptions outlined previously (i.e., dilute solutions and no resistance to mass and heat transfer in the liquid phase). In this work, mass and heat transfer coefficients are calculated for both the vapor and liquid phases by a procedure outlined by Treybal[28]. The data used in the computation of the profiles are presented in Table C-11.

Equilibrium data were not available in any of the literature surveyed for this study. An attempt was made to develop an equation to represent the equilibrium data from the heat of vaporization and activity coefficients as suggested by Sherwood and Pigford[24]. Since this method is, at best, an estimation, accurate results could not be expected. The model is not capable of reproducing the profiles estimated by Sherwood and Pigford (Figure C-11), probably due to the inaccuracy of the equilibrium data. This problem demonstrates the necessity of having an accurate representation of the equilibrium data if a model is used.

If the equilibrium data are accurately represented, the model is capable of predicting column heights and output compositions for absorber-reactors. A total of nine systems involving mass transfer with chemical reaction is used to test the mass and heat balance equations and their solutions. A summary of these systems is presented in Table C-13. In addition, a comparison of the column heights reported by the various investigators and the column heights predicted by the model is presented. The difference between the reported and predicted column height in most of the systems studied is six percent or under; and in over half of the systems studied, the difference is less than three percent.

A typical mass transfer problem with chemical reaction system is that of Tepe and Dodge[25]. In the 7.7 foot absorber-reactor filled with one-half inch Raschig rings, carbon dioxide in the air phase is transferring and reacting instantaneously with sodium hydroxide in the aqueous phase and is the only transferring component. The heats of reaction and vaporization are sufficiently large to require both mass and energy balance calculations. The concentration and temperature profiles calculated in this work are presented in Figure C-9. The data for this system are presented in Table C-9. The difference between the column height used by Tepe and Dodge[25] and that predicted by the model is six percent.

All compositions and temperatures are checked at the opposite end of the column from which the numerical integration procedure is started. The reported and predicted liquid phase compositions and vapor and liquid temperatures [i.e., $\underline{y}_{in}$, $\underline{x}_{out}$, $(t_V)_{in}$, $(t_L)_{out}$] differ by no more than ten percent and two percent, respectively. In most cases, the terminal conditions (i.e., at the opposite end of the column from which the numerical integration procedure was started) reported by the original investigators do not differ from the calculated terminal conditions by more than ten percent.

As a final demonstration of the versatility of the model and the resulting computer program, a problem which would incorporate all the features of the model (energy balance, chemical reaction, and multicomponent transfer) was desired; however, no such problem was available in the open literature. Therefore, a three component test problem was proposed and then simulated. Two of the components (y_1 and y_2) transfer from the vapor to the liquid phase and react instantaneously in the liquid film. The other transferring component (y_3) transfers from the vapor to the liquid phase and does not react. The heats of vaporization and reaction are chosen to necessitate using the energy balance calculations. A summary of the data is presented in Table C-10. The resulting concentration and temperature profiles, which appear to represent the typical behavior of three component nonisothermal absorption with chemical reaction accurately, are shown in Figure C-10.

TABLE C-1

PHYSICAL DATA -- SYSTEM 1

Carrier Liquid: Water

Carrier Gas: Air

Compositions:

$y_{in} = 0.001$ $x_{in} = 0.0$ $\hat{y}_{in} = 0.001$

$y_{out} = 0.0002$ $x_{out} = 0.000114$ $\hat{x}_{out} = 0.000109$

Temperature: Uniform throughout the column

Reaction: None

Flow Rates: $L' = 143.3$ lb moles/hr ft^2

$V' = 20.5$ lb moles/hr ft^2

Mass Transfer Coefficients (assumed constant):

$k_x a = 0.349$ lb moles/hr ft^3 (mole fraction)

$k_y a = 1.996$ lb moles/hr ft^3 (mole fraction)

Equilibrium Data:

$$y^i = 7.0\ x^i$$

Program Predicted Tower Height: 1465 ft

Reference: 16

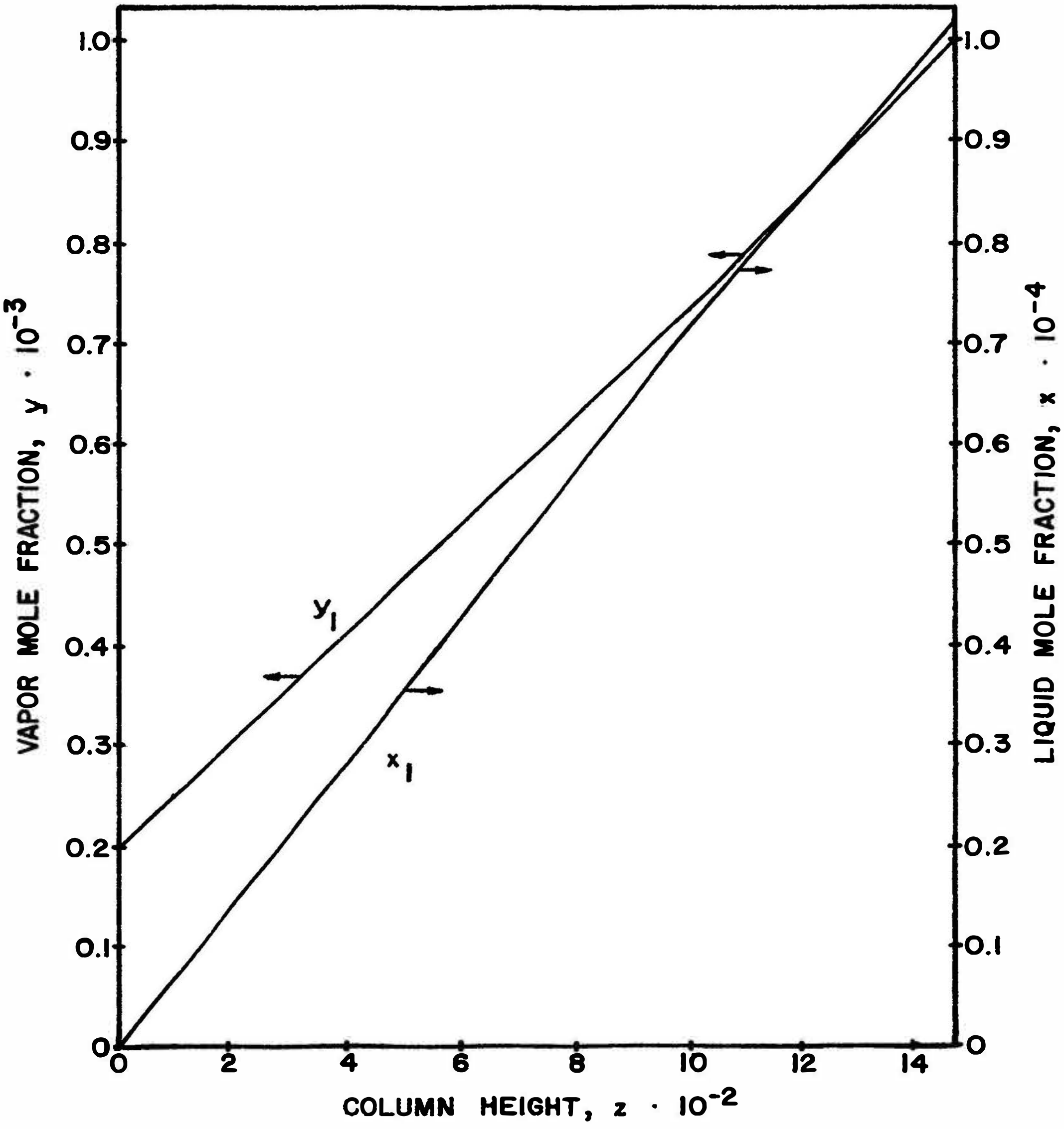

Figure C-1. Calculated Vapor and Liquid Concentration Profiles for System 1[16]

TABLE C-2

PHYSICAL DATA -- SYSTEM 2

Carrier Liquid: Water

Carrier Gas: Air

Column Height: 16.4 ft

Components: 1 = A, 2 = C, 3 = B

Reaction: $A+B \rightarrow C$ (instantaneous reaction)

Compositions:
$(y_{in})_1 = 0.001$ $(y_{out})_1 = 0.0002$
$(y_{in})_2 = 0.0$ $(y_{out})_2 = 0.0$
$(y_{in})_3 = 0.0$ $(y_{out})_3 = 0.0$
$(x_{in})_1 = 0.0$ $(x_{out})_1 = 0.0$
$(x_{in})_2 = 0.0$ $(x_{out})_2 =$ ---
$(x_{in})_3 = 0.0143$ $(x_{out})_3 = 0.0142$
$(\hat{y}_{in})_1 = 0.001003$ $(\hat{x}_{out})_1 = 0.0$
$(\hat{y}_{in})_2 = 0.0$ $(\hat{x}_{out})_2 = 0.000113$
$(\hat{y}_{in})_3 = 0.0$ $(\hat{x}_{out})_3 = 0.0142$

Temperature: Uniform throughout the column

Flow Rates: $L' = 143.3$ lb moles/hr ft^2
$V' = 20.5$ lb moles/hr ft^2

Mass Transfer Coefficients (assumed constant):
$(k_x a)_1 = 0.349$ lb moles/hr ft^3 (mole fraction)
$(k_y a)_1 = 1.996$ lb moles/hr ft^3 (mole fraction)

Equilibrium Data:

$$y_1^i = 7.0\ x_1^i$$

Program Predicted Tower Height: 16.55 ft

Reference: 16

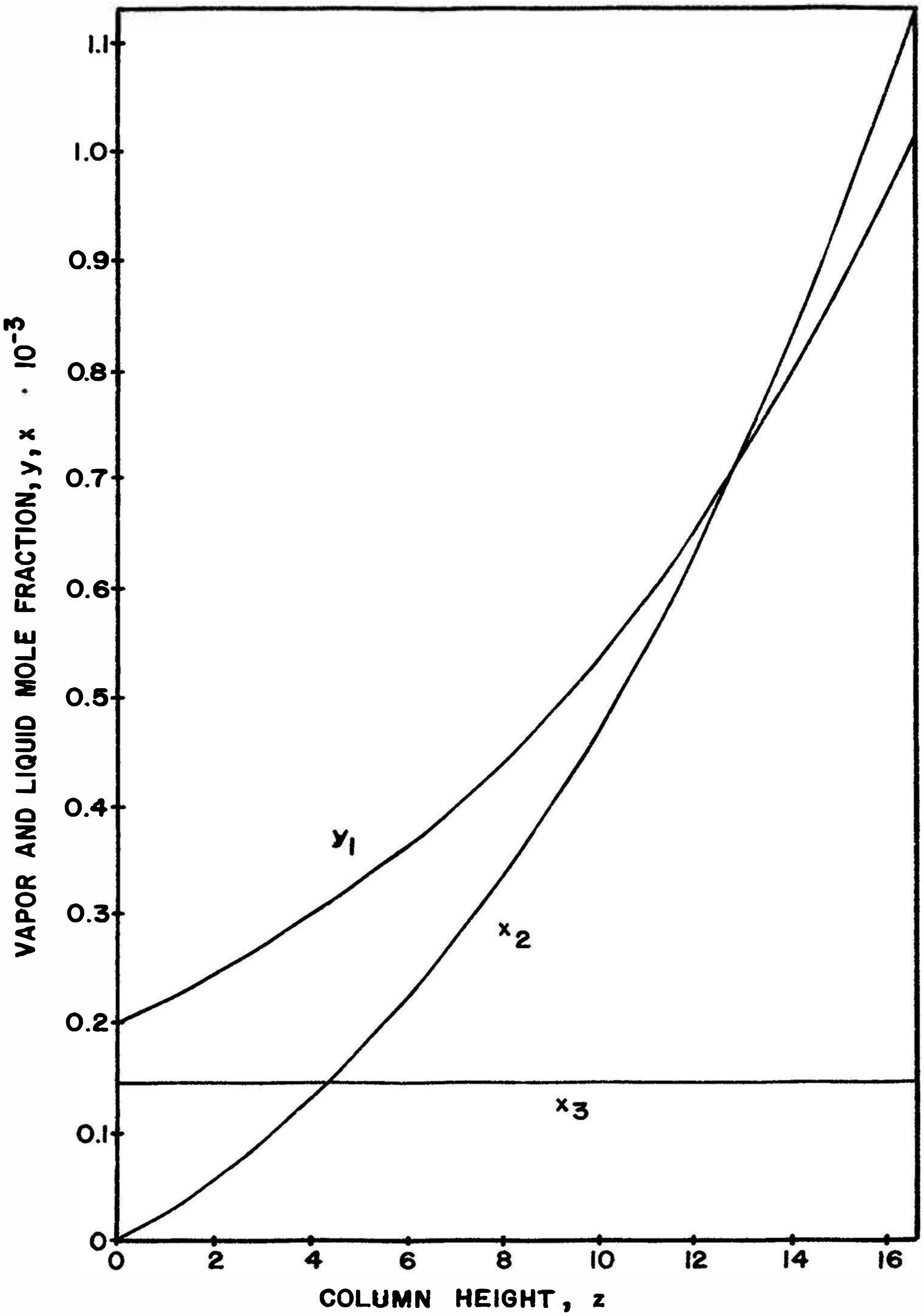

Figure C-2. Calculated Vapor and Liquid Concentration Profiles for System 2 (High Reactant Concentration)[16]

TABLE C-3

PHYSICAL DATA -- SYSTEM 3

Carrier Liquid: Water

Carrier Gas: Air

Column Height: 80 ft

Components: 1 = A, 2 = C, 3 = B

Reaction: $A+B \rightarrow C$ (instantaneous reaction)

Compositions:

$(y_{in})_1$	= 0.001	$(y_{out})_1$	= 0.0002
$(y_{in})_2$	= 0.0	$(y_{out})_2$	= 0.0
$(y_{in})_3$	= 0.0	$(y_{out})_3$	= 0.0
$(x_{in})_1$	= 0.0	$(x_{out})_1$	= 0.0
$(x_{in})_2$	= 0.0	$(x_{out})_2$	= ---
$(x_{in})_3$	= 0.0005714	$(x_{out})_3$	= 0.000457
$(\hat{y}_{in})_1$	= 0.001003	$(\hat{x}_{out})_1$	= 0.0
$(\hat{y}_{in})_2$	= 0.0	$(\hat{x}_{out})_2$	= 0.00012
$(\hat{y}_{in})_3$	= 0.0	$(\hat{x}_{out})_3$	= 0.000456

Temperature: Uniform throughout the column

Flow Rates: $L' = 143.3$ lb moles/hr ft^2

$V' = 20.5$ lb moles/hr ft^2

Mass Transfer Coefficients (assumed constant):

$(k_x a)_1 = 0.349$ lb moles/hr ft^3 (mole fraction)

$(k_y a)_1 = 1.996$ lb moles/hr ft^3 (mole fraction)

Equilibrium Data:

$$y_1^i = 7.0\ x_1^i$$

Program Predicted Tower Height: 81 ft

Reference: 16

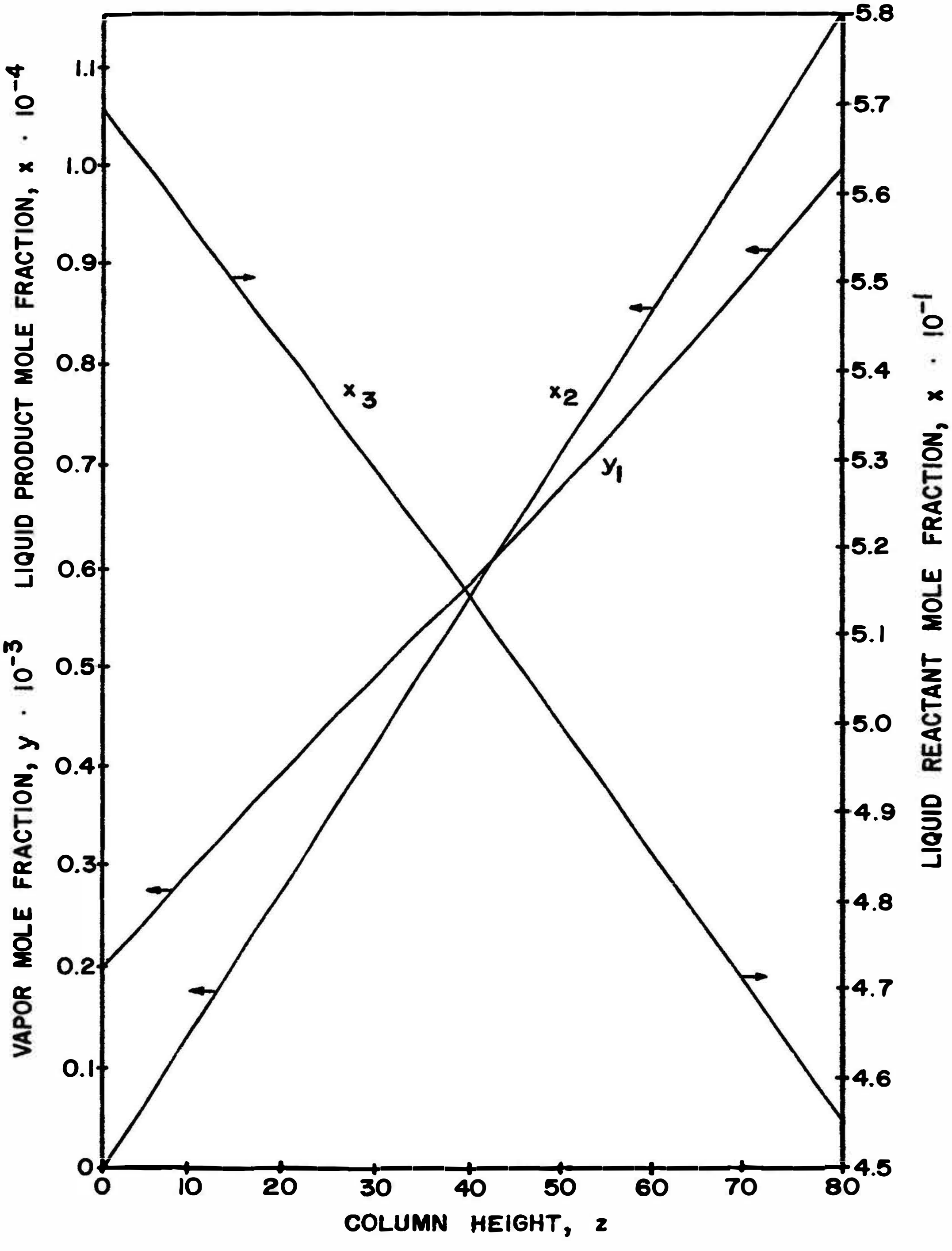

Figure C-3. Calculated Vapor and Liquid Concentration Profiles for System 3 (Low Reactant Concentration)[16]

TABLE C-4

PHYSICAL DATA -- SYSTEM 4

Carrier Liquid: Water

Carrier Gas: Air

Column Height: 23 ft

Components: 1 = A, 2 = C, 3 = B

Reaction: A+B→C (instantaneous reaction)

Compositions:
$(y_{in})_1 = 0.001$ $(y_{out})_1 = 0.0002$
$(y_{in})_2 = 0.0$ $(y_{out})_2 = 0.0$
$(y_{in})_3 = 0.0$ $(y_{out})_3 = 0.0$
$(x_{in})_1 = 0.002135$ $(x_{out})_1 = 0.0$
$(x_{in})_2 = 0.0$ $(x_{out})_2 =$ ---
$(x_{in})_3 = 0.0$ $(x_{out})_3 = 0.00217$
$(\hat{y}_{in})_1 = 0.001001$ $(\hat{x}_{out})_1 = 0.0$
$(\hat{y}_{in})_2 = 0.0$ $(\hat{x}_{out})_2 =$
$(\hat{y}_{in})_3 = 0.0$ $(\hat{x}_{out})_3 = 0.00202$

Temperature: Uniform throughout the column

Flow Rates: $L' = 143.3$ lb moles/hr ft^2
$V' = 20.5$ lb moles/hr ft^2

Mass Transfer Coefficients (assumed constant):

$(k_x a)_1 = 0.0349$ lb moles/hr ft^3 (mole fraction)
$(k_y a)_1 = 1.996$ lb moles/hr ft^3 (mole fraction)

Equilibrium Data:

$$y_1^i = 7.0\ x_1^i$$

Program Predicted Column Height: 25.4 ft

Reference: 16

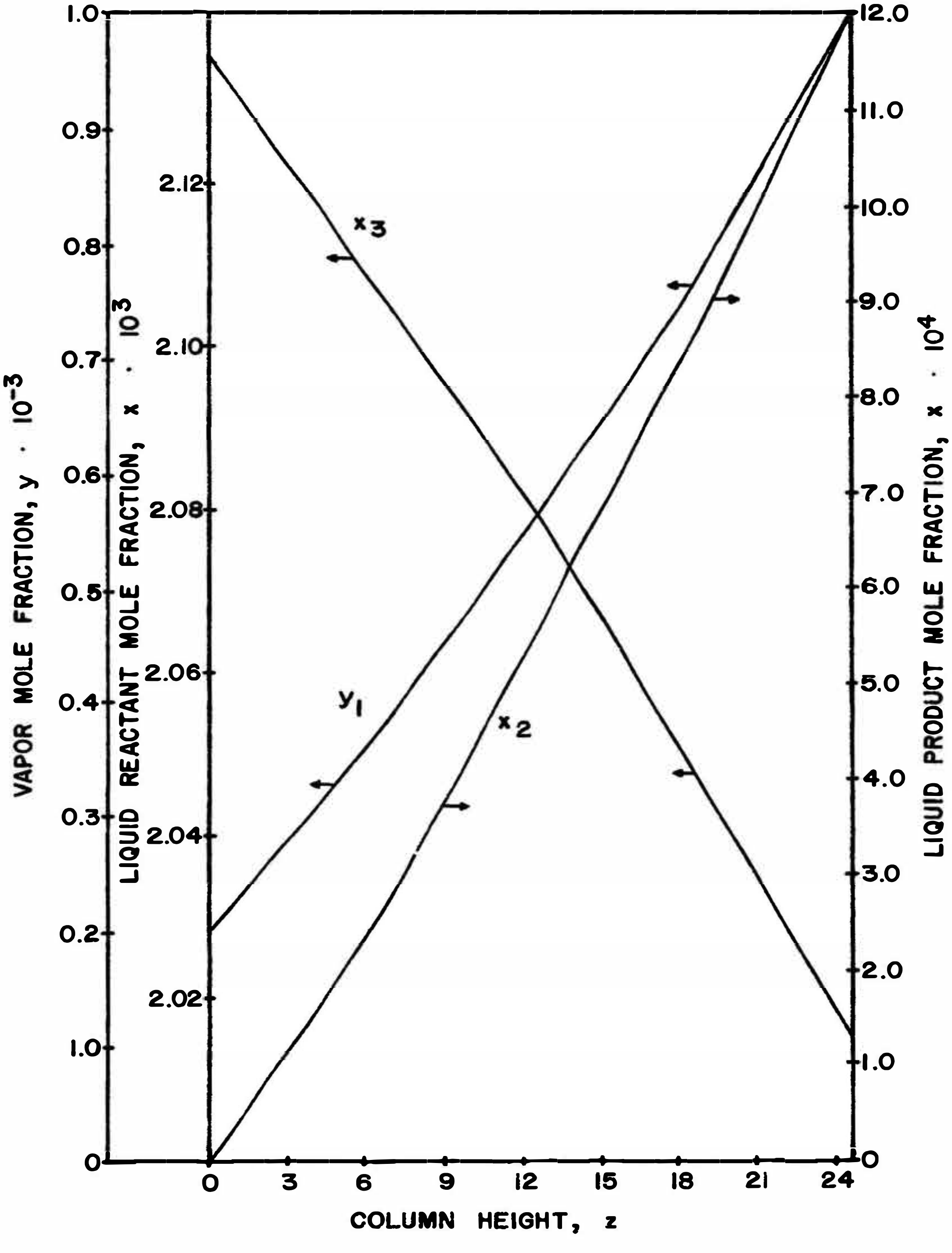

Figure C-4. Calculated Vapor and Liquid Concentration Profiles for System 4 (Intermediate Reactant Concentration)[16]

TABLE C-5

PHYSICAL DATA -- SYSTEM 5

Carrier Liquid: Water

Carrier Gas: Nitrogen-Hydrogen

Column Height: 22.9 ft

Components: 1 = CO_2, 2 = $KHCO_3$, 3 = K_2CO_3

Reaction: $CO_2+K_2CO_3+H_2O \rightarrow 2KHCO_3$

Compositions:

$(y_{in})_1 = 0.25$ $(y_{out})_1 = 0.005$

$(y_{in})_2 = 0.0$ $(y_{out})_2 = 0.0$

$(y_{in})_3 = 0.0$ $(y_{out})_3 = 0.0$

$(x_{in})_1 = 0.0$ $(x_{out})_1 = 0.0$

$(x_{in})_2 = 0.00704$ $(x_{out})_2 = 0.0480$

$(x_{in})_3 = 0.03169$ $(x_{out})_3 = 0.0130$

$(\hat{Y}_{in})_1 = 0.025$ $(\hat{X}_{out})_1 = 0.0$

$(\hat{Y}_{in})_2 = 0.0$ $(\hat{X}_{out})_2 = 0.0420$

$(\hat{Y}_{in})_3 = 0.0$ $(\hat{X}_{out})_3 = 0.0141$

Temperature: t = 140°F (uniform throughout the column)

Flow Rates: L' = 652 lb moles/hr ft^2

V' = 442 lb moles/hr ft^2

Mass Transfer Coefficients:

$(k_x a)_1$ = 190 lb moles/hr ft^3 (mole fraction)

$(k_y a)_1$ = 51 lb moles/hr ft^3 (mole fraction)

Diffusivities: $(D_V)_1 = 0.775$ ft^2/hr

$(D_L)_1 = 6.39 \times 10^{-5}$ ft^2/hr

$(D_L)_3 = 6.975 \times 10^{-5}$ ft^2/hr

TABLE C-5 (continued)

Equilibrium Data:

$$Y_1^i = 490.5\ x_1^i$$

Program Predicted Tower Height: 22.5 ft

Reference: 9

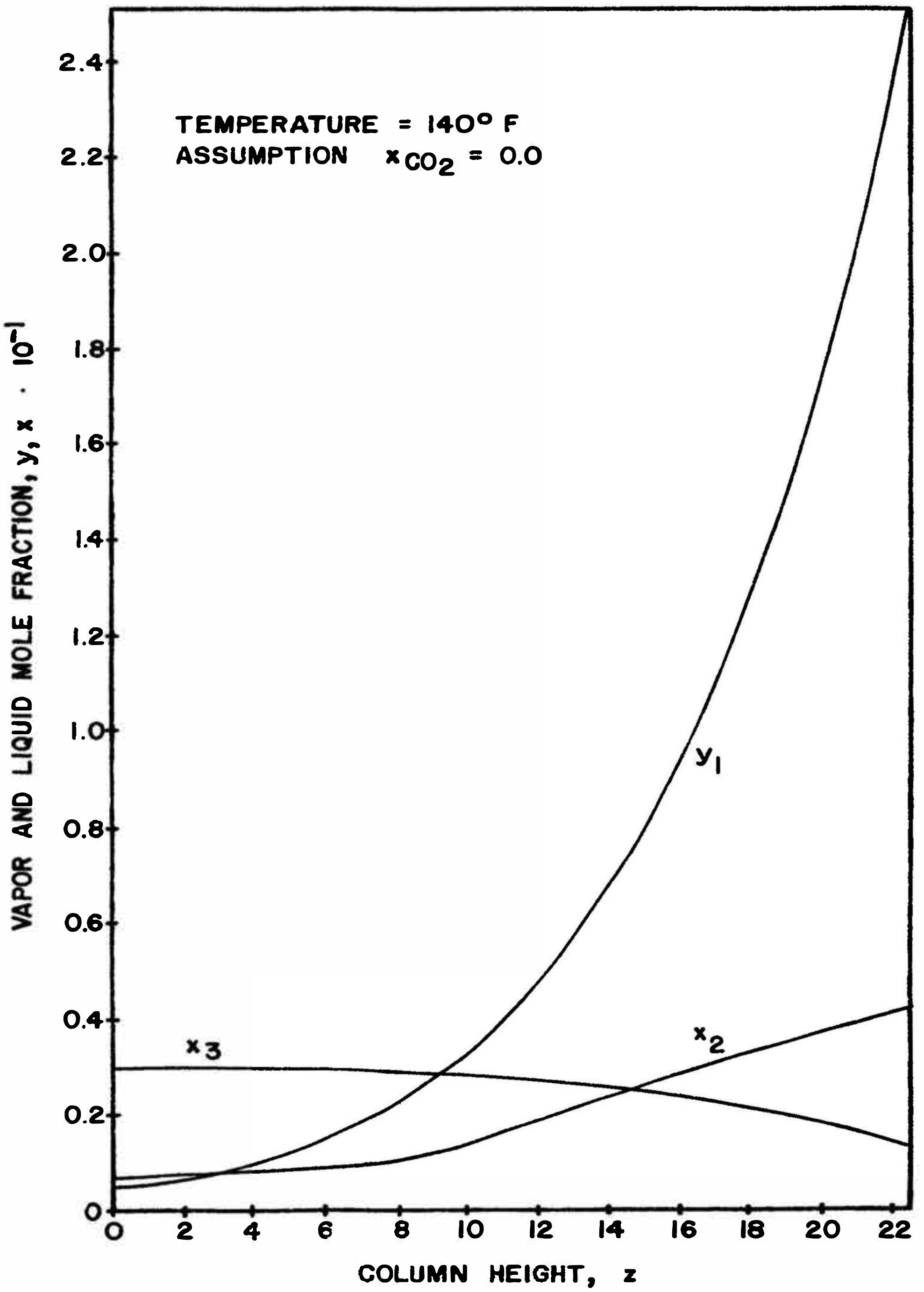

Figure C-5. Calculated Vapor and Liquid Concentration Profiles for System 5[9]

TABLE C-6

PHYSICAL DATA -- SYSTEM 6

Carrier Liquid: Water

Carrier Gas: Nitrogen-Hydrogen Mixture

Column Height: 22.9 ft

Components: $1 = CO_2$, $2 = KHCO_3$, $3 = K_2CO_3$

Reaction: $CO_2+K_2CO_3+H_2O \rightarrow 2KHCO_3$

Compositions: $(y_{in})_1 = 0.25$ $(y_{out})_1 = 0.005$
$(y_{in})_2 = 0.0$ $(y_{out})_2 = 0.0$
$(y_{in})_3 = 0.0$ $(y_{out})_3 = 0.0$
$(x_{in})_1 = 0.0$ $(x_{out})_1 = 0.0000183$
$(x_{in})_2 = 0.00704$ $(x_{out})_2 = 0.0480$
$(x_{in})_3 = 0.03169$ $(x_{out})_3 = 0.0130$
$(\hat{y}_{in})_1 = 0.2503$ $(\hat{x}_{out})_1 = 0.0000183$
$(\hat{y}_{in})_2 = 0.0$ $(\hat{x}_{out})_2 = 0.0420$
$(\hat{y}_{in})_3 = 0.0$ $(\hat{x}_{out})_3 = 0.0142$

$x_1 = x_{eq}$ where $x_{eq} = (.000151)(KHCO_3)^2/(K_2CO_3)$

Temperature: t = 140°F (uniform throughout the column)

Flow Rates: $L' = 652$ lb moles/hr ft^2
$V' = 442$ lb moles/hr ft^2

Mass Transfer Coefficients:

$(k_x a)_1 = 190$ lb moles/hr ft^3 (mole fraction)
$(k_y a)_1 = 51$ lb moles/hr ft^3 (mole fraction)

Diffusivities: $(D_V)_1 = 0.775\ ft^2/hr$
$(D_L)_1 = 6.39 \times 10^{-5}\ ft^2/hr$
$(D_L)_3 = 6.975 \times 10^{-5}\ ft^2/hr$

TABLE C-6 (continued)

Equilibrium Data:

$$y_1^i = 490.5\ x_1^i$$

Program Predicted Tower Height: 22.8 ft

Reference: 9

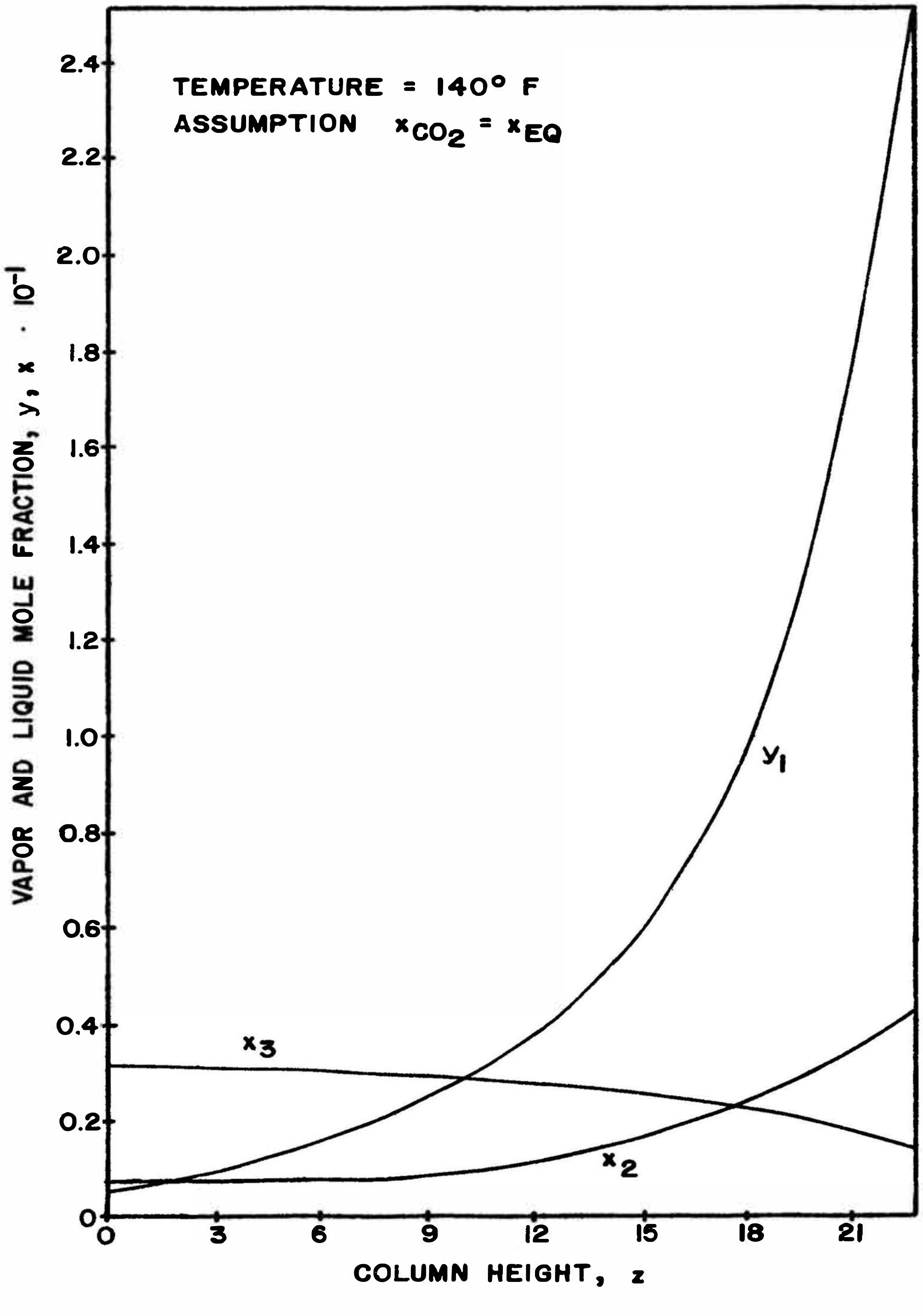

Figure C-6. Calculated Vapor and Liquid Concentration Profiles for System 6[9]

TABLE C-7

PHYSICAL DATA -- SYSTEM 7

Carrier Liquid: Water

Carrier Gas: Nitrogen-Hydrogen Mixture

Column Height: 10.5 ft

Components: 1 = CO_2, 2 = $RNH_2COO^{-}+RNH_3^{-}$, 3 = RNH_2 (MEA)

Reaction: $CO_2+2RNH_2 \rightarrow RNH_2COO^{-}+RNH_3^{+}$

Compositions: $(y_{in})_1 = 0.25$ $(y_{out})_1 = 0.00002$
$(y_{in})_2 = 0.0$ $(y_{out})_2 = 0.0$
$(y_{in})_3 = 0.0$ $(y_{out})_3 = 0.0$
$(x_{in})_1 = 0.0$ $(x_{out})_1 = 0.0$
$(x_{in})_2 = 0.01374$ $(x_{out})_2 = 0.0350$
$(x_{in})_3 = 0.03205$ $(x_{out})_3 = 0.00916$
$(\hat{y}_{in})_1 = 0.254$ $(\hat{x}_{out})_1 = 0.0$
$(\hat{y}_{in})_2 = 0.0$ $(\hat{x}_{out})_2 = 0.032$
$(\hat{y}_{in})_3 = 0.0$ $(\hat{x}_{out})_3 = 0.013$

Temperature: t = 86°F (uniform throughout the column)

Flow Rates: $L' = 677.8$ lb moles/hr ft^2
$V' = 23.2$ lb moles/hr ft^2

Mass Transfer Coefficients (assumed constant):

$(k_x a)_1 = 384.4$ lb moles/hr ft^3 (mole fraction)
$(k_y a)_1 = 36.4$ lb moles/hr ft^3 (mole fraction)

Diffusivities: $(D_V)_1 = 0.775\ ft^2/hr$
$(D_L)_1 = 5.425 \times 10^{-5}\ ft^2/hr$
$(D_L)_3 = 2.983 \times 10^{-5}\ ft^2/hr$

TABLE C-7 (continued)

Equilibrium Data:

$$y_1^i = 111.2\ x_1^i$$

Program Predicted Tower Height: 9.8 ft

Reference: 6

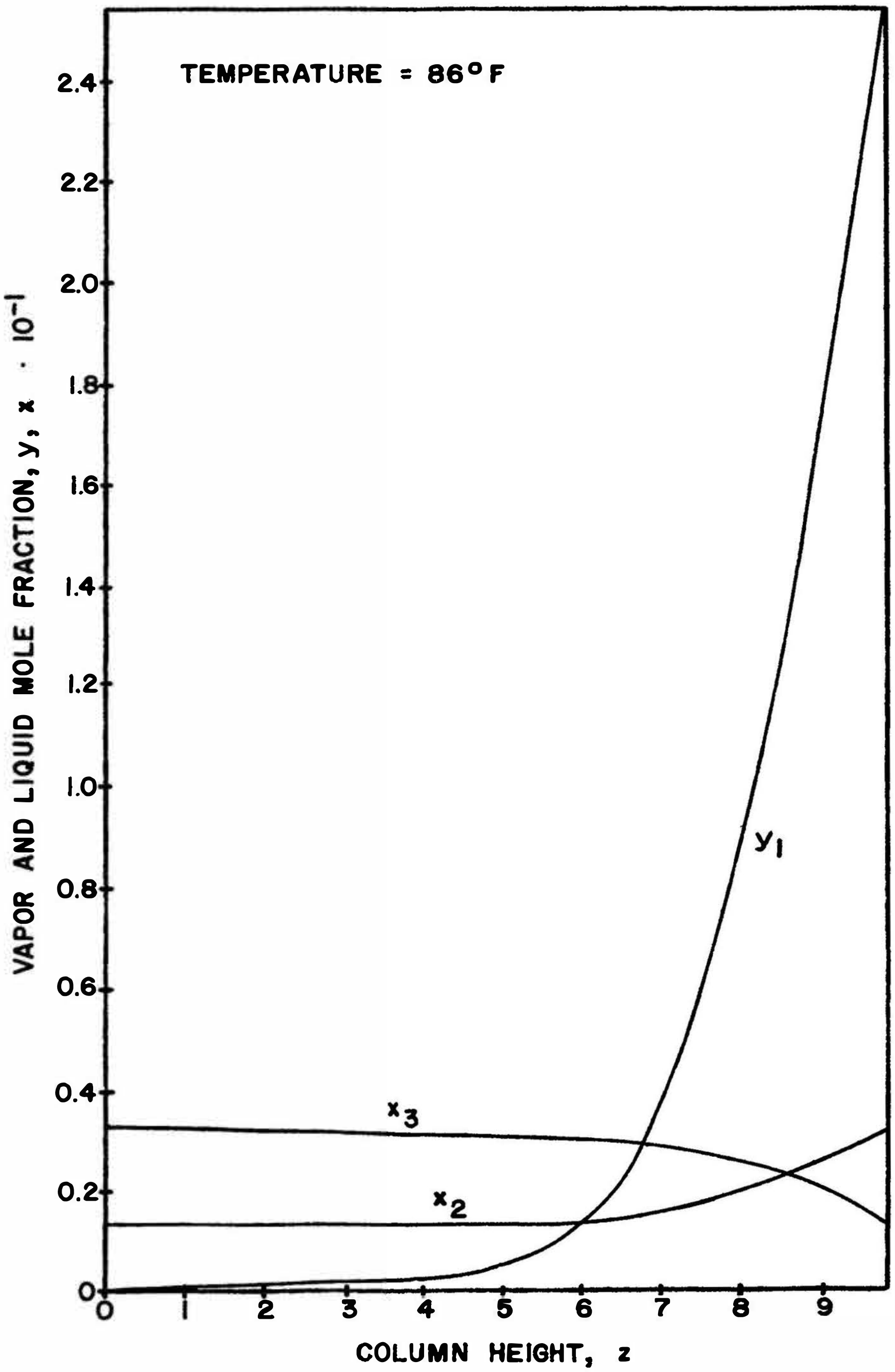

Figure C-7. Calculated Vapor and Liquid Concentration Profiles for System 7[9]

TABLE C-8

PHYSICAL DATA -- SYSTEM 8

Carrier Liquid: Water

Carrier Gas: Air

Column Height: 3.0 ft

Components: 1 = CO_2, 2 = Na_2CO_3, 3 = NaOH

Reaction: $CO_2+2NaOH \rightarrow Na_2CO_3+H_2O$

Compositions: $(y_{in})_1 = 0.0184$ $(y_{out})_1 = 0.0109$
$(y_{in})_2 = 0.0$ $(y_{out})_2 = 0.0$
$(y_{in})_3 = 0.0$ $(y_{out})_3 = 0.0$
$(x_{in})_1 = 0.0$ $(x_{out})_1 = 0.0$
$(x_{in})_2 = 0.0363$ $(x_{out})_2 = 0.0375$
$(x_{in})_3 = 0.0104$ $(x_{out})_3 = 0.0091$
$(\hat{y}_{in})_1 = 0.01841$ $(\hat{x}_{out})_1 = 0.0$
$(\hat{y}_{in})_2 = 0.0$ $(\hat{x}_{out})_2 = 0.0368$
$(\hat{y}_{in})_3 = 0.0$ $(\hat{x}_{out})_3 = 0.0093$

Temperature: t = 79°F (uniform throughout the column)

Flow Rates: L' = 91.17 lb moles/hr ft^2
V' = 6.55 lb moles/hr ft^2

Packing: 1/2" Raschig rings

Mass Transfer Coefficients[28] (assumed constant):

$(k_x a)_1 = 120.27$ lb moles/hr ft^3 (mole fraction)
$(k_y a)_1 = 5.27$ lb moles/hr ft^3 (mole fraction)

TABLE C-8 (continued)

Diffusivities: $(D_V)_1 = 0.6355$ ft^2/hr

$(D_L)_1 = 6.85 \times 10^{-5}$ ft^2/hr

$(D_L)_3 = 5.85 \times 10^{-5}$ ft^2/hr

Equilibrium Data:

$$y_1^i = 1680\ x_1^i$$

Program Predicted Tower Height: 3.08 ft

Reference: 24

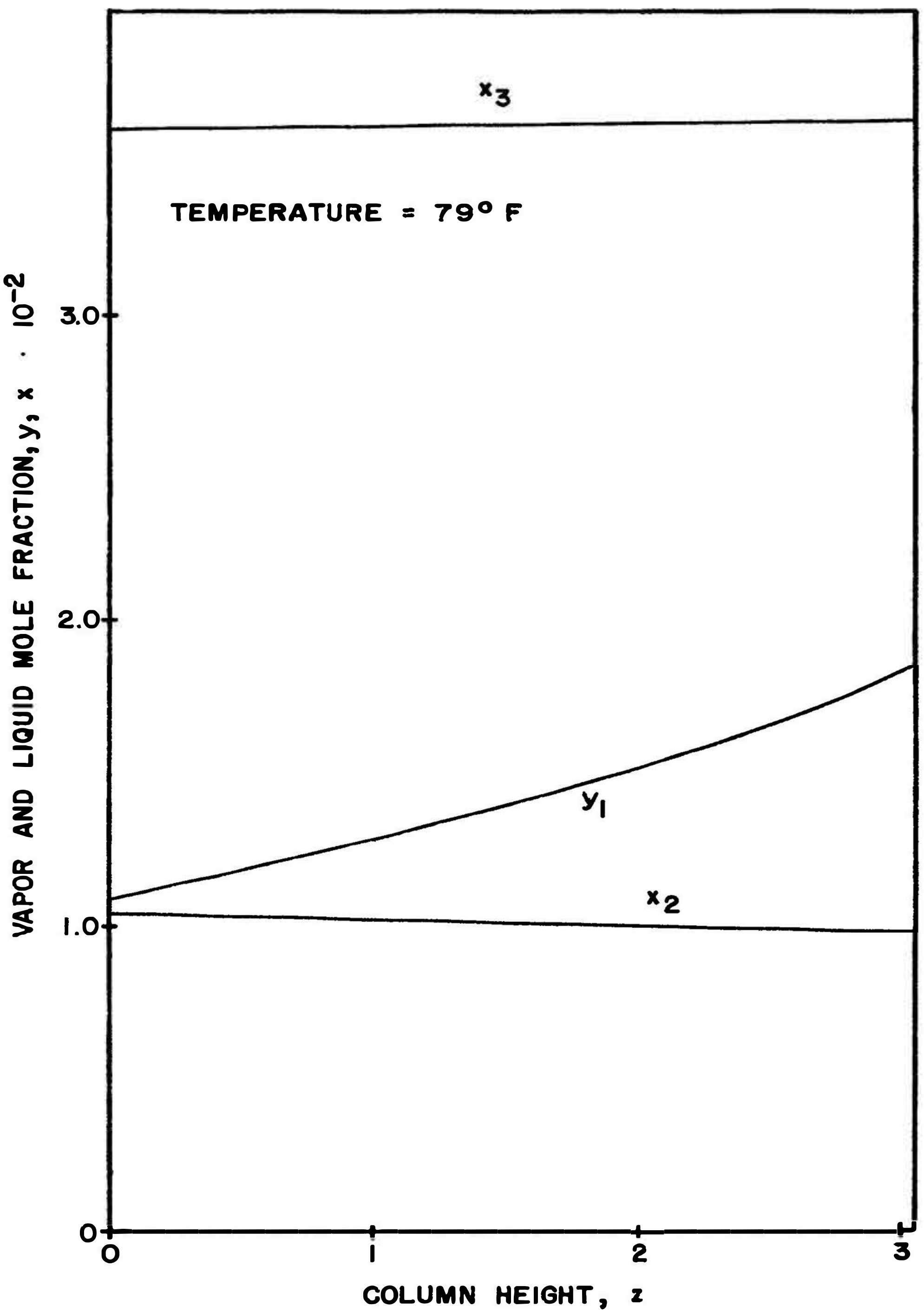

Figure C-8. Calculated Vapor and Liquid Concentration Profiles for System 8[25]

TABLE C-9

PHYSICAL DATA -- SYSTEM 9

Carrier Liquid: Water

Carrier Gas: Air

Column Height: 7.7 ft

Components: 1 = CO_2, 2 = Na_2CO_3, 3 = NaOH

Reaction: $CO_2 + 2NaOH \rightarrow Na_2CO_3 + H_2O$

Compositions:

$(y_{in})_1 = 0.0472$	$(y_{out})_1 = 0.0099$
$(y_{in})_2 = 0.0$	$(y_{out})_2 = 0.0$
$(y_{in})_3 = 0.0$	$(y_{out})_3 = 0.0$
$(x_{in})_1 = 0.0$	$(x_{out})_1 = 0.0$
$(x_{in})_2 = 0.000427$	$(x_{out})_2 = 0.00685$
$(x_{in})_3 = 0.01883$	$(x_{out})_3 = 0.00539$
$(\hat{y}_{in})_1 = 0.0472$	$(\hat{x}_{out})_1 = 0.0$
$(\hat{y}_{in})_2 = 0.0$	$(\hat{x}_{out})_2 = 0.00619$
$(\hat{y}_{in})_3 = 0.0$	$(\hat{x}_{out})_3 = 0.00741$

Temperature:

$(t_L)_{in} = 63°F$	$(t_L)_{out} = 80°F$	$(\hat{t}_L)_{out} = 79.0°F$
$(t_V)_{in} = 80°F$	$(t_V)_{out} = 69°F$	$(\hat{t}_V)_{in} = 80.1°F$

Flow Rates: L' = 40.1 lb moles/hr ft^2

V' = 6.15 lb moles/hr ft^2

Packing: 1/2" Raschig rings

TABLE C-9 (continued)

Transfer Coefficients[28] (assumed constant):

$(k_x a)_1$ = 52.5 lb moles/hr ft^3 (mole fraction)

$(k_y a)_1$ = 2.99 lb moles/hr ft^3 (mole fraction)

$h_L a$ = 8758 BTU/hr ft^3 °F

$h_V a$ = 24.6 BTU/hr ft^3 °F

Diffusivities (at 79°F): $(D_V)_1 = 0.6355$ ft^2/hr

$(D_L)_1 = 6.85 \times 10^{-5}$ ft^2/hr

$(D_L)_3 = 5.85 \times 10^{-5}$ ft^2/hr

Equilibrium Data:

$y_1^i = h\ (10^4)\ x_1^i$ where $h = 0.025499 + 0.00122338\ t^i + 0.0000073484\ (t^i)^2$

Program Predicted Tower Height: 8.2 ft

Reference: 24

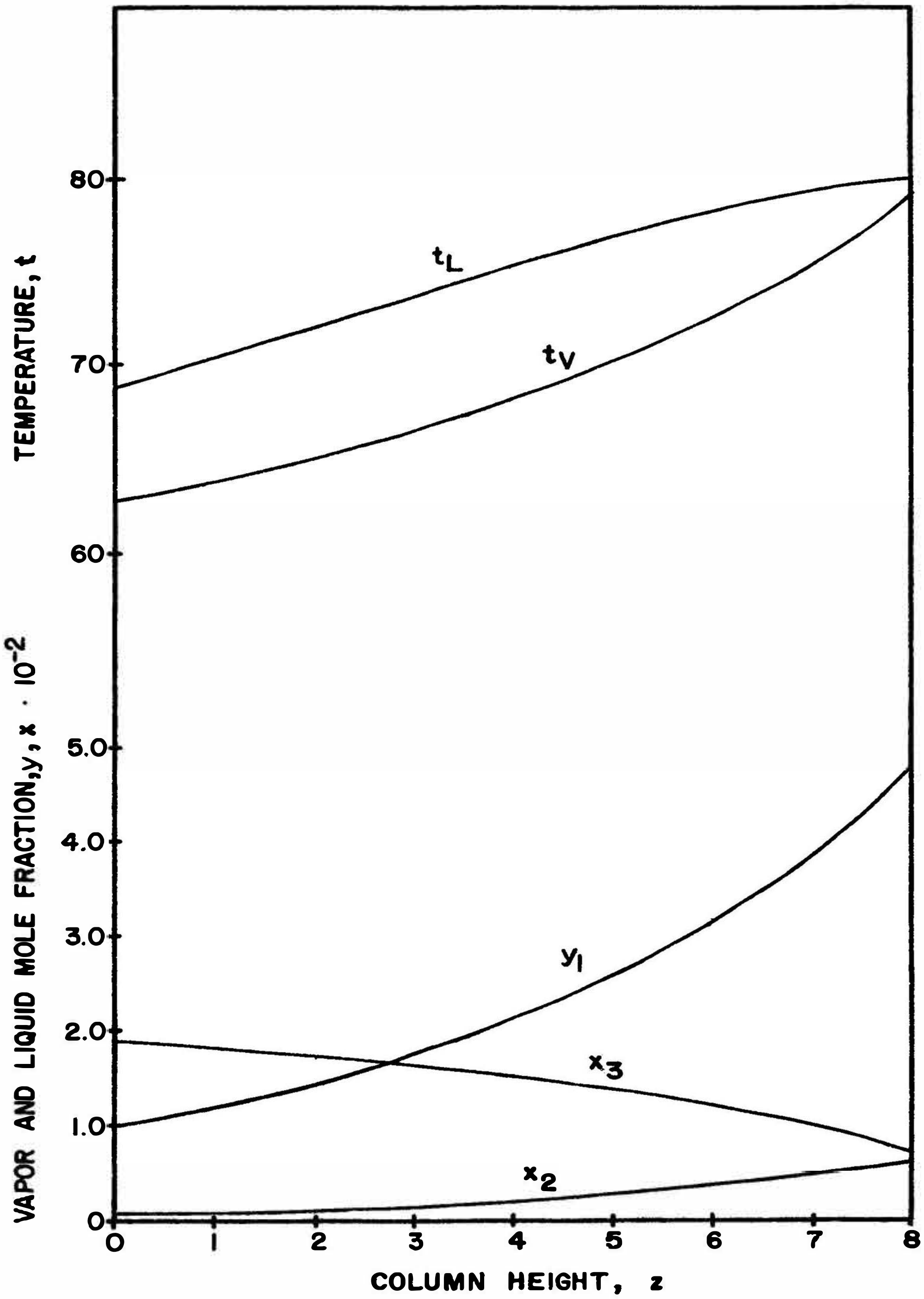

Figure C-9. Calculated Concentration and Temperature Profiles for System 9[25]

TABLE C-10

PHYSICAL DATA -- SYSTEM 10

Carrier Liquid: Water

Carrier Gas: Air

Components: 1 = A, 2 = C, 3 = D, 4 = E, 5 = F, 6 = B

Reactions: $A+2B \rightarrow E$, $C+B$ F

Compositions:

$(y_{in})_1 = 0.05$ $(y_{out})_1 = 0.01$ $(x_{in})_1 = 0.00$

$(y_{in})_2 = 0.075$ $(y_{out})_2 = 0.02$ $(x_{in})_2 = 0.00$

$(y_{in})_3 = 0.014$ $(y_{out})_3 = 0.01$ $(x_{in})_3 = 0.00$

$(y_{in})_4 = 0.00$ $(y_{out})_4 = 0.00$ $(x_{in})_4 = 0.0001$

$(y_{in})_5 = 0.00$ $(y_{out})_5 = 0.00$ $(x_{in})_5 = 0.00015$

$(y_{in})_6 = 0.00$ $(y_{out})_6 = 0.00$ $(x_{in})_6 = 0.02$

Temperature:

$(t_L)_{in} = 60°F$ $(t_V)_{in} = 65°F$

$(t_L)_{out} = 87°F$ $(t_V)_{out} = 58°F$

Flow Rates: $L' = 45$ lb moles/hr ft^2

$V' = 5$ lb moles/hr ft^2

Packing: 1" Raschig rings

Transfer Coefficients (at 79°F, assumed constant):

$(k_x a)_1 = 50$ lb moles/hr ft^3 (mole fraction)

$(k_y a)_1 = 3$ lb moles/hr ft^3 (mole fraction)

$(k_x a)_2 = 45$ lb moles/hr ft^3 (mole fraction)

$(k_y a)_2 = 2.5$ lb moles/hr ft^3 (mole fraction)

$(k_x a)_3 = 332$ lb moles/hr ft^3 (mole fraction)

TABLE C-10 (continued)

Transfer Coefficients (continued):

$(k_y a)_3 = 14$ lb moles/hr ft^3 (mole fraction)

$h_L a = 9000$ BTU/hr ft^3 °F

$h_V a = 10$ BTU/hr ft^3 °F

Diffusivities: $(D_V)_1 = 0.64$ ft^2/hr

$(D_L)_1 = 7.0 \times 10^{-5}$ ft^2/hr

$(D_V)_2 = 0.70$ ft^2/hr

$(D_L)_2 = 7.5 \times 10^{-5}$ ft^2/hr

$(D_L)_6 = 6.0 \times 10^{-5}$ ft^2/hr

Equilibrium Data:

$$y_1^i = [0.025 + 0.0012\ t^i + 0.000007\ (t^i)^2]\ 10^4\ x_1^i$$

$$y_2^i = [0.030 + 0.020\ t^i + 0.00010\ (t^i)^2]\ 10^4\ x_2^i$$

$$y_3^i = 29\ x_3^i$$

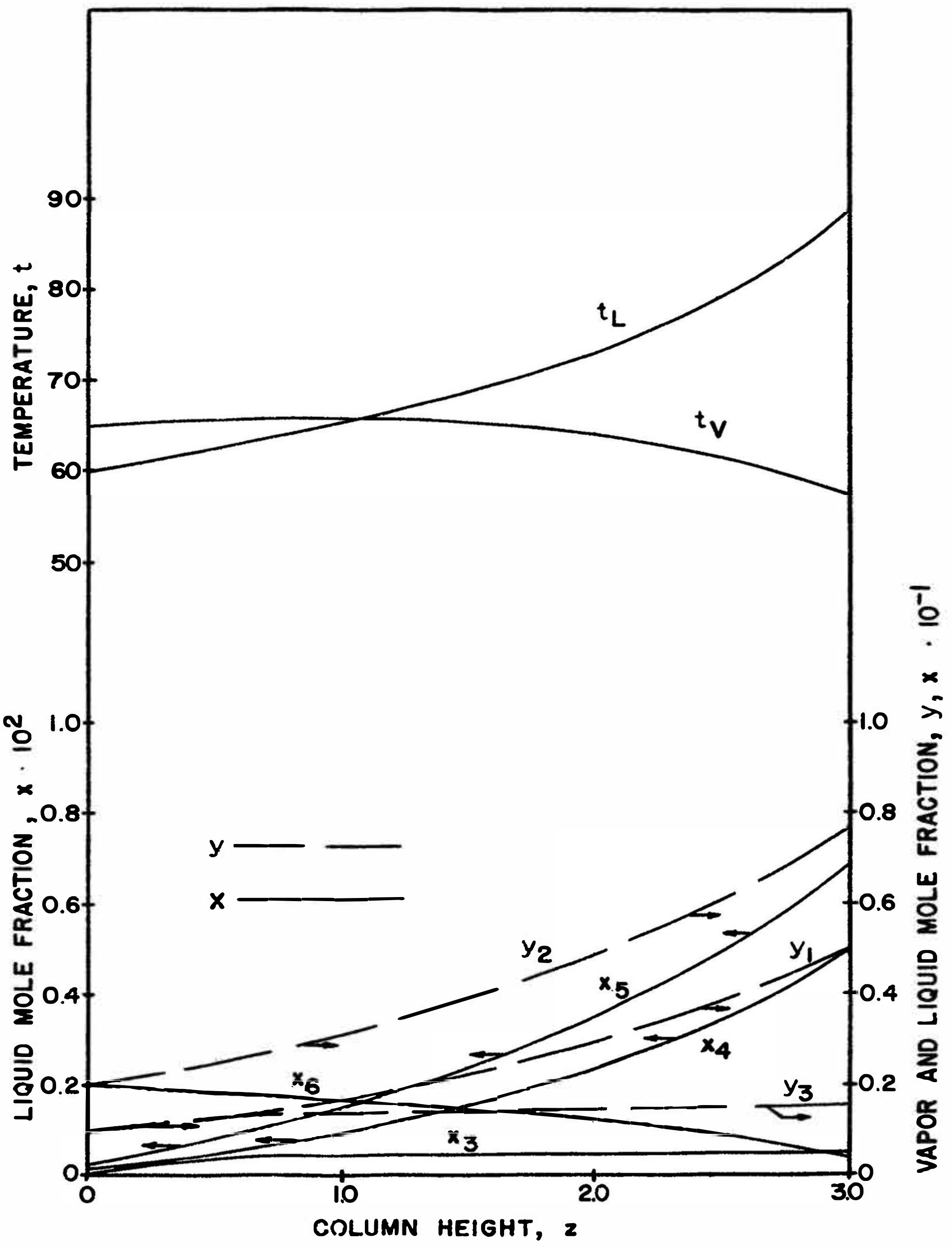

Figure C-10. Calculated Concentration and Temperature Profiles for System 10

TABLE C-11

PHYSICAL DATA -- SYSTEM 11

Carrier Liquid: Water

Carrier Gas: Air

Components: 1 = Acetone, 2 = Water

Reaction: None

Compositions: $(y_{in})_1 = 0.0309$ $(y_{out})_1 = 0.00231$

$(y_{in})_2 = 0.0116$ $(y_{out})_2 = 0.0265$

$(x_{in})_1 = 0.0$ $(x_{out})_1 = 0.0114$

$(x_{in})_2 = 0.0$ $(x_{out})_2 = 0.9886$

$(\hat{y}_{out})_1 = 0.00227$ $(\hat{x}_{in})_1 = 0.0$

$(\hat{y}_{out})_2 = 0.0186$ $(\hat{x}_{in})_2 = 1.0$

Temperature:

$(t_L)_{in} = 54.5°F$ $(t_L)_{out} = 69.3°F$ $(\hat{t}_L)_{in} = 56.8°F$

$(t_V)_{in} = 58.8°F$ $(t_V)_{out} = 72°F$ $(\hat{t}_V)_{out} = 58°F$

Flow Rates: $L' = 38.33$ lb moles/hr ft^2

$V' = 15.24$ lb moles/hr ft^2

Packing: 1" Ceramic rings

Mass Transfer Coefficients[28] (at 65°F, assumed constant):

$(k_xa)_1 = 21.65$ lb moles/hr ft^3 (mole fraction)

$(k_xa)_2 = 39.4$ lb moles/hr ft^3 (mole fraction)

$(k_ya)_1 = 4.36$ lb moles/hr ft^3 (mole fraction)

$(k_ya)_2 = 7.93$ lb moles/hr ft^3 (mole fraction)

$h_La = 120.0$ BTU/hr ft^3 °F

$h_Va = 6.93$ BTU/hr ft^3 °F

TABLE C-11 (continued)

Equilibrium Data:

$y_1^i = \gamma_1 \; P^o \; x_1^i/P$ (see Appendix D)

$$y_2^i = [0.027721 - 0.000733\, t^i + 0.0000112819\, (t^i)^2][1-\sum_{j=1}^{N} x_j]$$

Reference: 23

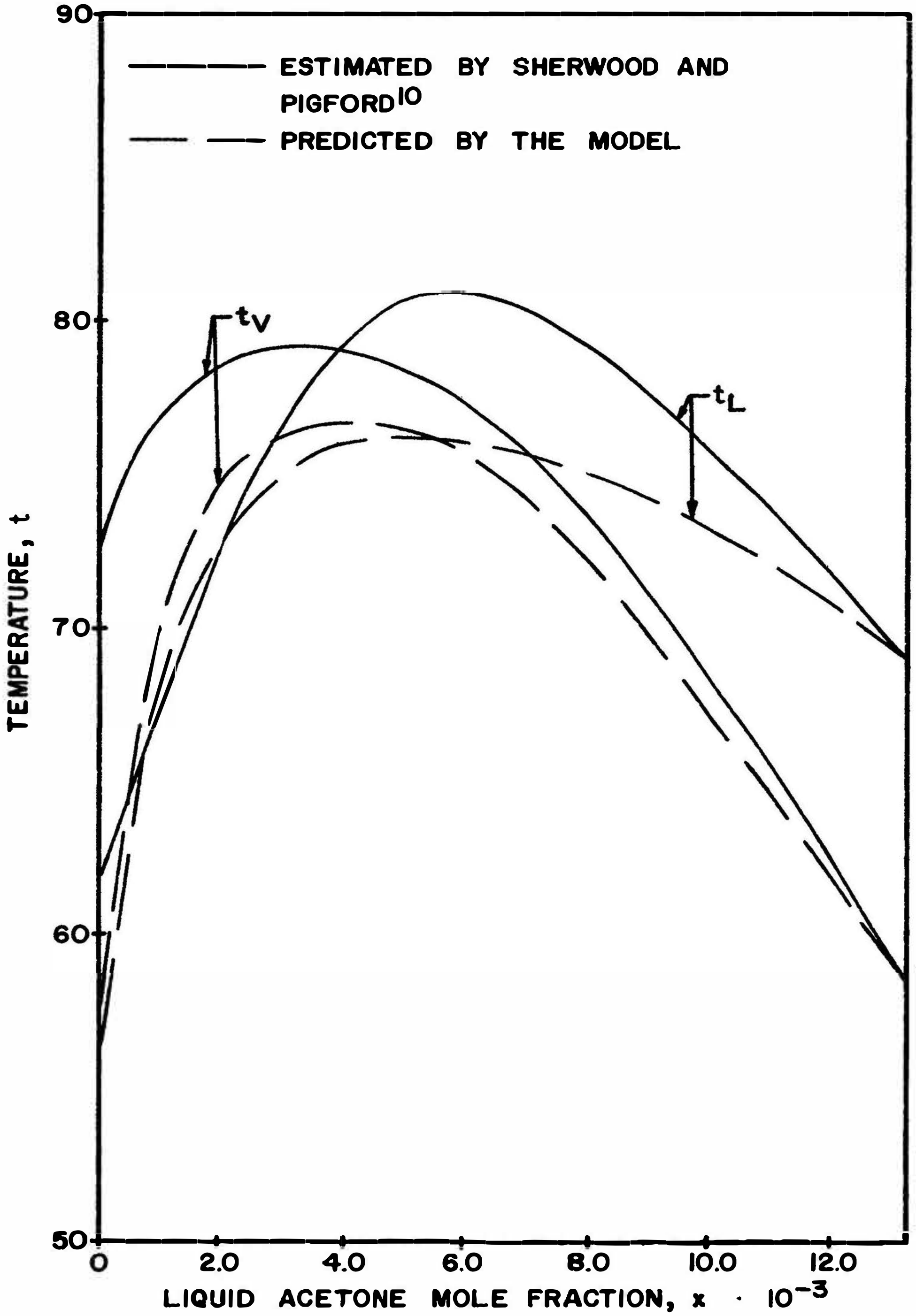

Figure C-11. Vapor and Liquid Temperature Profiles for an Adiabatic Absorption of Acetone in Water[24]

TABLE C-12

PHYSICAL DATA -- SYSTEM 12

Carrier Liquid: Water

Carrier Gas: Air

Components: 1 = Ammonia, 2 = Water

Reaction: None

Compositions:

$(y_{in})_1 = 0.0049$ $(y_{out})_1 = 0.0881$

$(y_{in})_2 = 0.025$ $(y_{out})_2 = 0.0305$

$(x_{in})_1 = 0.0$ $(x_{out})_1 = 0.0302$

$(x_{in})_2 = 1.0$ $(x_{out})_2 = 0.9698$

Temperature:

$(t_L)_{in} = 61.3°F$ $(t_L)_{out} = 92.1°F$

$(t_V)_{in} = 77°F$ $(t_V)_{out} = 68.3°F$

Flow Rates: $L' = 65.1$ lb moles/hr ft^2

$V' = 24.6$ lb moles/hr ft^2

Packing: 1" Raschig rings

Transfer Coefficients^{12} (at 77°F, assumed constant):

$(k_x a)_1 = 126.0$ $(k_y a)_1 = 23.1$

$(k_x a)_2 = 143.7$ $(k_y a)_2 = 26.5$

$h_L a = 12600$ $h_V a = 23.2$

Equilibrium Data:

$$y_1^i = [10^{(7.6657+\frac{1222.2}{t+230} - \log\{(\frac{1000}{c} - 1.6)(0.7574+\frac{62.51}{t+230})\}}]/760$$

TABLE C-12 (continued)

Equilibrium Data (continued):

$$y_2^i = [0.027721 - 0.000733\, t^i + 0.0000112819\, (t^i)^2][1-\sum_{j=1}^{N} x_j]$$

Reference: 23

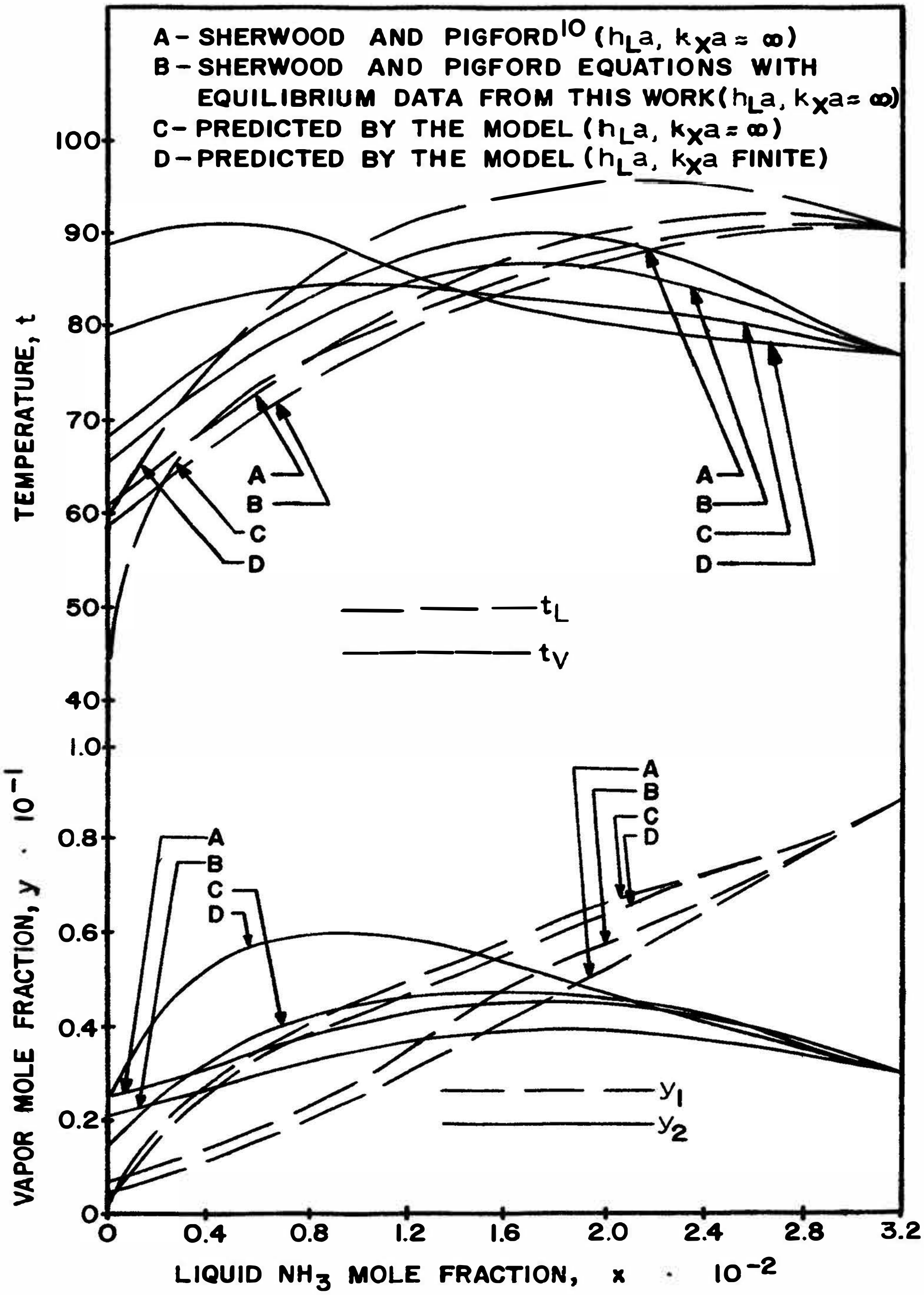

Figure C-12. Concentration and Temperature Profile for an Adiabatic Absorption of Ammonia in Water[24]

TABLE C-13

REACTION SYSTEMS STUDIED WITH REPORTED AND CALCULATED COLUMN HEIGHTS

System	Reaction	Carrier Liquid	Carrier Gas	Transferring Component	Heat Effects	Reported Column Height (ft)	Program Predicted Height (ft)	% Error	Reference
1	None	H_2O	Air	A	Isothermal	1550	1465	5.5	6
2	A+B→C	H_2O	Air	A	Isothermal	16.4	16.55	0.9	6
3	A+B→C	H_2O	Air	A	Isothermal	80.0	81.0	1.2	6
4	A+B→C	H_2O	Air	A	Isothermal	23.0	25.4	9.4	6
5	$CO_2+K_2CO_3+H_2O \rightarrow 2KHCO_3$	H_2O	N_2	CO_2	Isothermal	22.9	22.5	1.7	4
6	$CO_2+K_2CO_3+H_2O \rightarrow 2KHCO_3$	H_2O	N_2	CO_2	Isothermal	22.9	22.8	0.4	4
7	$CO_2+2RNH_3 \rightarrow RNH_2COO^- + RNH_2$	H_2O	N_2	CO_2	Isothermal	10.5	9.8	6.7	4

TABLE C-13 (continued)

System	Reaction	Carrier Liquid	Carrier Gas	Transferring Component	Heat Effects	Reported Column Height (ft)	Program Predicted Height (ft)	% Error	Reference
8	$CO_2+2NaOH\rightarrow$ $Na_2CO_3+H_2O$	H_2O	Air	CO_2	Isothermal	3.0	3.08	2.7	11
9	$CO_2+2NaOH\rightarrow$ $Na_2CO_3+H_2O$	H_2O	Air	CO_2	Adiabatic	7.7	8.2	6.1	11
10	$A+2B\rightarrow C$ $A+B\rightarrow C$	H_2O	Air	A,B,C	Adiabatic	---	3.1	---	

APPENDIX D

EQUILIBRIUM DATA

In the numerical solution of mass transfer equations, one of the most important considerations is the accuracy of the equilibrium data. Where data is available, it is generally reliable.

For example, Perry[21] gives equilibrium data for ammonia, sulfer dioxide, and many others. For isothermal conditions, it is most convenient to curve fit the data using least squares to the form:

$$y^i = a + bx^i + c(x^i)^2 + \ldots \qquad \text{(D-1)}$$

For nonisothermal conditions, the data may be correlated by a graphical technique presented by Davis[8]. The Stern equation (Appendix C, System 12) was developed using this technique. If Henry's Law constants are available, they can be fit to:

$$H = a + bt + ct^2 + \ldots \qquad \text{(D-2)}$$

by least squares and used in:

$$y^i = H(t)x^i \text{ (see Appendix C, System 9).} \qquad \text{(D-3)}$$

All of these methods can represent the equilibrium data quite well. A problem arises when equilibrium data are not available and must be estimated from other known quantities.

For an acetone absorption (Appendix C, System 11), equilibrium data could not be found in the literature. Sherwood and Pigford[24] suggest that the equilibrium relationship be estimated from activity coefficient data.

The activity coefficient may be calculated from:

$$\gamma = y^i P / x^i P^o \tag{D-4}$$

where γ = activity coefficient; P = total pressure, mmHg; P^o = vapor pressure, mmHg. The vapor pressure of a substance changes with temperature by the Clausius-Clapeyron equation:

$$\frac{d\ell n P^o}{dT} = \frac{\Delta Q_V}{RT^2} \; . \tag{D-5}$$

Integrating from T to T_R gives:

$$\ell n P^o_T = \ell n P^o_{T_R} + [\frac{T-T_R}{TT_R}] \; . \tag{D-6}$$

If $P^o_{T_R}$ = 200 mmHg (T_R = 22.7°C) is used as a reference, then Equation D-6 becomes:

$$P^o = \exp\,[\ell n\ 200 + \frac{7590}{1.99}\,(\frac{T-295.7}{295.7T})] \tag{D-7}$$

where:

$$\Delta Q_V^{T=22.7} = 7590 \text{ cal/gmole.}$$

In addition, the activity coefficient also changes with temperature according to:

$$\frac{d\ln\gamma}{dT} = -\frac{\Delta Q_s}{RT^2} \qquad \text{(D-8)}$$

where ΔQ_s = heat of solution. Integrating Equation D-8 gives:

$$\ln\gamma = \ln\gamma_R - \frac{\Delta Q_s}{R}\left[\frac{T-T_R}{TT_R}\right]. \qquad \text{(D-9)}$$

For a reference temperature of T_R = 17.6°C, Hartley[15] gives $\gamma_R = 6$. Equation D-9 becomes:

$$\gamma = \exp\left[1.79208 + 1256.28\left(\frac{T-290.6}{290.6T}\right)\right] \qquad \text{(D-10)}$$

for $x < 0.002$. If $x > 0.002$, Carlson and Colburn[6] suggest a slightly different form of:

$$\gamma = \exp\left\{2.303\,(1-x)^2\left[0.77815 + 545.497\left(\frac{T-290.6}{290.6T}\right)\right]\right\}. \qquad \text{(D-11)}$$

By rearranging Equation D-4, the equilibrium relationship may be estimated by:

$$y^i = \frac{\gamma P^o}{P}\,x^i. \qquad \text{(D-12)}$$

Figure C-10 shows the resulting profiles using the above representation of the equilibrium data. The estimation of the equilibrium relationship was not accurate enough for the particular problem. In addition, the temperature (59°F - 80°F) and concentration (y^i; 0 - 0.0205) ranges may have been too broad for this method to give adequate results.

Obviously, the importance of accurate equilibrium data cannot be stressed too strongly. An accurate representation of the equilibrium data is essential to reliable results.

APPENDIX E

INSTRUCTIONAL USE OF THE NUMERICAL SOLUTION OF THE ONE COMPONENT EQUATIONS

For the equations:

$$\frac{dy}{dz} = \frac{k_y a}{V} (y-y^i) \qquad \text{(A-16a)}$$

$$\frac{dx}{dz} = \frac{k_x a}{L} (x^i-x) \qquad \text{(A-16b)}$$

there are three methods to obtain tower height -- numerical, analytical, and graphical solutions. The graphical technique is still primarily covered in undergraduate courses in mass transfer. Foust[12] and others have detailed the procedure for the graphical technique. The tower height can be found from:

$$z = H_G N_G \qquad \text{(E-1)}$$

where H_G is the height of the transfer unit and N_G is the number of transfer units. Equation E-1 is further defined by:

$$H_G = \frac{V}{k_y a (1-y)_{1m}} \qquad \text{(E-2a)}$$

and

$$N_G = \int_{y_{in}}^{y_{out}} \frac{(1-y)_{1m} dy}{(1-y)(y^i-y)} \; . \qquad \text{(E-2b)}$$

Equation E-2b must be graphically integrated to obtain the value for the number of transfer units.

Since graphical calculations are time consuming, the use of the graphical technique to demonstrate anything other than simple tower height calculations is not practical. However, properly programmed, Equation A-16 can be solved in a matter of seconds using a digital computer. But far more effective (if the facilities are available) is to program the equations on an interactive terminal. The user may supply the required data and receive the requested answer all in a matter of minutes.

The types of one component problems that can be handled by the properly programmed equations are numerous. Figure 1 shows the general column model. The various problems possible are:

Case I:

Quantity Sought: Tower height (z)

Known: All terminal compositions, the flow rates, transfer coefficients, and equilibrium data.

Case II:

Quantity Sought: Output compositions (y_{out} and x_{out})

Known: y_{in}, x_{in}, flow rates, transfer coefficients, equilibrium data, and tower height. An initial guess of y_{out} must be supplied to the program. For an initial guess try y_{out} = 0.001 unless a better approximation to y_{out} is known.

Case III:

Quantity Sought: L' and x_{out}

Known: x_{in}, y_{in}, y_{out}, V', transfer coefficients, equilibrium data, and total tower height. (L' should be read in as zero and x_{out} as -1.)

Case IV:

Quantity Sought: V' and y_{out}

Known: x_{in}, x_{out}, y_{in}, L', transfer coefficients, equilibrium data, and total tower height. (V' should be read in as zero and y_{out} as -1.)

Case V:

Quantity Sought: Either overall transfer coefficient

Known: All terminal compositions, flow rates, total tower height, and equilibrium data. (The coefficient not under consideration should be read as zero and an initial guess of the desired coefficient should be read in.)

Sample outputs from an interactive terminal are presented in Tables E-1 through E-4.

Case I would be a straightforward numerical integration to determine tower height. However, Cases II through V require the numerical integration to be nested inside a Newton-Raphson method to search for the unknown variable.

For a one variable search, Newton's equation is:

$$S_{i+1} = S_i - \frac{f(S_i)}{\frac{d[f(S_i)]}{dS_i}} \qquad \text{(E-3)}$$

where S is the independent variable and f(S) is the dependent variable. An estimate of the independent variable is supplied with the initial data to the program. Newton's method is then used to improve on that value until the exact value is determined.

Newton's method requires a function, f, and the function must be differentiable. For a continuous contactor the function may be represented by:

$$f = (y_{in} - \hat{y}_{in}) \qquad \text{(E-4)}$$

where $\hat{y}_{in}$ = the estimate of y_{in} for a particular value of the independent variable ($k_x a$, $k_y a$, L, V, y_{out}). The differential of the function with respect to the independent variable may be estimated by:

$$\frac{d[f(S_i)]}{dS_i} = \frac{(y_{in}-\hat{y}_{in})_2 - (y_{in}-\hat{y}_{in})_1}{S_2 - S_1}. \qquad \text{(E-5)}$$

Substitution of Equations C-6 and C-7 into Equation E-5 yields:

$$S_3 = S_2 - \frac{(y_{in}-\hat{y}_{in})_2}{\left[\frac{(y_{in}-\hat{y}_{in})_2 - (y_{in}-\hat{y}_{in})_1}{S_2 - S_1}\right]}. \qquad \text{(E-6)}$$

From Equation E-6 it is obvious that two functional evaluations are necessary to start the search procedure. The initial estimate is supplied in data given to the program. The other starting value is calculated from the initial value by multiplying it by a factor (e.g., 1.05). Figure E-1 is a simplified flow diagram demonstrating the construction of the program.

Having a computer solution available for the student serves a two-fold purpose. The instructor may demonstrate principles that were previously too time consuming to do by the graphical technique. For example, the instructor may wish to show the effect on tower height of changing the L/V ratio. The student may also fabricate problems on his own to help answer questions that arise during his study time. The only mistake he could make would be to formulate a problem in which the operating and equilibrium lines crossed. That, too, would be a learning experience.

The computer solution of the one component differential equations can be a valuable teaching tool for the instructor and learning device for the student.

TABLE E-1

CALCULATION OF COLUMN HEIGHT (CASE I)

```
xeq
nal
0
na2
1
na3
1
na4
1
na5
1
na6
0
na7
0
na8
0
na9
0
na10
0
nall
1
      YOU HAVE SPECIFIED OVERALL TRANSFER COEFFICIENTS AND
                   X DRIVING FORCES


a
0,29.3,0,0,0,0
  GIVEN EQUILIBRIUM STRAIGHT LINE DATA      SLOPE=.29300000E02      INTERCEPT=.0
```

TABLE E-1 (continued)

```
xin
0,.00088,.001,.06,332,13.8,473,6.56,.05,0,0
  INITIAL CONDITIONS   XIN=0.   XOUT=.00088   YOUT=.00100   YIN=.06000   DH=.0500
                       LP=473.0000


CALCULATED OVERALL KX = 182.308282
TOWER HEIGHT = 6.750   X CALCULATED = .00087628   Y CALCULATED = .06036160117
**  41. XEQ "STOP".
```

TABLE E-2

SEARCH FOR CORRECT LIQUID PHASE FLOW RATE (CASE III)

```
load(chel33,res)user2


lp=0
xeq 31 thru ...
  INITIAL CONDITIONS   XIN=0.   XOUT=-1.00000   YOUT=.00100   YIN=.06000   DH=.5000
                       LP=0.


  YOU HAVE REQUESTED MINIMUM FLOW CALCULATIONS


THE TOWER IS OPERATING AT 1.50 TIMES THE MINIMUM L PHASE FLOW RATE   LP=301.2866484
CALCULATED OVERALL KX = 182.308282
ASSUMED FLOW RATE         CALCULATED YIN        YIN ACTUAL = .0600000000
   301.28664835              .03038013
   376.60831044              .04988410
NEW L FLOW RATE PREDICTED FROM THESE VALUES = 415.67452320
TOWER HEIGHT = 8.000   X CALCULATED = .00099050   Y CALCULATED = .05999689174
**  41. XEQ "STOP".
```

TABLE E-3

SEARCH FOR CORRECT OUTPUT COMPOSITIONS (CASE II)

```
load(chel33,res)
xeq
nal
0,1,1,1,1,0,0,0,1,0,1
     YOU HAVE SPECIFIED OVERALL TRANSFER COEFFICIENTS AND
                  X DRIVING FORCES


a
0,29.3,0,0,0,0
  GIVEN EQUILIBRIUM STRAIGHT LINE DATA   SLOPE = .29300000E02   INTERCEPT = .0


xin
0,.00088,.0001,.06,332,1388,473,6.56,.05,6.75,0
  INITIAL CONDITIONS   XIN=0.   XOUT=.00088   YOUT=.00010   YIN=.06000   DH=.0500
                       LP=473.0000


CALCULATED OVERALL KX = 182.308282
      CALCULATIONS FROM NEWTON'S ITERATION
      .00010000          .00715274
      .00010500          .00750370
  NEW YOUT PREDICTED FROM THESE VALUES = .000852882
      .00010500          .00750370
      .00085288          .05389807
  NEW YOUT PREDICTED FROM THESE VALUES = .000951246
```

TABLE E-3 (continued)

```
      .00085288           .05389807
      .00095125           .05922714
  NEW YOUT PREDICTED FROM THESE VALUES = .00096551l
TOWER HEIGHT = 6.750   X CALCULATED = .00087089   Y CALCULATED = .05998722097
**  4l. XEQ "STOP".
```

TABLE E-4

CALCULATION OF TOWER HEIGHT WITH LEAST SQUARES CURVE FITTED EQUILIBRIUM DATA

```
load(che133,res)user2
xeq
nal
1,2,1,0,1,2,0,0,0,0,1
     YOU HAVE SPECIFIED INDIVIDUAL TRANSFER COEFFICIENTS AND
                  X DRIVING FORCES


npowr
5,8
x(1)
0,0
x(2)
0,0
x(3)
.000056,.00079
x(4)
.000141,.00224
x(5)
.000281,.0062
x(6)
.000422,.0107
x(7)
.000565,.01566
x(8)
.000844,.0259
```

TABLE E-4 (continued)

```
LEAST SQUARES CURVE FIT AND DATA COMPARISON
  THE BEST FIT OBTAINED WITH AN EQUATION OF DEGREE 3
         A( 0) =       -.270274E04
         A( 1) =        .121918E02
         A( 2) =        .398960E05
         A( 3) =       -.212873E08
  Y CALCULATED          Y KNOWN           X KNOWN
  -.000027              0.                0.
  -.000027              0.                0.
   .000777               .0007900          .000056
   .002426               .0022400          .000141
   .006077               .0062000          .000281
   .010623               .0107000          .000422
   .015758               .0156600          .000565
   .025884               .0259000          .000844
     THE AAPD IS .166368007660E01


xin
0,.00088,.001,.06,332,13.8,473,6.56,.05,0,0
  INITIAL CONDITIONS   XIN=0.   XOUT=.00088   YOUT=.00100   YIN=.06000   DH=.0500
                       LP=473.0000


  INDIVIDUAL COEFFICIENTS      KX = 332.000000      KY = 13.800000
TOWER HEIGHT = 5.300      X CALCULATED = .00094140      Y CALCULATED = .06449691795
**  41. XEQ "STOP".
```

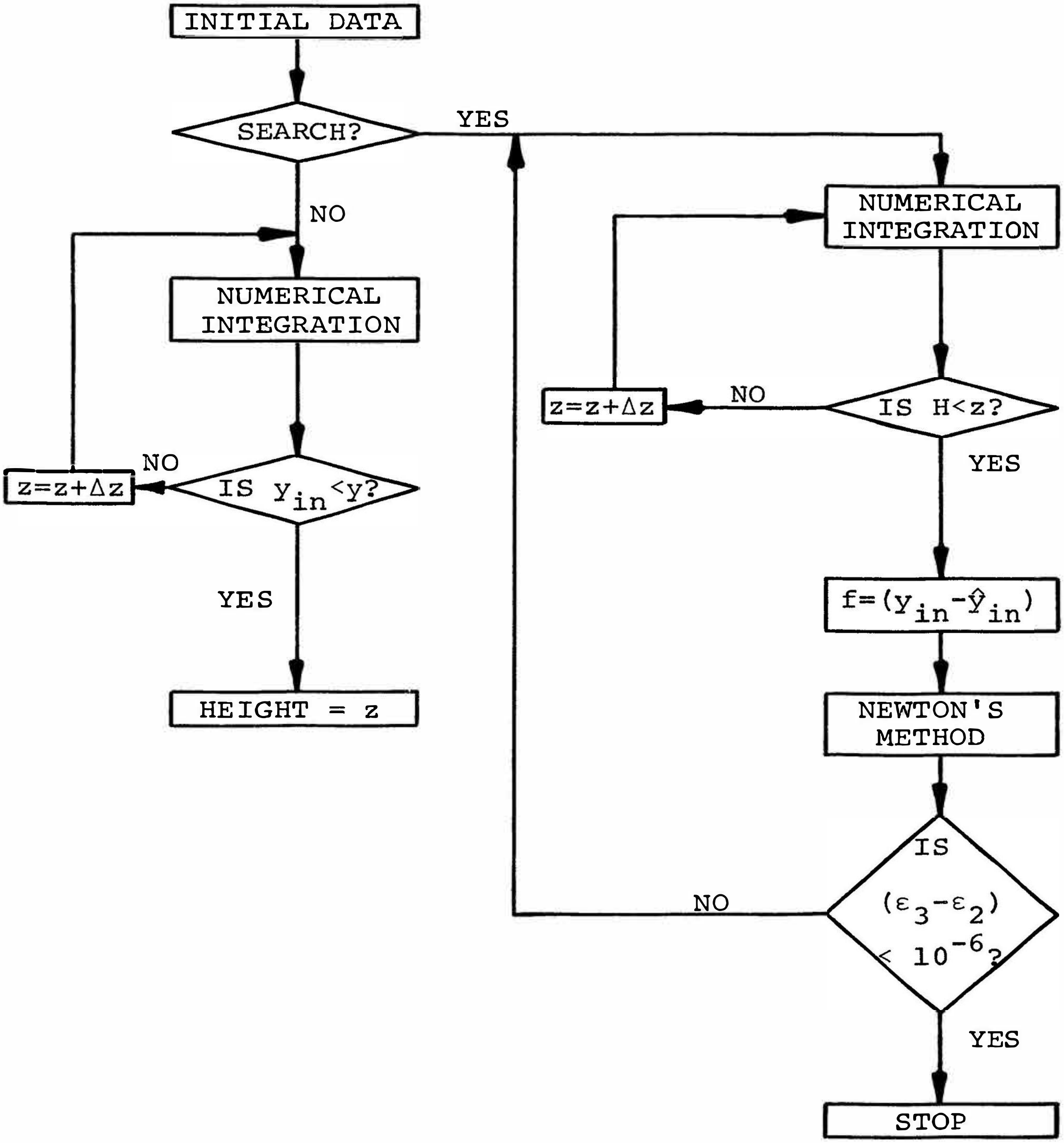

Figure E-1. Flow Diagram for One Component Transfer Computer Program Including Newton's Method

APPENDIX F

COMMENTS ON THE WORK OF CALLIHAN

Often the work of the design engineer requires him to not only design equipment (i.e., establish operating conditions and determine tower height) but to determine the capabilities and characteristics of equipment already existing in the plant. This is particularly true when a new product will be made in an installation already established. Here, the design engineer would be concerned with throughput, percent recovery, output compositions, and other operating parameters for a known absorber and absorber height. Callihan[5] has proposed such a technique and it is an objective of this work to generalize the Callihan method for multicomponent absorbers and for absorber-reactors.

Callihan built his computer program around the numerical solution of:

$$\frac{dy}{dz} = \frac{(1-y)}{V'} k_y a \ (y-y^i) \qquad \text{(A-15a)}$$

$$\frac{dx}{dz} = \frac{(1-x)}{L'} k_x a \ (x^i-x) \qquad \text{(A-15b)}$$

using the Runge-Kutta method (described in detail in Appendix B). These equations describe one component mass transfer in a continuous contactor.

The numerical solution would generate compositions at various points in the column. These compositions would be

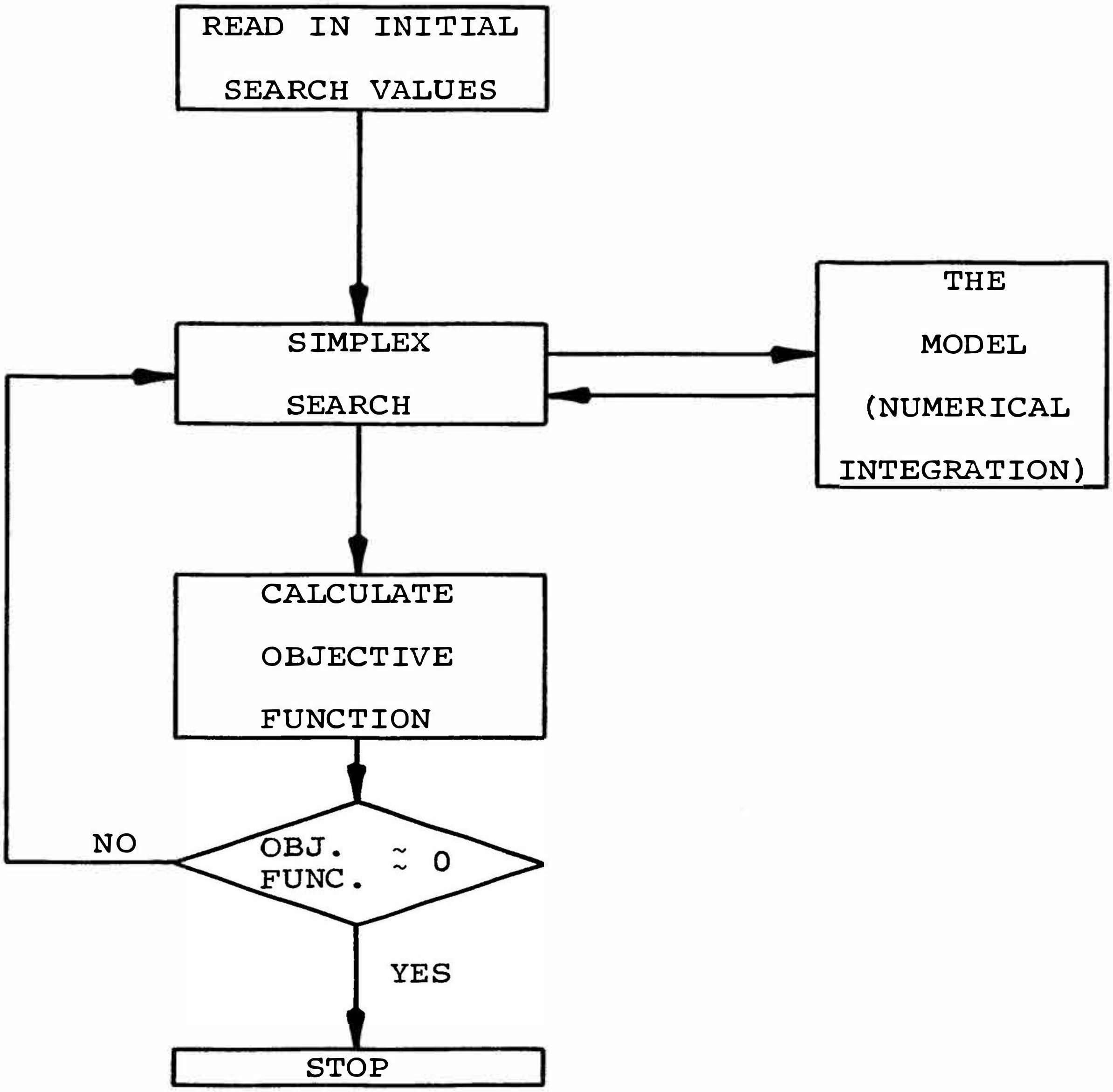

Figure F-1. Simplified Flow Diagram of Callihan's Program used to calculate the objective function (Figure F-1). The objective function chosen was:

$$S = \sum_{j=1}^{NDATA} (y_j - \hat{y}_j)^2 = g\ (k_y a,\ k_x a) \qquad \text{(F-1)}$$

where y_j is the known vapor composition at a given column height and $\hat{y}_j$ is the calculated vapor composition at a given column height. Using the Nelder-Mead[17] technique, a search was performed to find the minimum value of S $(k_x a,\ k_y a)$.

An example may better illustrate this technique. Consider the equation:

$$y = 100 - (10 - x_1)^2 - (5 - x_2)^2 = g\ (x_1,\ x_2). \qquad \text{(F-2)}$$

If the Nelder-Mead method were used to find a minimum of Equation F-2, then:

$$S = (y - \hat{y})^2 \qquad \text{(F-3)}$$

where y is the desired value of the function and $\hat{y}$ is the calculated value of the function for a given $x_1 x_2$. The object is to minimize S. The initial guess of x_1 and x_2 would be made; the Nelder-Mead would calculate two other sets of the independent variables, calculate the y's and proceed to minimize S. The function $g(x_1, x_2)$ represents the numerical solution of the model. Every time the Nelder-Mead requests a value, y, numerical integration must be performed to calculate the vapor composition profile.

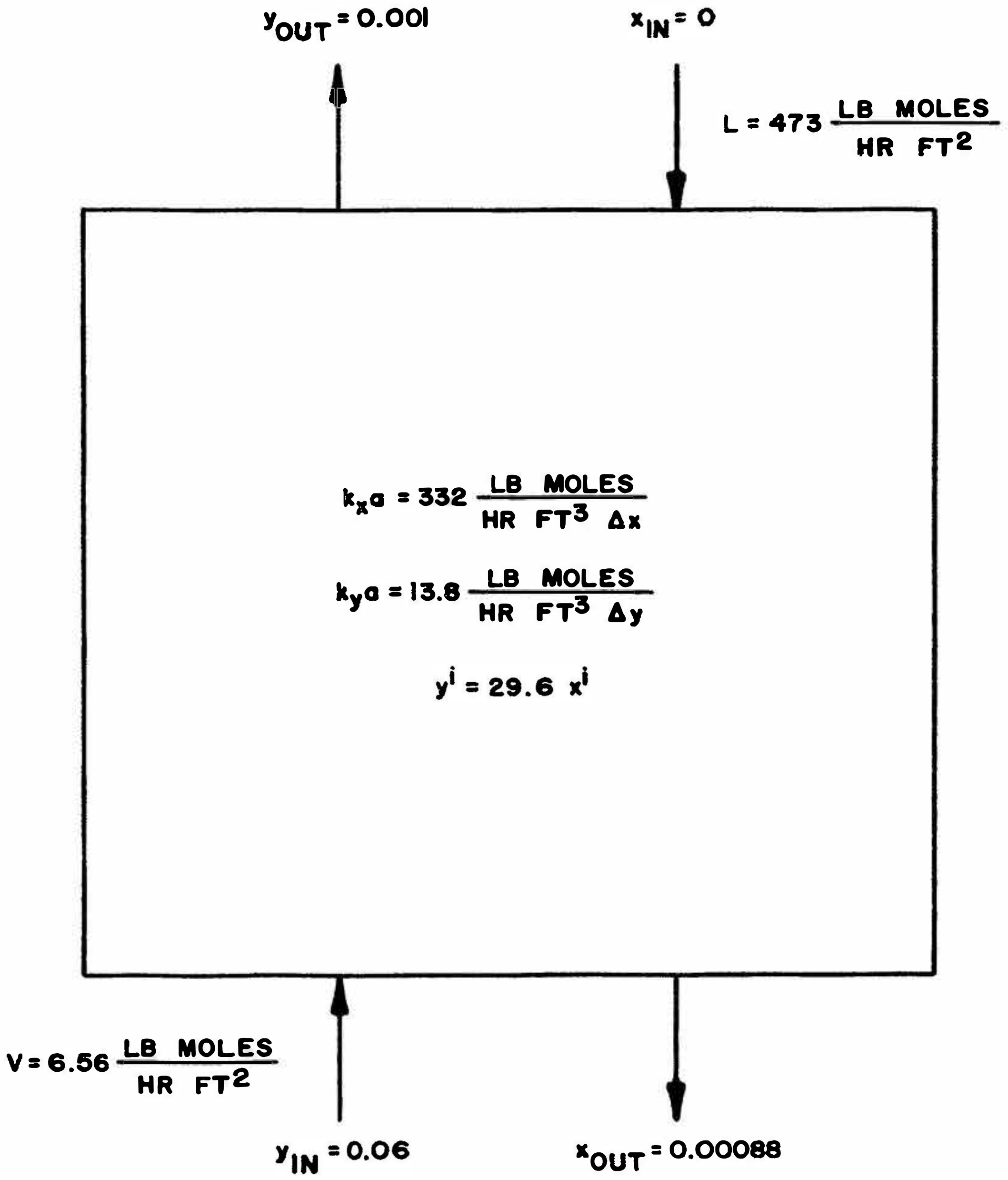

Figure F-2. Operating Conditions for Callihan's Problem

Although vapor composition profiles were unavailable from actual plant columns, the data required were simulated using a problem from Foust[12] and are presented in Figure F-2. The vapor composition profile in the column was generated using a computer and calculated from the formula:

$$\text{Random Error} = st\left(\frac{12}{M}\right)^{0.5}\left(r-\frac{M}{2}\right) \qquad \text{(F-4)}$$

where st is the standard deviation of desired experimental error, M is the number of increment at which the data are taken, and r is $\sum_{j=1}^{M}$ (random number between 0 and 1). Random error was added to each of the points in the vapor composition profile to make the profile more closely represent one that had been obtained experimentally.

The operating conditions of interest (i.e., $k_y a$, $k_x a$) are assumed unknown and an "estimate" of their value (e.g., 1.15 $k_y a$, 1.15 $k_x a$) is used as the starting values for the search which is continued until S (the value of the objective function) is reduced to nearly zero.

Callihan chose four different search techniques -- the sequential simplex, accelerated simplex, complex method of Box, and the Nelder-Mead. Callihan demonstrated that the Nelder-Mead was more efficient than any other method chosen and, therefore, it is the only method considered in this work. A flow diagram of the Nelder-Mead method is presented in Figure F-3 (in the nomenclature of Callihan).

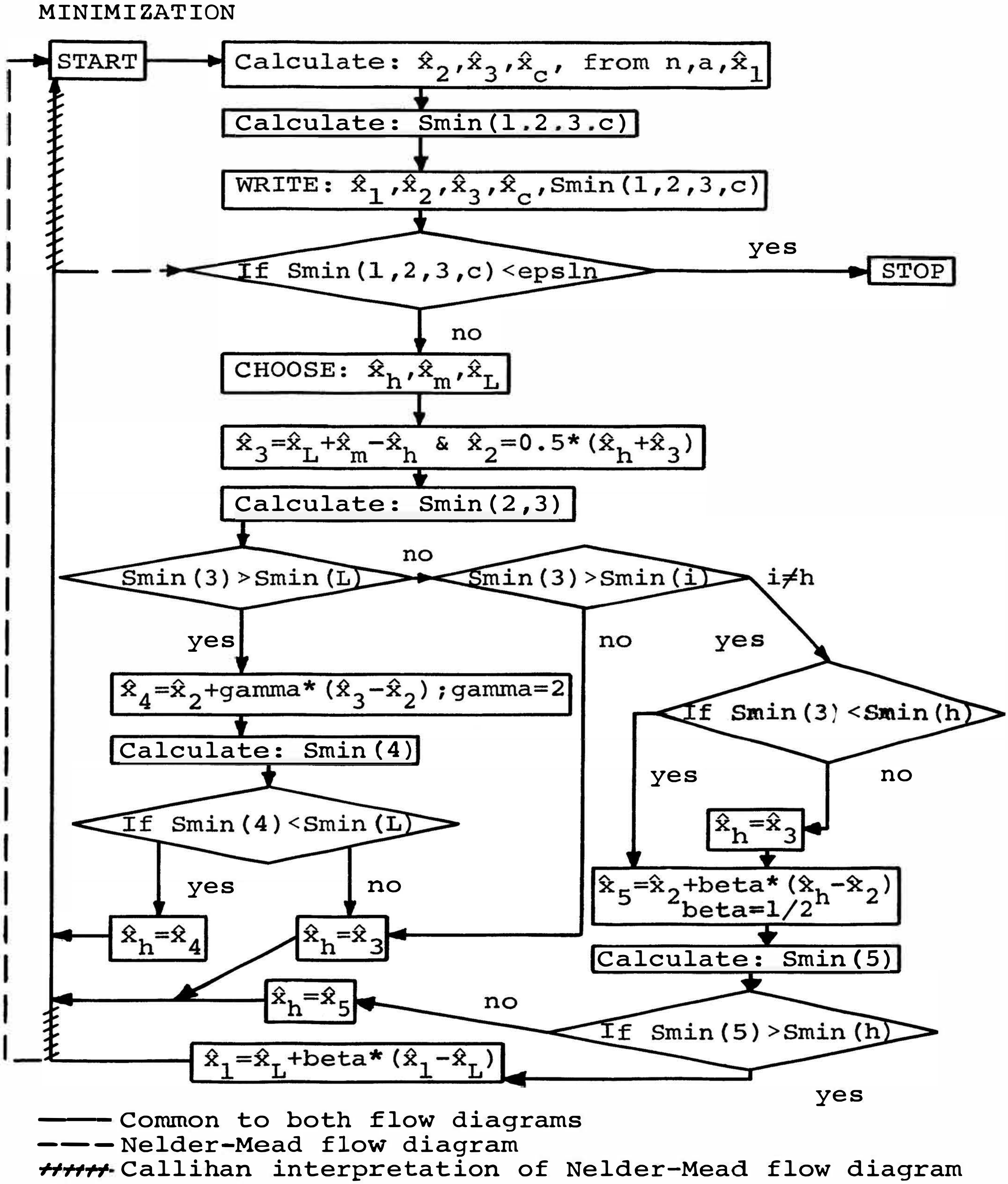

Figure F-3. Comparison of the Nelder-Mead Flow Diagram with Callihan's Interpretation of the Nelder-Mead Method

Figure F-1 illustrates how the equations of the search technique and of the model are integrated. The search procedure calculates a better approximation to the optimum of the search variables (i.e., k_ya, k_xa). The updated values are used by the model to calculate new values for the vapor composition profile which is used to evaluate a new value of the objective function. With the updated values the search begins again until the objective function, S, is found, as above, to be below some predetermined value and the search is discontinued.

Unfortunately the searching technique to determine operating parameters (in this case, k_ya and k_xa) failed to find the optimal values for any problem attempted. A close examination of Callihan's development of his method and his data in addition to the data generated in this work will conclusively show that Callihan's method never functioned properly and probably the idea of searching for operating variables in this manner will never work.

Callihan's development must be considered first, for it is precisely that which caused his data to be generated in such a way that it gave erroneous results and caused him to draw false conclusions.

Callihan has apparently misinterpreted the flow chart presented by Nelder-Mead[17]. Although the chart is somewhat misleading, the text of the article makes clear the procedure for generating a new simplex. The discussion (p. 308 ff.) details a procedure to replace the search variable (x) in the simplex with the largest value of the objective function. The new simplex is used to calculate a better approximation of the search variables. The process is continued until the objective function, S, is minimized.

Callihan, however, appears to have misinterpreted Nelder-Mead's figure 1 (p. 309). His method calculates a new simplex each iteration from the search variable with the smallest value of the objective function. The procedure is not incorrect; it is just not the Nelder-Mead method. The differences between the two methods are illustrated in the nomenclature of Callihan in Figure F-3. The result is that the Callihan procedure performs three times as many functional evaluations at each increment as the Nelder-Mead. Therefore, when Callihan claims his Nelder-Mead converged in nine iterations it is equivalent to a normal Nelder-Mead of twenty-seven iterations.

Callihan was also fortunate in his choice of starting values. The chosen values cause the altered Nelder-Mead to give the illusion of proceeding to and finding the optimum. From the Foust example problem the optimum values of $k_x a$ and $k_y a$ are 332 lb moles/hr ft^3 Δx and 13.8 lb moles/hr ft^3 Δy respectively. The starting values chosen (for the case of starting above the optimum) are $k_xa = 400$ and $k_ya = 50$. The starting value for k_xa is approximately 20 percent and k_ya is approximately 260 percent above the optimum although Callihan claimed to be starting at 15 percent above the optimum. Since k_ya was a great distance from the answer, the Nelder-Mead will cause the simplex to expand for the first few iterations in an attempt to bring the search closer to the answer. These large steps toward the optimum plus the special method Callihan used to calculate the simplex of points used in the search (to be discussed next) forced the value of k_xa toward the optimum.

Schechter and Beveridge[4] present a scheme for calculating the starting values of the simplex from the initial estimate of the unknown variables. For a two variable search the scheme would be:

		Variable	
		1	2
Points in the Simplex	1	k_xa	k_ya
	2	$k_xa + p$	$k_ya + q$
	3	$k_xa + q$	$k_ya + p$

where

$$p = \frac{a}{n\sqrt{2}} [\sqrt{n+1} + n-1] = \frac{a}{2\sqrt{2}} (\sqrt{3}+1)$$

$$q = \frac{a}{n\sqrt{2}} [\sqrt{n+1} - 1] = \frac{a}{2\sqrt{2}} (\sqrt{3}-1)$$

$p \neq q$

n = number of variables ($n=2$)

a = length of a side of the initial simplex

Callihan[5] presents the calculation of the starting simplex in the form of a flow chart. Translating the flow chart into a table as above gives:

		Variable	
		1	2
Points in the Simplex	1	$k_x a$	$k_y a$
	2	$k_x a + p$	$k_y a + p$
	3	$k_x a + q$	$k_y a + q$

The first iteration of each of the starting simplex of Callihan's data[5] substantiates the above.

The slight alteration made in the generation of the starting simplex, the fortunate choice of starting values, and the minor modification of the Nelder-Mead itself is precisely what makes the method appear to find the optimum. In reality, the above errors work together to "guide" the search technique close to the optimum.

Table F-1 shows that a different choice of starting values will not produce the same optimum but an entirely different one. If the search technique is not "guided", it locates a local optimum which is away from the global

TABLE F-1

A SUMMARY OF THE RESULTS OF SCHWAB AND CALLIHAN USING THE NELDER-MEAD METHOD

Description	Starting Values			Final Values		
	k_xa	k_ya	Obj. Function	k_xa	k_ya	Obj. Function
Callihan's Thesis						
1% error	400	50	0.3573E-01	364.15	14.15	0.5868E-04
1% error	320	5	0.9736E-03	345.27	15.27	0.6013E-04
1% error	500	100	0.2220E-00	376.59	13.59	0.5839E-04
15% error	500	100	0.7480E-03	371.85	21.49	0.6338E-04
15% error	1800	500	0.7497E-00	371.65	21.65	0.2288E-03
This work 1% error using Callihan procedure for calculating new simplex.	400	50	0.3470E-00	362.61	12.61	0.4171E-6
	380	50	0.6475E-01	343.3	13.31	0.6673E-7
	400	20	0.1983E-01	391.73	11.74	0.1655E-6
	350	20	0.2166E-01	343.29	13.29	0.4623E-8
This work 1% error using normal N-M method.	350	20	0.1476E-03	359.08	12.68	0.4066E-4
	300	9.0	0.4906E-02	305.91	15.33	0.5712E-4

optimum.

THE NATURE OF THE SURFACE

The nature of the surface is the real problem in attempting to make the technique work. The surface generated by the objective function:

$$y = \sum_{j=1}^{NDATA} (y_j - \hat{y}_j)^2 = g\ (\underline{A}) \qquad (F-5)$$

has multiple optima. Tables D-7 through D-9 clearly show the presence of multiple optima. Once the value of k_ya approaches the global optimum within 4-5 percent, the k_xa value ceases to change even though it may be more than 15 percent away from the global optimum. The search technique ceases to move because it has encountered a local optimum. The method begins to contract the search area once it discovers a local optimum and never moves from the area. Table D-9 shows the results of starting the search at various locations around the global optimum. It is impossible to locate the global optimum because it is surrounded by local optima.

If k_ya is fixed and values of the objective function are calculated for a number of k_xa values, the presence of the multiple optima is revealed. An abundance of local optima exist around the global optimum as is indicated by a careful study of Tables F-2, F-3, and F-4. A surface with multiple optima in close proximity to each other

TABLE F-2

STARTING AND FINAL VALUES FOR A NELDER-MEAD SEARCH USING THE CALLIHAN PROBLEM

Random Error	Starting Values		Obj. Function	Final Values		Obj. Function	Itera-tions
	k_xa	k_ya		k_xa	k_ya		
0% Error	332	13.8	0.4548E-16	332	13.8	0.4548E-16	3
1% Error ABS($y-\hat{y}$)	300	3.0	0.5418E-01	307.54	15.2	0.8337E-5	31
1% Error	307.32	14.959	0.1450E-02	307.84	15.18	0.1439E-6	31
	300	3.0	0.6791E-02	307.69	15.19	0.3150E-8	22
1% Error	350	20.0	0.1476E-03	359.08	12.68	0.4066E-4	30
1% Error	300	9.0	0.4906E-02	305.91	15.33	0.5712E-4	35
0% Error	332	13.8	0.1087E-11	332	13.8	0.1087E-11	3
1% Error	350	13.8	0.1599E-01	350.17	13.01	0.1892E-4	33
1% Error	332	15.0	0.2980E-01	332.38	13.78	0.9549E-8	33
0% Error	332	14.0	0.8077E-01	333.7	13.72	0.2197E-6	33
Callihan's starting method							
1% Error	400	50.0	0.3469E-00	362.61	12.61	0.4171E-6	17
1% Error	380	50.0	0.2632E-00	343.3	13.31	0.6673E-7	13
1% Error	400	20.0	0.1983E-01	391.73	11.74	0.1655E-6	14
1% Error	350	20.0	0.2166E-01	343.29	13.29	0.4623E-8	24

TABLE F-3

STARTING AND FINAL VALUES USING ANALYTIC EQUATIONS AND ZERO PERCENT RANDOM ERROR (FOUST[12] ILL. 16.3)

Starting Values		Obj. Function	Final Values		Obj. Function
k_xa	k_ya		k_xa	k_ya	
332	13.8	0.1635E-15	332	13.8	0.1635E-15
350	8.0	0.3004E-02	353.58	12.85	0.4781E-12
339	7.0	0.4150E-02	342.49	13.31	0.2222E-12
360	14.0	0.3739E-03	361.03	12.58	0.4844E-12
310	14.0	0.1037E-03	310.25	15.07	0.2691E-13
350	20.0	0.1016E-01	350.55	12.97	0.7562E-13
300	20.0	0.1298E-02	300.43	15.80	0.4708E-13
339	20.0	0.7228E-02	337.57	13.53	0.1563E-15
300	8.0	0.3807E-02	303.44	15.57	0.1467E-12

(Final values are 40 iterations of Nelder-Mead except for first set.)

TABLE F-4

STARTING AND FINAL VALUES USING ANALYTIC EQUATIONS AND FIVE PERCENT RANDOM ERROR (FOUST[12] ILL. 16.3)

Starting Values		Obj. Function	Final Values		Obj. Function
k_xa	k_ya		k_xa	k_ya	
332	13.8	0.1350E-04	332.32	13.7	0.1263E-04
360	14.0	0.4238E-03	360.67	12.52	0.1263E-04
300	8.0	0.3706E-02	302.64	15.52	0.1263E-04
339	7.0	0.4044E-02	342.25	13.24	0.1263E-04
350	8.0	0.2915E-02	353.25	12.79	0.1263E-04
310	4.0	0.9810E-04	311.50	14.89	0.1263E-04
350	20.0	0.1037E-01	350.21	12.91	0.1263E-04
339	20.0	0.7398E-02	337.99	13.43	0.1263E-04
300	20.0	0.1379E-02	300.72	15.67	0.1263E-04

(Final values are 40 iterations of Nelder-Mead.)

prohibits the use of any searching technique. Several attempts were made at smoothing the surface, but smoothing would not remove the local optima.

Because of the slight error introduced at each step of the Runge-Kutta numerical integration, Equation 16 was solved analytically and used to replace the numerical integration in the computer program. The data, presented in Tables F-3 and F-4, show the multiple optima on the surface.

There can be only one conclusion -- multiple optima. Let those who use similar techniques beware, since the same misfortune may befall them.

APPENDIX G

ANALYTIC SOLUTION OF THE ONE COMPONENT DILUTE SOLUTION EQUATIONS

The analytic solution of the one component dilute solution equations developed in Appendix A:

$$\frac{dy}{dz} = \frac{k_y a}{V'} (y-y^i) \qquad \text{(A-16a)}$$

$$\frac{dx}{dz} = \frac{k_x a}{L'} (x^i-x) \qquad \text{(A-16b)}$$

can be of extreme value especially in verifying results obtained from a numerical solution. Equation A-16 can be solved with Laplace transforms.

An overall material balance on the transferring component yields:

$$V' \frac{dy}{dz} = L' \frac{dx}{dz} \ . \qquad \text{(G-1)}$$

Substitution of Equation A-16 into Equation G-1 gives:

$$k_y a \ (y-y^i) = k_x a \ (x^i-x) . \qquad \text{(G-2)}$$

If the equilibrium data is linear of the form:

$$y^i = mx^i , \qquad \text{(G-3)}$$

Equation G-2 may be solved for x^i and y^i to give:

$$y^i = \frac{k_x a \ x + k_y a \ y}{k_x a + k_y a} \qquad \text{(G-4a)}$$

$$x^i = \frac{k_x a \ x + k_y a \ y}{k_x a + k_y a \ m} \ . \qquad \text{(G-4b)}$$

Insertion of Equations G-4 and G-5 into Equations A-16a and A-16b respectively gives:

$$\frac{dy}{dz} - \left[\frac{k_y a\ y}{V'} - \frac{k_y a}{V'}\left(\frac{k_x a\ x + k_y a\ x}{\frac{k_x a}{m} + k_y a}\right)\right] = 0 \qquad \text{(G-5a)}$$

$$\frac{dx}{dz} - \left[\frac{k_x a}{L'}\left(\frac{k_x a\ x + k_y a\ y}{k_x a + k_y a\ m}\right) - \frac{k_x a\ x}{L'}\right] = 0. \qquad \text{(G-5b)}$$

Taking the Laplace transform of the above gives:

$$s\bar{y}(s) - y(0) - \frac{KY}{V'}\bar{y}(s) + \frac{KY\ KX\ m}{V'M} + \frac{(KY)^2 m}{V'M} = 0 \qquad \text{(G-6a)}$$

$$s\bar{x}(s) - x(0) - \frac{(KX)^2}{L'M}\bar{x}(s) + \frac{KX\ KY}{L'M}\bar{y}(s) + \frac{KX}{L'}\bar{x}(s) = 0, \qquad \text{(G-6b)}$$

where

$$KX = k_x a$$

$$KY = k_y a$$

$$M = k_y a + k_x a\ m$$

$$x(0) = x_{in}$$

$$y(0) = y_{out}$$

Rearranging Equation G-6 yields:

$$\bar{x}(s)\frac{KX\ KY\ m}{V'M} + \bar{y}(s)\left[s + \frac{(KY)^2 m}{V'M} - \frac{KY}{V'}\right] = y_{out} \qquad \text{(G-7a)}$$

$$\bar{x}(s)\left[s + \frac{KX}{L'} - \frac{(KX)^2}{L'M}\right] + \bar{y}(s)\frac{KX\ KY}{L'M} = x_{in} \qquad \text{(G-7b)}$$

and solving for $\bar{x}(s)$ and $\bar{y}(s)$ results in:

$$\bar{y}(s) = \frac{y_{out}\ s + \frac{KX\ KY\ m}{M}\left[\frac{y_{out}}{L'} - \frac{x_{in}}{V'}\right]}{s\ \left(s + \frac{KX\ KY\ m}{L'M} - \frac{KX\ KY}{V'M}\right)} \tag{G-8a}$$

$$\bar{x}(s) = \frac{x_{in}\ s + \frac{KX\ KY}{M}\left(\frac{y_{out}}{L'} - \frac{x_{in}}{V'}\right)}{s\ \left(s + \frac{KX\ KY\ m}{L'M} - \frac{KX\ KY}{V'M}\right)}\ . \tag{G-8b}$$

The Laplace Equation (G-8) can be solved by partial fractions for x and y:

$$y = \frac{\left[\frac{m\ y_{out}}{L'} - \frac{m\ x_{in}}{V'}\right]}{\frac{m}{L'} - \frac{1}{V'}} + \frac{\frac{x_{in}\ m}{V'} - \frac{y_{out}}{V'}}{\frac{m}{L'} - \frac{1}{V'}}\ e^{-\left(\frac{k_x a\ k_y a\ m}{L'M} - \frac{k_x a\ k_y a}{V'M}\right) z} \tag{G-9a}$$

$$x = \frac{\frac{y_{out}}{L'} - \frac{x_{in}}{V'}}{\frac{m}{L'} - \frac{1}{V'}} + \frac{\frac{x_{in}\ m}{L'} - \frac{y_{out}}{L'}}{\frac{m}{L'} - \frac{1}{V'}}\ e^{-\left(\frac{k_x a\ k_y a\ m}{L'M} - \frac{k_x a\ k_y a}{V'M}\right) z}\ . \tag{G-9b}$$

In Equation G-9, vapor and liquid compositions are represented as a function of column height and can be used to validate computer results for one component transferring systems.

APPENDIX H

APPLICATION OF THE GENERAL MULTICOMPONENT MASS AND ENERGY BALANCE EQUATIONS WITH CHEMICAL REACTION

The purpose of this section is to apply the general equations for multicomponent mass and energy transfer with chemical reaction to a specific example. For the purpose of this development, consider a three transferring component nonisothermal problem with two of the components reacting with a reactant from the liquid phase. Equation 12 describes the stoichiometry of the reaction and Equation 13 describes the rate of reaction. The carrier gas is noncondensing and the carrier liquid is nonvolatile.

Equation A-37, which describes the change in the vapor phase concentration with respect to column height, becomes:

$$\frac{dy_1}{dz} = \frac{(1-y_1-y_2-y_3)}{V'} [(1-y_1)\ (k_ya)_1\ (y_1-y_1^i) - y_1\ (k_ya)_2\ (y_2-y_2^i) - y_1\ (k_ya)_3\ (y_3-y_3^i)] \tag{H-1a}$$

$$\frac{dy_2}{dz} = \frac{(1-y_1-y_2-y_3)}{V'} [(1-y_2)\ (k_ya)_2\ (y_2-y_2^i) - y_2\ (k_ya)_1\ (y_1-y_1^i) - y_2\ (k_ya)_3\ (y_3-y_3^i)] \tag{H-1b}$$

$$\frac{dy_3}{dz} = \frac{(1-y_1-y_2-y_3)}{V'} [(1-y_3)\ (k_ya)_3\ (y_3-y_3^i) - y_3\ (k_ya)_1\ (y_1-y_1^i) - y_3\ (k_ya)_2\ (y_2-y_2^i)] \tag{H-1c}$$

$$\frac{dy_4}{dz} = 0 \tag{H-1d}$$

$$\frac{dy_5}{dz} = 0 \tag{H-1e}$$

$$\frac{dy_6}{dz} = 0 \tag{H-1f}$$

Equation A-48, which describes the change of concentration with respect to column height, in the liquid phase becomes:

$$\frac{dx_1}{dz} = \frac{(1-x_1-x_2-x_3-x_4-x_5-x_6)}{L'} \{(1-x_1)\ [E_1\ (k_x a)_1\ (x_1^i-x_1) - r_1] - x_1\ [E_2\ (k_x a)_2\ (x_2^i-x_2) - r_2] - x_1\ (k_x a)_3\ (x_3^i-x_3) - x_1\ p_1\ r_1 - x_1\ p_2\ r_2 - x_1\ [-\ b_1\ r_1 - b_2\ r_2]\} \tag{H-2a}$$

$$\frac{dx_2}{dz} = \frac{(1-x_1-x_2-x_3-x_4-x_5-x_6)}{L'} \{(1-x_2)\ [E_2\ (k_x a)_2\ (x_2^i-x_2) - r_2] - x_2\ [E_1\ (k_x a)_1\ (x_1^i-x_1) - r_1] - x_2\ (k_x a)_3\ (x_3^i-x_3) - x_2\ p_1\ r_1 - x_2\ p_2\ r_2 - x_2\ [-\ b_1\ r_1 - b_2\ r_2]\} \tag{H-2b}$$

$$\frac{dx_3}{dz} = \frac{(1-x_1-x_2-x_3-x_4-x_5-x_6)}{L'} \{(1-x_3)\ (k_x a)_3\ (x_3^i-x_3) - x_3\ [E_1\ (k_x a)_1\ (x_1^i-x_1) - r_1] - x_3\ [E_2\ (k_x a)_2\ (x_2^i-x_2) - r_2] - x_3\ p_1\ r_1 - x_3\ p_2\ r_2 - x_3\ [-\ b_1\ r_1 - b_2\ r_2]\} \tag{H-2c}$$

$$\frac{dx_4}{dz} = \frac{(1-x_1-x_2-x_3-x_4-x_5-x_6)}{L'} \{(1-x_4)\ p_1\ r_1 - x_4\ [E_1\ (k_xa)_1\ (x_1^i-x_1) - r_1] - x_4\ [E_2\ (k_xa)_2\ (x_2^i-x_2) - r_2] - x_4\ (k_xa)_3\ (x_3^i-x_3) - x_4\ p_2\ r_2 - x_4\ [-\ b_1\ r_1 - b_2\ r_2]\} \tag{H-2d}$$

$$\frac{dx_5}{dz} = \frac{(1-x_1-x_2-x_3-x_4-x_5-x_6)}{L'} \{(1-x_5)\ p_2\ r_2 - x_5\ [E_1\ (k_xa)_1\ (x_1^i-x_1) - r_1] - x_5\ [E_2\ (k_xa)_2\ (x_2^i-x_2) - r_2] - x_5\ (k_xa)_3\ (x_3^i-x_3) - x_5\ p_1\ r_1 - x_5\ [-\ b_1\ r_1 - b_2\ r_2]\} \tag{H-2e}$$

$$\frac{dx_6}{dz} = \frac{(1-x_1-x_2-x_3-x_4-x_5-x_6)}{L'} \{(1-x_6)\ [-\ b_1\ r_1 - b_2\ r_2] - x_6\ [E_1\ (k_xa)_1\ (x_1^i-x_1) - r_1] - x_6\ [E_2\ (k_xa)_2\ (x_2^i-x_2) - r_2] - x_6\ (k_xa)_3\ (x_3^i-x_3) - x_6\ p_1\ r_1 - x_6\ p_2\ r_2\} \tag{H-2f}$$

To fully describe the problem, the energy equations must also be presented. For the vapor phase, Equation A-54 would become:

$$
\begin{aligned}
\frac{dt_V}{dz} = \{ & h_V a\ (t_V - t^i) + \frac{V'}{(1-y_1-y_2-y_3)} \frac{dy_1}{dz} [(Cp_L)_1\ (t^i - t_R) + \\
& (Q_V)_1 + (Cp_V)_1\ (t_V - t^i)] + \frac{V'}{(1-y_1-y_2-y_3)} \frac{dy_2}{dz} [(Cp_L)_2 \\
& (t^i - t_R) + (Q_V)_2 + (Cp_V)_2\ (t_V - t^i)] - \frac{V'}{(1-y_1-y_2-y_3)} \frac{dy_3}{dz} \\
& [(Cp_L)_3\ (t^i - t_R) + (Q_V)_3 + (Cp_V)_3\ (t_V - t^i)] - V'\ (t_V - \\
& t_R) \frac{d(Cp_V)_{N+1}}{dz} - V'\ (t^i - t_R) \frac{y_1}{(1-y_1-y_2-y_3)} \frac{d(Cp_L)_1}{dz} - V' \\
& (t^i - t_R) \frac{y_2}{(1-y_1-y_2-y_3)} \frac{d(Cp_L)_2}{dz} - V'\ (t^i - t_R) \\
& \frac{y_3}{(1-y_1-y_2-y_3)} \frac{d(Cp_L)_3}{dz} - V'\ (t_V - t^i) \frac{y_1}{(1-y_1-y_2-y_3)} \\
& \frac{d(Cp_V)_1}{dz} - V'\ (t_V - t^i) \frac{y_2}{(1-y_1-y_2-y_3)} \frac{d(Cp_V)_2}{dz} - V'\ (t_V - \\
& t^i) \frac{y_3}{(1-y_1-y_2-y_3)} \frac{d(Cp_V)_3}{dz} - V'\ [(Cp_L)_1\ (t^i - t_L) + \\
& (Q_V)_1 + (Cp_V)_1\ (t_V - t^i)]\ [\frac{(1-y_2-y_3)}{(1-y_1-y_2-y_3)^2} \frac{dy_1}{dz} + \\
& \frac{y_1}{(1-y_1-y_2-y_3)^2} \frac{dy_2}{dz} + \frac{y_1}{(1-y_1-y_2-y_3)^2} \frac{dy_3}{dz}] - V'\ [(Cp_L)_2 \\
& (t^i - t_L) + (Q_V)_2 + (Cp_V)_2\ (t_V - t^i)]\ [\frac{(1-y_1-y_3)}{(1-y_1-y_2-y_3)^2} \\
& \frac{dy_2}{dz} + \frac{y_2}{(1-y_1-y_2-y_3)^2} \frac{dy_1}{dz} + \frac{y_2}{(1-y_1-y_2-y_3)^2} \frac{dy_3}{dz}] - V'
\end{aligned}
$$

$$[(Cp_L)_3 \ (t^i - t_L) + (Q_V)_3 + (Cp_V)_3 \ (t_V - t^i)]$$

$$[\frac{(1-y_1-y_2)}{(1-y_1-y_2-y_3)^2} \frac{dy_3}{dz} + \frac{y_3}{(1-y_1-y_2-y_3)^2} \frac{dy_1}{dz} +$$

$$\frac{y_3}{(1-y_1-y_2-y_3)^2} \frac{dy_2}{dz}]\} \ / \ [V' \ (Cp_V)_{N+1} + V' \ (Cp_V)_1$$

$$\frac{y_1}{(1-y_1-y_2-y_3)} + V' \ (Cp_V)_2 \ \frac{y_2}{(1-y_1-y_2-y_3)} + V' \ (Cp_V)_3$$

$$\frac{y_3}{(1-y_1-y_2-y_3)}] \qquad \text{(H-3a)}$$

and for the liquid phase, Equation A-61 would become:

$$\frac{dt_L}{dz} = \{h_L a \ (t^i - t_L) + \frac{L'}{(1-x_1-x_2-x_3-x_4-x_5-x_6)} \frac{dx_1}{dz} [(Cp_L)_1$$

$$(t^i - t_R) + (Q_V)_1 + (Q_s)_1 + (Cp_V)_1 \ (t_V - t^i)] +$$

$$\frac{L'}{(1-x_1-x_2-x_3-x_4-x_5-x_6)} \frac{dx_2}{dz} [(Cp_L)_2 \ (t^i - t_R) + (Q_V)_2 +$$

$$(Q_s)_2 + (Cp_V)_2 \ (t_V - t^i)] + \frac{L'}{(1-x_1-x_2-x_3-x_4-x_5-x_6)} \frac{dx_3}{dz}$$

$$[(Cp_L)_3 \ (t^i - t_R) + (Q_V)_3 + (Q_s)_3 + (Cp_V)_3 \ (t_V - t^i)]$$

$$\frac{L'}{(1-x_1-x_2-x_3-x_4-x_5-x_6)} \frac{dx_1}{dz} \Delta H_{rx_1} +$$

$$\frac{L'}{(1-x_1-x_2-x_3-x_4-x_5-x_6)} \frac{dx_2}{dz} \Delta H_{rx_2} +$$

$$\frac{L'}{(1-x_1-x_2-x_3-x_4-x_5-x_6)} [\frac{dx_4}{dz} p_1 \ (Cp_L)_4 - \frac{dx_1}{dz} (Cp_V)_1]$$

$$(t^i-77) + \frac{L'}{(1-x_1-x_2-x_3-x_4-x_5-x_6)} [\frac{dx_5}{dz} p_2 \ (Cp_L)_5 - \frac{dx_2}{dz}$$

$$(Cp_V)_2] \ (t^i-77) - L' \ (t_L-t_R) \ \frac{x_1}{(1-x_1-x_2-x_3-x_4-x_5-x_6)}$$

$$\frac{d(Cp_L)_1}{dz} L' \ (t_L-t_R) \ \frac{x_2}{(1-x_1-x_2-x_3-x_4-x_5-x_6)} \ \frac{d(Cp_L)_2}{dz} -$$

$$L' \ (t_L-t_R) \ \frac{x_3}{(1-x_1-x_2-x_3-x_4-x_5-x_6)} \ \frac{d(Cp_L)_3}{dz} - L' \ (t_L-$$

$$t_R) \ \frac{x_4}{(1-x_1-x_2-x_3-x_4-x_5-x_6)} \ \frac{d(Cp_L)_4}{dz} - L' \ (t_L-t_R)$$

$$\frac{x_5}{(1-x_1-x_2-x_3-x_4-x_5-x_6)} \ \frac{d(Cp_L)_5}{dz} - L' \ (t_L-t_R)$$

$$\frac{x_6}{(1-x_1-x_2-x_3-x_4-x_5-x_6)} \ \frac{d(Cp_L)_6}{dz} - L' \ (t_L-t_R) \ \frac{d(Cp_L)_{N+1}}{dz}$$

$$- \frac{L'}{(1-x_1-x_2-x_3-x_4-x_5-x_6)} \ (Cp_L)_1 \ (t^i-t_R)$$

$$[\frac{(1-x_2-x_3-x_4-x_5-x_6)}{(1-x_1-x_2-x_3-x_4-x_5-x_6)^2} \frac{dx_1}{dz} + \frac{x_1}{(1-x_1-x_2-x_3-x_4-x_5-x_6)^2}$$

$$(\frac{dx_2}{dz} + \frac{dx_3}{dz} + \frac{dx_4}{dz} + \frac{dx_5}{dz} + \frac{dx_6}{dz})] -$$

$$\frac{L'}{(1-x_1-x_2-x_3-x_4-x_5-x_6)} \ (Cp_L)_2 \ (t^i-t_R)$$

$$[\frac{(1-x_1-x_3-x_4-x_5-x_6)}{(1-x_1-x_2-x_3-x_4-x_5-x_6)^2} \frac{dx_2}{dz} + \frac{x_2}{(1-x_1-x_2-x_3-x_4-x_5-x_6)^2}$$

$$(\frac{dx_1}{dz} + \frac{dx_3}{dz} + \frac{dx_4}{dz} + \frac{dx_5}{dz} + \frac{dx_6}{dz})] -$$

$$\frac{L'}{(1-x_1-x_2-x_3-x_4-x_5-x_6)} (Cp_L)_3 \quad (t^i-t_R)$$

$$[\frac{(1-x_1-x_2-x_4-x_5-x_6)}{(1-x_1-x_2-x_3-x_4-x_5-x_6)^2} \frac{dx_3}{dz} + \frac{x_3}{(1-x_1-x_2-x_3-x_4-x_5-x_6)^2}$$

$$(\frac{dx_1}{dz} + \frac{dx_2}{dz} + \frac{dx_4}{dz} + \frac{dx_5}{dz} + \frac{dx_6}{dz})] -$$

$$\frac{L'}{(1-x_1-x_2-x_3-x_4-x_5-x_6)} (Cp_L)_4 \quad (t^i-t_R)$$

$$[\frac{(1-x_1-x_2-x_3-x_5-x_6)}{(1-x_1-x_2-x_3-x_4-x_5-x_6)^2} \frac{dx_4}{dz} + \frac{x_4}{(1-x_1-x_2-x_3-x_4-x_5-x_6)^2}$$

$$(\frac{dx_1}{dz} + \frac{dx_2}{dz} + \frac{dx_3}{dz} + \frac{dx_5}{dz} + \frac{dx_6}{dz})] -$$

$$\frac{L'}{(1-x_1-x_2-x_3-x_4-x_5-x_6)} (Cp_L)_5 \quad (t^i-t_R)$$

$$[\frac{(1-x_1-x_2-x_3-x_4-x_6)}{(1-x_1-x_2-x_3-x_4-x_5-x_6)^2} \frac{dx_5}{dz} + \frac{x_5}{(1-x_1-x_2-x_3-x_4-x_5-x_6)^2}$$

$$(\frac{dx_1}{dz} + \frac{dx_2}{dz} + \frac{dx_3}{dz} + \frac{dx_4}{dz} + \frac{dx_6}{dz})] -$$

$$\frac{L'}{(1-x_1-x_2-x_3-x_4-x_5-x_6)} (Cp_L)_6 \quad (t^i-t_R)$$

$$[\frac{(1-x_1-x_2-x_3-x_4-x_5)}{(1-x_1-x_2-x_3-x_4-x_5-x_6)^2} \frac{dx_6}{dz} + \frac{x_6}{(1-x_1-x_2-x_3-x_4-x_5-x_6)^2}$$

$$(\frac{dx_1}{dz} + \frac{dx_2}{dz} + \frac{dx_3}{dz} + \frac{dx_4}{dz} + \frac{dx_5}{dz})]\} \; / \; \{L' \quad (Cp_L)_{N+1} +$$

$$\frac{L'}{(1-x_1-x_2-x_3-x_4-x_5-x_6)} [x_1 \quad (Cp_L)_1 + x_2 \quad (Cp_L)_2 +$$

$$x_3 \quad (Cp_L)_3 + x_4 \quad (Cp_L)_4 + x_5 \quad (Cp_L)_5 + x_6 \quad (Cp_L)_6]\} \text{(H-3b)}$$

Equations H-1, H-2, and H-3 are solved numerically by the Runge-Kutta method described in detail in Appendix B.

Before the above equations can be integrated, the interfacial compositions and temperature must be determined. The interfacial equations are:

$$(1-y_1)\ (k_ya)_1\ (y_1-y_1^i) - y_1\ (k_ya)_2\ (y_2-y_2^i) - y_1\ (k_ya)_3\ (y_3-y_3^i) - \{(1-x_1)\ [E_1\ (k_xa)_1\ (x_1^i-x_1) - r_1] - x_1\ [E_2\ (k_xa)_2\ (x_2^i-x_2) - r_2]\ x_1\ (k_xa)_3\ (x_3^i-x_3) - x_1\ p_1\ r_1 - x_1\ p_2\ r_2 - x_1\ [-\ b_1\ r_1 - b_2\ r_2]\} = 0 \tag{H-4a}$$

$$(1-y_2)\ (k_ya)_2\ (y_2-y_2^i) - y_2\ (k_ya)_1\ (y_1-y_1^i) - y_2\ (k_ya)_3\ (y_3-y_3^i) - \{(1-x_2)\ [E_2\ (k_xa)_2\ (x_2^i-x_2) - r_2] - x_2\ [E_1\ (k_xa)_1\ (x_1^i-x_1) - r_1]\ x_2\ (k_xa)_3\ (x_3^i-x_3) - x_2\ p_1\ r_1 - x_2\ p_2\ r_2 - x_2\ [-\ b_1\ r_1 - b_2\ r_2]\} = 0 \tag{H-4b}$$

$$(1-y_3)\ (k_ya)_3\ (y_3-y_3^i) - y_3\ (k_ya)_1\ (y_1-y_1^i) - y_3\ (k_ya)_2\ (y_2-y_2^i) - \{(1-x_3)\ (k_xa)_3\ (x_3^i-x_3) - x_3\ [E_1\ (k_xa)_1\ (x_1^i-x_1) - r_1] - x_3\ [E_2\ (k_xa)_2\ (x_2^i-x_2) - x_3\ p_1\ r_1 - x_3\ p_2\ r_2] - x_3\ [-\ b_1\ r_1 - b_2\ r_2]\} = 0 \tag{H-4c}$$

$$\begin{aligned}
& h_V a\ (t_V - t^i) + \frac{V'}{(1-y_1-y_2-y_3)} \frac{dy_1}{dz} (H_V)_1 + \frac{V'}{(1-y_1-y_2-y_3)} \frac{dy_2}{dz} \\
& (H_V)_2 + \frac{V'}{(1-y_1-y_2-y_3)} \frac{dy_3}{dz} (H_V)_3 - \{h_L a\ (t^i - t_L) + \\
& \frac{L'}{(1-x_1-x_2-x_3-x_4-x_5-x_6)} [\frac{dx_1}{dz} (H_L)_1 + \frac{dx_2}{dz} (H_L)_2 + \frac{dx_3}{dz} (H_L)_3 + \\
& \frac{dx_4}{dz} (H_L)_4 + \frac{dx_5}{dz} (H_L)_5 + \frac{dx_6}{dz} (H_L)_6] + \frac{L'}{(1-x_1-x_2-x_3-x_4-x_5-x_6)} \\
& [\frac{dx_1}{dz} (\Delta H_{rx})_1 + \frac{dx_2}{dz} (\Delta H_{rx})_2] + \frac{L'}{(1-x_1-x_2-x_3-x_4-x_5-x_6)} [\frac{dx_4}{dz} \\
& p_1\ (Cp_L)_4 - \frac{dx_1}{dz} (Cp_V)_1]\ [t^i - 77] + \frac{L'}{(1-x_1-x_2-x_3-x_4-x_5-x_6)} \\
& [\frac{dx_5}{dz} p_2\ (Cp_L)_5 - \frac{dx_2}{dz} (Cp_V)_1]\ [t^i - 77]\} = 0 \qquad \text{(H-5)}
\end{aligned}$$

Equations H-4 and H-5 are solved for the interfacial compositions, $\underline{x}^i$, and interfacial temperature, t^i, using Newton's method, detailed in Appendix B, and permit Equations H-1, H-2, and H-3 to be solved for $\underline{x}$, $\underline{y}$, t_L, and t_V as a function of column height.

APPENDIX I

USER'S GUIDE

For any computer program, a user's guide is just as important as the documentation. In addition to supplying instructions for the use of the program, the guide also defines all terms used in the Fortran program. The input data required are listed below with the required format noted in parentheses.

Card 1 (15I5)

NXFER, NREACT, NHEAT, IRXTRZ, NDIRCT, IVAPOR, IEQDAT, INTGRT, NPACK, NWATER, KONTAC, KIND, KCOEFF, NDRIVE

NXFER - Number of transferring components

NREACT - Number of reacting components (NREACT XNFER)

NHEAT - 0, if no energy calculations are required
1, if energy calculations are required

IRXTRZ - 0, if reactant is also the carrier liquid
1, if reactant only a component in the liquid phase

NDIRCT - 0, for countercurrent flow
1, for cocurrent flow

IVAPOR - 0, if the carrier liquid does not vaporize
- component number for vaporizing carrier liquid

IEQDAT - 0, for equilibrium data of the form $y^i=a+bx^i+c(x^i)^2+\ldots$

1, for equilibrium data supplied (requires the inclusion of the equation for the data in function subroutine F and the derivative of the equation in subroutine FP)

INTGRT - 0, for numerical integration from bottom to top of the column

1, for numerical integration from top to bottom of the column

NPACK - 0, if transfer coefficients are supplied

1, 0.5 in. Ceramic Raschig rings

2, 1.0 in. Ceramic Raschig rings

3, 1.5 in. Ceramic Raschig rings

4, 2.0 in. Ceramic Raschig rings

5, 2.5 in. Ceramic Raschig rings (no data available)

6, 0.5 in. Carbon Raschig rings (no data available)

7, 1.0 in. Carbon Raschig rings

8, 1.5 in. Carbon Raschig rings

9, 2.0 in. Carbon Raschig rings

10, 2.5 in. Carbon Raschig rings (no data available)

11, 0.5 in. Ceramic Berl Saddles

12, 1.0 in. Ceramic Berl Saddles

13, 1.5 in. Ceramic Berl Saddles
14, 2.0 in. Ceramic Berl Saddles (no data available)
15, 2.5 in. Ceramic Berl Saddles (no data available)

NWATER - 0, for no calculation of transfer coefficients
1, for absorption with aqueous solutions
2, for absorption with nonaqueous solutions
3, for absorption with pure water (for vaporization)
4, for absorption with pure water (for vaporization)

KIND - 0, for calculation of column height
1, for a search for mass and heat transfer coefficient
2, for a search for mass transfer coefficient
3, for a search for heat transfer coefficient
4, for a search for flow rates

KCOEFF - 1, for individual coefficients
2, for overall coefficients

NDRIVE - 0, for individual coefficients
1, for overall coefficients, Y driving forces
2, for overall coefficients, X driving forces

Card 2 (15I5)

NRX(J) J=1, NXFER

NRX - 0, no reaction

1, instantaneous reaction

2, finite reaction, pseudo first order

3, finite reaction, second order

4, slow reaction

5, very slow reaction

Card 3 (8F10.0)

LP, VP, DH, HL, HV, TLIN, TVOUT, TR

LP - liquid flow rate, lb moles/hr ft^2

VP - vapor flow rate, lb moles/hr ft^2

DH - numerical integration height increment, ft

HL - liquid heat transfer coefficient, BTU/hr ft^3

HV - vapor heat transfer coefficient, BTU/hr ft^3

TLIN - temperature of liquid in, °F

TVOUT - temperature of vapor out, °F

TR - reference temperature, °F

Card 4 (8F10.0)

XIN(J)' J=1,N where N=NXFER+NREACT

XIN - mole fraction of the incoming liquid components

Card 5 (8F10.0)

YIN(J)' J=1,N

YIN - mole fraction of the incoming vapor components

Card 6* (8F10.0)

YOUT(J) 8 values per card

YOUT - mole fraction of the outgoing vapor components

Next N cards (if IEQDAT=1, no cards are required)**

(8F10.0)

COX(J,M) 6 values per card, NXFER cards

Equilibrium data of the form $y^i=a+bx^i+C(x^i)^2+\ldots$

Next NXFER cards (2F10.0)

V(M,J) 2 values per card, NXFER cards

stoichiometric reaction coefficients: A+V(1,J)B, V(2,J)C

*Integration is performed from the top to the bottom of the column. If integration is from the bottom to the top, then: for XIN the compositions of the outgoing liquid should be given, for YIN the compositions of the outgoing vapor should be given, for YOUT the compositions of the incoming vapor should be given.

**If the user has an unusual representation of the equilibrium data, the functions F and FP must be changed in the program. The function F is used to represent the equilibrium data and calculate y^i from a given x^i. Function FP is the derivative of F with respect to both x^i and t^i.

Next NXFER cards (2F10.0)

KX(J), KY(J) 2 values per card, NXFER cards

KX - liquid mass transfer coefficient, lb moles/hr ft^3

KY - vapor mass transfer coefficient, lb moles/hr ft^3

Next NXFER cards (2F10.0)

KRX(M,J) 2 values per card

KRX - reaction rate constant

Next N+1 cards (2F10.0)

D(M,J)

D(1,J) - vapor phase diffusivities

D(2,J) - liquid phase diffusivities

(On card N+1 the diffusivities of the carrier gas and liquid respectively are given.)

Next card(s) (8F10.0) (omit if NHEAT=0)

QV(J) N values

QV - heat of vaporization, BTU/lb moles

Next card(s) (8F10.0) (omit if NHEAT=0)

QS(J) N values

QS - heat of solution, BTU/lb moles

Next card(s) (8F10.0) (omit if NHEAT=0)

DELHRX(J) NXFER values

DELHRX - heat of reaction, BTU/lb moles

Next 3(N+1) cards (3E20.8) (omit if NHEAT=0)

COCP(JJ,M,J)

For heat capacity data of the form:

$Cpj = COCP(JJ,1,J) + COCP(JJ,2,J)\ t + COCP(JJ,3,J)\ t^3$

where t is temperature in °F

COCP(1,M,J) - heat capacity coefficient for a component in the vapor

COCP(2,M,J) - heat capacity coefficient for a component in the liquid

Next card (15I5)

IREF(J) N values

IREF - reference state of the component

1, if component has vapor reference state

2, if component has liquid reference state

Next card (8F10.0) (omit if NPACK=0)

UL, UV, RHOL, RHOV, SIGMA, TCONDL, TCONDV, PRESS

UL - viscosity of the liquid

UV - viscosity of the vapor

RHOL - liquid density

RHOV - vapor density

SIGMA - surface tension dynes/cm^2

TCONDL - liquid thermal conductivity

TCONDV - vapor thermal conductivity

PRESS - total pressure of the column, atm.

Next card (8F10.0) (omit if NPACK=0)

CPL, CPV

CPL - heat capacity of the liquid phase

CPV - heat capacity of the vapor phase

Next N+1 cards (2F10.0) (omit if NPACK=0)

AMW(I,J)

AMW(1,J) - vapor component molecular weight

AMW(2,J) - liquid component molecular weight

Next card (8F10.0) (omit if NPACK≠0)

RHOL, PRESS, AREA, AVEMWL

RHOL - liquid density, lb/ft^3

PRESS - total pressure of the column, atm.

AREA - interfacial area per cubic foot of contactor volume, ft^2/ft^3

AVEMWL - average molecular weight of the liquid, lb/lb mole

Next card (15I5) (omit if KIND=0)

NNV, NDATA, NPTS, NTYPE

NNV - number of search variables

NDATA - number of sets of data to be used in the minimization

NPTS - number of points in each set of data

NTYPE - variable used in the objective function

1, for y and t_V

2, for x and t_L

3, for y only

4, for x only

5, for t_V only

6, for t_L only

Next card (8F10.0) (omit if KIND=0)

ASIDE, EPSLN, ALPHA, BETA, GAMMA, H

ASIDE - length of a side in the starting

EPSLN - stopping criteria

ALPHA, BETA, GAMMA - Nelder-Mead constants

H - column height

Next NDATA (NPYS/4) cards (4E20.8) (omit if KIND=0)

YS(I,J)

YS - experimental data to be used in the objective function

Next card (8F10.0) (omit if KIND=0)

SCALE(I)

SCALE - scale factor for each variable

COMPLETE NOMENCLATURE

a	Interfacial area per cubic foot of contactor volume, ft^2/ft^3
a,b,p	Stoichiometric coefficients of the reactants and product
A	A transferring-reacting component from the vapor phase
$\underline{A}$	Independent search variables
A_c	Cross-sectional area of the column, ft^2
B	The reacting component in the liquid phase
c	Concentration, lb NH_3/1000 lb H_2O
Cp	Heat capacity, BTU/lb mole
D	Diffusivity, ft^2/hr
e,f,g,h	Indicators of functions
E	Enhancement factor
E_i	Instantaneous enhancement factor
F,M	Defined by Equation F-17
h_L	Liquid heat transfer coefficient, BTU/hr ft^2 °F
h_V	Vapor heat transfer coefficient, BTU/hr ft^2 °F
H_G	Height of a transfer unit, ft
H_{rx}	Heat of reaction, BTU/lb mole
H	Henry's Law constant
H	Enthalpy, BTU/lb mole
KX	Defined by Equation B-6

k_x	Liquid mass transfer coefficient, lb moles/hr ft^2 mole fraction
KY	Defined by Equation B-6
k_y	Vapor mass transfer coefficient, lb moles/hr ft^2 mole fraction
k_{rx}	Reaction rate constant
k	Iteration counter
L	Total liquid flow rate, lb moles/hr ft^2
L'	Flow rate of the solvent liquid, lb moles/hr ft^2
ℓn	Natural logarithm
M	Defined by Equation 16
M	Defined by Equation B-6
m,n	Reaction order
m	Equilibrium constant
N	Total number of components
NDATA	Number of data points
N_G	Number of transfer units
N_M	Defined by Equation C-1
N_r	Number of transferring-reacting components
N_x	Number of transferring-reacting and transferring-nonreacting components
P	Reaction product or pressure, atm
P^o	Vapor pressure, atm
p,q	Simplex search variables
Q_s	Heat of solution, BTU/lb mole

Q_V	Heat of vaporization, BTU/lb mole
r	Rate of reaction, lb moles of A/hr ft^3
r	Random number between 0 and 1
R	Defined by Equation 10
R	Gas law constant
S	Independent search variable
s	Designates a function
st	Standard deviation
t	Temperature, °F
T	Temperature, °K
V	Total vapor flow rate, lb moles/hr ft^2
V'	Flow rate of the noncondensing carrier gas, lb moles/hr ft^2
x	Component concentration in the liquid phase, mole fraction
$\underline{x}$	A vector representing all liquid phase compositions
y	Component concentration in the vapor phase, mole fraction
$\underline{y}$	A vector representing all vapor phase compositions
z	Column height, ft
$\bar{\rho}$	Molar density, lb moles/ft^3

Subscripts

C	Centroid
H	The search variable which gives the

	largest value of the objective function
L	The search variable which gives the smallest value of the objective function
L	Liquid phase
lm	Log mean
N+1	Component number of the carrier gas and carrier liquid
R	Reference
V	Vapor phase
x	Liquid phase
y	Vapor phase
α,β,γ	Parameters of the Nelder-Mead method
α,β	Defined by Equation C-1
γ	Activity coefficient
1,2,...N	Component numbers
0	Initial value

Superscripts

i	Interface
^	Values predicted by the model

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