11. Mischke, R. A., and J. M. Smith, *Ind. Eng. Chem. Fundamentals*, **1**, 288 (1962).
12. Kennard, E. H., "Kinetic Theory of Gases with an Introduction to Statistical Mechanics," McGraw-Hill, New York (1938).
13. Dushman, S., and J. M. Lafferty, "Scientific Foundations of Vacuum Technique," Wiley, New York (1962).
14. Masamune, S., and J. M. Smith, *Ind. Eng. Chem. Fundamentals*, **2**, 136 (1963).
15. Wilhelm, R. H., W. C. Johnson, R. Wynkoop, and D. W. Collier, *Chem. Eng. Progr.*, **44**, 105 (1948).
16. Woodside, W., and J. H. Messmer, *J. Appl. Phys.*, **32**, 1688 (1961).
17. Tsao, G. T., *Ind. Eng. Chem.*, **53**, 395 (1961).
18. Warren, J. E., and J. H. Messmer, *Ind. Eng. Chem. Fundamentals*, **1**, 222 (1962).

Manuscript received March 2, 1964; revision received August 5, 1964; paper accepted August 7, 1964.

Solution of Problems Involving Conventional and Complex Distillation Columns at Unsteady State Operation

R. C. WAGGONER and C. D. HOLLAND

Texas A&M University, College Station, Texas

The θ method of convergence has been applied to conventional and complex columns at unsteady state operation. A different holdup for each stage may be specified in terms of molal, mass, or volumetric units. Plate efficiencies were used, and the K values and enthalpies were taken to be polynomials in temperature.

The combination of the calculational procedure of Thiele and Geddes (*27*) and the θ method of convergence (*11*) has been applied to solve problems involving conventional and complex distillation columns at unsteady state operation. A conventional column is one which has one feed stream and two product streams, the distillate and the bottoms. A complex column has any number of feeds and/or one or more side stream withdrawals in addition to the distillate and bottoms. In the interest of simplicity, the equations are developed for a conventional column, and then a brief description of their extension to include complex columns is presented.

The differential equations that represent a component-material balance, a total-material balance, and an enthalpy balance for plate j are as follows:

$$v_{j+1,i} + l_{j-1,i} - v_{ji} - l_{ji} = \frac{du_{ji}}{dt} \qquad (1)$$

$$V_{j+1} + L_{j-1} - V_j - L_j = \frac{dU_j}{dt} \qquad (2)$$

$$V_{j+1}H_{j+1} + L_{j-1}h_{j-1} - V_jH_j - L_jh_j = \frac{d(U_jh_j)}{dt} \qquad (3)$$

These differential-difference equations were first presented by Marshall and Pigford (*13*). In the statement of the material and enthalpy balances, the holdup in the vapor phase was omitted because it is generally negligible. Equation (1) implies that the composition of the liquid is the same at each point on plate j at any time t. This assumption is made throughout the course of the developments.

In order to complete the description of a plate, the equilibrium relationship

$$y_{ji} = E_{ji}K_{ji}x_{ji} \qquad (4)$$

is needed. The instantaneous vaporization efficiency (*7, 26*) is defined as

$$E_{ji} = y_{ji}/Y_{ji}, \text{ and } Y_{ji} = K_{ji}x_{ji} \qquad (5)$$

R. C. Waggoner is with Humble Oil and Refining Company, Baytown, Texas.

where K_{ji} is evaluated at the temperature and composition of the liquid leaving plate j. This efficiency is related to the modified Murphree efficiency (*7, 15*)

$$E^M_{ji} = \frac{y_{ji} - y_{j+1,i}}{Y_{ji} - y_{j+1,i}} \tag{6}$$

in the following manner:

$$E_{ji} = E^M_{ji} + (1 - E^M_{ji}) \frac{y_{j+1,i}}{Y_{ji}} \tag{7}$$

The temperature of the liquid leaving plate j is that $T_j > 0$ which makes $f(T_j) = 0$, where

$$f(T_j) = \sum_{i=1}^{c} E_{ji} K_{ji} x_{ji} - 1 \tag{8}$$

Many authors have used various combinations of Equations (1), (2), (3), and some form of an equilibrium relationship in the investigation of the behavior of multistage processes. Much of the work has been directed toward finding either an analytical solution or a numerical method for solving relatively simple problems (*1, 18, 20, 22, 29*). These workers made use of one or more of the following simplifying assumptions: binary mixtures, constant relative volatility, linear equilibrium relationships, and constant flow rates. For the case of binary mixtures, the remaining restrictions were removed by Huckaba et al. (*8, 9*).

Among the first to consider multicomponent mixtures were Rose et al. (*21*). In their method, Equation (1) was solved by a procedure called the *relaxation method*. Although the relaxation method was proposed to determine the final steady state solution, it could be used to obtain approximations of transient conditions. Modifications of this procedure for the solution of steady state problems have been presented by Ball (*3*) (see also reference 7). Mah et al. (*12*) presented a solution in matrix form for the material-balance matrix for each component. Within each time interval, the matrix coefficients which contained combinations of K_{ji}, V_j, and L_j were held constant. Sargent (*24*) extended the approach of Mah et al. to include the case where the coefficients in the material balances were supposed to be at least linear functions of time. It was proposed to find the correct linear functions for each time period by an iterative procedure. Recently, several applications of the unsteady state distillation relationships have been made in the area of process control (*5, 17, 23*). Before the development of the equations is presented, a brief description of the overall approach is given. Suppose that at the particular time $t = t_n$, the temperatures, compositions, and flow rates are known throughout the column, and that it is desired to find the values of the variables at some time later $t = t_n + \Delta t$.

By use of a numerical technique, the differential-difference equations for each component are converted into a set of difference equations for each time period Δt. The equations so obtained are of the same general form as those for columns at steady state. For each time period, these equations are solved by a procedure analogous to that used to solve the corresponding sets of steady state equations. This procedure consists of a combination of the Thiele and Geddes (*27*) calculational procedure and the θ method of convergence (*11*). The temperatures at the end of the time period (time $t_n + \Delta t$) are taken to be the independent variables. On the basis of an assumed temperature profile for the column at time $t_n + \Delta t$, the component-material balances are solved for the component flow rates and holdups. The θ method of convergence is then applied to find a set of component-distillate rates d_i and component holdups u_{ji} that are both in component-material balance and in agreement with the specified values of the total distillate rate and all of the holdups at time $t_n + \Delta t$. Next the corrected compositions and temperatures are computed. Then the total flow rates are found by use of enthalpy and material balances. This procedure is repeated for each time period until component flow rates and holdups of the desired degree of accuracy are obtained, and then the procedure is repeated for the next increment of time.

The equations for a conventional column are developed in the same order in which they were mentioned in the general approach. After the equations have been developed for a conventional column, the required modifications of these equations for the description of complex columns are presented.

COMPONENT-MATERIAL BALANCES

Two general methods for the statement of the component-material balance exist. In the first method each material balance includes only one plate, Equation (1). In the second method, the top (or bottom) of the column and all plates between the top (or bottom) of the column and the given plate are enclosed by each material balance. Both of them were investigated and found to be about equally reliable.

Method I: Enclosure of One Plate by Each Component-Material Balance

The differential-difference equation for each component was converted to a linear difference equation with variable coefficients by use of a numerical technique called the *implicit method*. This method is similar to the well-known implicit method for the numerical solution of partial differential equations such as the classical problem of unsteady state heat conduction (*10, 19*). One of the first applications of this method to multicomponent distillation problems was made by Ball (*3*) as described in reference 7, and a variation of this method was used by Rosenbrock (*22*).

In this method, the difference quotient for the derivative is approximated by use of a weighted average of the values of the derivatives at times t_n and $t_n + \Delta t$ as

$$\mu \left.\frac{du_{ji}}{dt}\right|_{t_n+\Delta t} + (1-\mu) \left.\frac{du_{ji}}{dt}\right|_{t_n} = \frac{u_{ji}|_{t_n+\Delta t} - u_{ji}|_{t_n}}{\Delta t} \tag{9}$$

where the weighting factor μ lies in the interval $0 \leqq \mu \leqq 1$. When the derivatives of Equation (9) are replaced by their values as given by Equation (1), the result

$$\mu(v_{j+1,i} + l_{j-1,i} - v_{ji} - l_{ji})|_{t_n+\Delta t} + (1-\mu)(v_{j+1,i} + l_{j-1,i} - v_{ji} - l_{ji})|_{t_n} = \frac{u_{ji}|_{t_n+\Delta t} - u_{ji}|_{t_n}}{\Delta t} \tag{10}$$

is obtained. A far simpler way to obtain identically the same result [Equation (10)] is to restate Equation (1) as an integral-difference equation

$$\int_{t_n}^{t_n+\Delta t} (v_{j+1,i} + l_{j-1,i} - v_{ji} - l_{ji})\,dt = u_{ji}\Big|_{t_n+\Delta t} - u_{ji}\Big|_{t_n} \tag{11}$$

and then to replace the integral by an approximation whereby the values of the integrand at $t_n + \Delta t$ and t_n are given the weights μ and $(1 - \mu)$, respectively.

Note than when $\mu = 1/2$, the implicit method reduces to the well-known trapezoidal rule for the approximation of an integral; this rule is also called a *two-point* or *trapezoidal corrector* (*14*). Because of the directness of the second approach used to obtain Equation (10), this approach is employed in the remainder of the development.

Each component-material balance may be stated in terms of either the v_{ji}'s, l_{ji}'s, or u_{ji}'s by use of the following relationships:

$$l_{ji} = A_{ji}v_{ji}; \quad v_{ji} = S_{ji}l_{ji}; \quad \text{and } u_{ji} = \frac{U_j}{L_j}A_{ji}v_{ji} \tag{12}$$

Let the values of the variables at the end of each time increment (time $t_n + \Delta t$) be denoted by v_{ji}, l_{ji}, and u_{ji}, and let the values of the variables at the beginning of each time increment be identified by superscript o, for example, v_{ji}^{o}, l_{ji}^{o}, and u_{ji}^{o}. When stated in terms of the v_{ji}'s the component-material balances for a column are as follows:

$$\left.\begin{array}{l} -\rho_{0i}\, v_{0i} + v_{1i} = -P_{0i} \\ A_{j-1,i}v_{j-1,i} - \rho_{ji}v_{ji} + v_{j+1,i} = -P_{ji}, \ (1 \leqq j \leqq N) \\ A_{Ni}v_{Ni} - \rho_{N+1,i}\, v_{N+1,i} = -P_{N+1,i} \end{array}\right\} \tag{13}$$

where

$$\rho_{ji} = 1 + A_{ji}(1 + \tau_j/\mu)$$

$$P_{ji} = z + \sigma[z^o + v^o_{j+1,i} - (A^o_{ji} + 1)v^o_{ji} + A^o_{j-1,i}\, v^o_{j-1,i}] + \frac{\tau_j{}^o A^o_{ji}v^o_{ji}}{\mu}; \text{ for } j = f - 1,$$

$$z = v_{Fi}; \text{ for } j = f, z = l_{Fi}; \text{ for all other } j, \ z = 0$$

For any given set of values for the L/V's, efficiencies, and temperatures at the end of the time increment, the component-material balances for each component i constitute a set of linear algebraic equations in the v_{ji}'s. For equations such as these, which are tridiagonal in form, recursion formulas are readily available (*6, 10*) for determining the unknown vapor rates. The use of the formulas has been demonstrated by Ball (*3*) as described in reference *7*.

Method II: Enclosure of the Top of the Column and Each Plate by the Component-Material Balance

For a conventional column, the material balance enclosing the top of the column and plate j (for $j < f - 1$) is given by

$$\int_{t_n}^{t_n+\Delta t} (v_{j+1,i} - l_{ji} - v_{0i})\, dt = \sum_{k=0}^{j} u_{ki} \Big|_{t_n+\Delta t} - \sum_{k=0}^{j} u_{ki} \Big|_{t_n} \tag{14}$$

Similar equations may be stated for $j = f - 1$ through $j = N$. When the values of the integrals are approimxated by use of the implicit method, and when the l_{ji}'s and u_{ji}'s are stated in terms of the v_{ji}'s a set of simultaneous equations in the v_{ji}'s is obtained. For any component i, these equations may be represented in matrix notation as

$$\overline{A}\ \overline{v} = \overline{P} \tag{15}$$

where the matrix $\overline{A}$ is a supertriangular matrix (*10*) of the form

$$\begin{bmatrix} a_{11} & 1 & 0 & 0 \ldots 0 \\ a_{21} & a_{22} & 1 & 0 \ldots 0 \\ \cdots & \cdots & \cdots & \cdots \\ a_{n-1,1} & a_{n-1,2} & a_{n-1,3} & \ldots 1 \\ a_{n1} & a_{n2} & a_{n3} & \ldots a_{nn} \end{bmatrix}$$

Matrix $\overline{A}$ is of order $(N + 2)$ and contains the coefficients of the v_{ji}'s The matrices $\overline{v}$ and $\overline{P}$ are column vectors of order $(N + 2)$. Matrix $\overline{v}$ contains the unknown v_{ji}'s, and $\overline{P}$ contains a set of terms (whose values are known) which are similar to those that appear in the P_{ji}'s of Equation (13). This system of equations may be solved by Crout's method, described elsewhere (*6, 10, 16*).

CONVERGENCE METHOD

If, after the component flow rates and holdups have been calculated, the values so obtained are not in agreement with the specified values of the total distillate rate and the holdups at time $t_n + \Delta t$, the correct set of temperatures was not selected. The θ method of convergence is an indirect method for choosing a new set of temperatures. This method alters or corrects the mole fractions, and on the basis of these mole fractions, new temperatures are computed as described in the next section. The corrected sets of mole fractions reflect the certainties that each component must be in overall material balance and in agreement with the specified values for the total distillate rate and the total holdups. By specified values is meant that at the beginning of a time increment (time t_n), the values of say D and the U_j's are known at time $t_n + \Delta t$. That is, at time t_n, the specified values must either be known at time $t_n + \Delta t$ or be calculable from previous sets of transient conditions at time t_n or any number of times $t < t_n$. The situation where the specified values at time $t_n + \Delta t$ depend upon the transient conditions at time $t_n + \Delta t$ is not treated. The θ method of convergence for molal, mass, and volumetric holdup specifications follows.

θ Method of Convergence Where Molal Holdups Are Specified

The θ method of convergence for columns at unsteady state operation is similar to the θ method of convergence for the steady state problem of a column with any number of side streams. For each side stream withdrawn, the additional information (or specification) consisting of its flow rate gives rise to a θ multiplier (*11*). For a column at unsteady state operation, the molal holdup specification for each plate or stage (except the reboiler) gives rise to a θ multiplier. These multipliers are determined such that the corrected set of d_i's and u_{ji}'s are both in overall material balance and in agreement with the specifications

$$D, U_0, U_1, \ldots, U_{N+1}$$

The θ method of convergence is related in spirit to the concept of the Lagrangian multipliers (*25*) in that for each condition of restraint or specification made on the system there exists a multiplier. However, at this point the similarity ends.

In the Appendix, a development leading to the following consistant set of multipliers is presented:

$$\left.\begin{array}{l} \left(\dfrac{b_i}{d_i}\right)_{co} = \theta_{-1}\left(\dfrac{b_i}{d_i}\right)_{ca} \\ \left(\dfrac{u_{ji}}{d_i}\right)_{co} = \theta_j\left(\dfrac{u_{ji}}{d_i}\right)_{ca}, 0 \leqq j \leqq N \end{array}\right\} \tag{16}$$

The knowledge of the holdup U_{N+1} of the reboiler does not give rise to a θ which would carry the subscript $(N + 1)$ because $(u_{N+1,i}/d_i)_{co}$ may be expressed in terms of $(b_i/d_i)_{co}$ as follows:

$$\left(\frac{u_{N+1,i}}{d_i}\right)_{co} = \left(\frac{U_{N+1}}{B}\right)\left(\frac{b_i}{d_i}\right)_{co} = \theta_{-1}\left(\frac{U_{N+1}}{B}\right)\left(\frac{b_i}{d_i}\right)_{ca} \tag{17}$$

[Note that the specification of L_o (or V_1) does not lead to a multiplier because this specification is used to compute the condenser duty.]

Also, as shown in the Appendix, this set of θ's is consistent with the following formula for the calculation of the corrected mole fractions:

$$(x_{ji})_{co} = \frac{\left(\frac{l_{ji}}{d_i}\right)_{ca} (d_i)_{co}}{\sum_{i=1}^{c} \left(\frac{l_{ji}}{d_i}\right)_{ca} (d_i)_{co}} \tag{18}$$

By use of a procedure analogous to the one presented in the Appendix, it is readily shown that

$$(y_{ji})_{co} = \frac{\left(\frac{v_{ji}}{d_i}\right)_{ca} (d_i)_{co}}{\sum_{i=1}^{c} \left(\frac{v_{ji}}{d_i}\right)_{ca} (d_i)_{co}} \tag{19}$$

The formula for $(d_i)_{co}$ is found by use of the overall material balance

$$\int_{t_n}^{t_n+\Delta t} [FX_i - (b_i)_{co} - (d_i)_{co}]dt = \sum_{j=0}^{N+1} (u_{ji})_{co} \Big|_{t_n+\Delta t} - \sum_{j=0}^{N+1} u_{ji} \Big|_{t_n} \tag{20}$$

When the integral is approximated by the implicit method and the resulting expression is solved for $(d_i)_{co}$, the following result is obtained upon replacing the corrected ratios by their equivalents as given by Equation (16):

$$(d_i)_{co} = \frac{FX_i + \sigma[F^oX_i^o - d_i^o - b_i^o] + \left(\frac{1}{\mu\,\Delta t}\right) \sum_{j=0}^{N+1} u^o_{ji}}{1 + \theta_{-1}\left(\frac{b_i}{d_i}\right)_{ca} \left[1 + \frac{U_{N+1}/B}{\mu\,\Delta t}\right] + \left(\frac{1}{\mu\,\Delta t}\right) \sum_{j=0}^{N} \theta_j \left(\frac{u_{ji}}{d_i}\right)_{ca}} \tag{21}$$

Except for the θ_j's, all other quantities appearing in Equation (21) will be known after each trial calculation through the column. Likewise, by use of Equations (16) and (21), the $(u_{ji})_{co}$'s may be stated in terms of the unknown θ_j's. The desired set of θ_j's is that set of positive numbers that makes $g_{-1} = g_o = g_1 = \ldots = g_N = 0$, simultaneously, where

$$\left.\begin{aligned} g_{-1}(\theta_{-1}, \theta_0, \theta_1, \ldots, \theta_N) &= \sum_{i=1}^{c} (d_i)_{co} - D \\ g_j(\theta_{-1}, \theta_0, \theta_1, \ldots, \theta_N) &= \sum_{i=1}^{c} (u_{ji})_{co} - U_j,\ 0 \leqq j \leqq N \end{aligned}\right\} \tag{22}$$

These equations apply for a column with a partial condenser. When a total condenser is employed, g_o is excluded and $(u_{0i}/d_i)_{co}$ is replaced wherever it appears by its equivalent U_0/D. The desired set of θ_j's was found by use of the Newton-Raphson method (*16*), also called *Newton's method* (*10*). This application of the Newton-Raphson method parallels that presented in reference 7 for complex columns at steady state operation.

θ Method of Convergence Where Mass Holdups Are Specified

If instead of molal holdups the total mass holdups are specified, then the specifications to be satisfied are as follows:

$$D, \mathcal{M}_0, \mathcal{M}_1, \mathcal{M}_2, \ldots, \mathcal{M}_{N+1}$$

The development for this case is shortened by using the results of the previous case. Let the corrected mass holdup of component i on plate j be denoted by $(m_{ji})_{co}$, which is related to $(u_{ji})_{co}$ as follows: $(m_{ji})_{co} = (u_{ji})_{co}M_i$, where M_i = molecular weight of component i. The formula for $(m_{ji})_{co}$ in terms of θ_j is obtained by replacing $(u_{ji})_{co}$ by its equivalent as given by Equation (16).

$$(m_{ji})_{co} = \theta_j \left(\frac{u_{ji}}{d_i}\right)_{ca} (d_i)_{co} M_i \tag{23}$$

The formula for $(d_i)_{co}$ is obtained by replacing the denominator of Equation (21) by

$$1 + \theta_{-1}\left(\frac{b_i}{d_i}\right)_{ca} + \frac{1}{\mu\,\Delta t} \sum_{j=0}^{N+1} \theta_j \left(\frac{u_{ji}}{d_i}\right)_{ca}$$

Thus, for the case where the mass holdups are specified, the specification $\mathcal{M}_{N+1}$ leads to the independent θ, namely θ_{N+1}. This results from the fact that when the $\mathcal{M}_j$'s are specified, the term U_{N+1}/B of Equation (17) depends upon the θ_j's.

Hence, for the case where mass holdups are specified, the g functions to be satisfied are as follows:

$$\left.\begin{aligned} g_{-1}(\theta_{-1}, \theta_0, \theta_1, \ldots, \theta_{N+1}) &= \sum_{i=1}^{c} (d_i)_{co} - D \\ g_j(\theta_{-1}, \theta_0, \theta_1, \ldots, \theta_{N+1}) &= \sum_{i=1}^{c} (m_{ji})_{co} - \mathcal{M}_j,\ 0 \leqq j \leqq N + 1 \end{aligned}\right\} \tag{24}$$

The desired set of θ_j's is that set of positive numbers that makes $g_{-1} = g_0 = g_1 = \ldots = g_{N+1} = 0$, simultaneously.

When the $\mathcal{M}_j$'s are specified, the corresponding U_j's at times t_n and $t_n + \Delta t$ are needed in the component-material balances. The value of U_j at time t_n is the value obtained at the end of the calculational procedure for the previous time increment. At the end of the first and all subsequent trials for any given time increment, the value of U_j at time $t_n + \Delta t$ is computed as follows:

$$U_j \Big|_{t_n+\Delta t} = \sum_{i=1}^{c} \frac{(m_{ji})_{co}}{M_i} \tag{25}$$

θ Method of Convergence Where Volumetric Holdups Are Specified

If the volumetric holdups of the condenser, each plate, and the reboiler are specified, and it is supposed that the volumes are additive, the θ method is applied in the same manner as described for the previous case. Also, the same equations apply provided the symbols M_i, m_{ji}, and $\mathcal{M}_j$ are redefined to mean the molal volume of component i in the liquid on plate j, the volume of component i on plate j, and the total volume of liquid on plate j, respectively.

DETERMINATION OF THE TEMPERATURES

After the θ_j's have been determined, the corresponding values of $(d_i)_{co}$ are used to compute a corrected set of mole fractions [Equations (18) and (19)] for each plate. These mole fractions are used to compute a new set of temperatures by use of the K_b method (*7, 26*). This method consists of a procedure for approximating the temperature of each plate and thereby eliminating the trial and error involved in the use of the conventional bubble-point expression, Equation (8). As described in Chapter 15 of reference 7, when the K_b method for the determination of $T_{j,n+1}$ is employed, the x_{ji}'s and y_{ji}'s given by Equation (18) and (19) form a consistent set in that the temperature predicted for the next trial $(n+1)$ for a given time period Δt is the same regardless of whether x_{ji}'s or y_{ji}'s are employed.

ENTHALPY AND TOTAL-MATERIAL BALANCES

The corrected x_{ji}'s and the corresponding temperatures found by the K_b method are used to determine a new set of total flow rates by use of enthalpy and total-material balances. Thus, as in the calculation of the temperatures, the most recently calculated values of the variables are used in subsequent equations. Such an iterative process is recognized as the Gauss-Seidel method (*10*) for solving simultaneous equations.

As illustrated for the material balances, each enthalpy balance may either enclose only one plate or it may enclose the top (or bottom) of the column and each given plate. Both of these methods were investigated and found to be equally reliable. The expression for the liquid rate L_j $(1 \leqq j \leqq f-2)$ as given by the constant-composition method (7) is developed in the following manner. An enthalpy balance enclosing the top of the column and plate j is represented by

$$\int_{t_n}^{t_n+\Delta t} (V_{j+1} H_{j+1} - L_j h_j - DH_D - Q_c)\, dt = \sum_{k=0}^{j} (U_k h_k - U_k^{\circ} h_k^{\circ}) \qquad (26)$$

When the value of the integral is approximated by the implicit method and when the quantity $V_{j+1}H_{j+1}$ is replaced by it equivalent

$$\begin{aligned} V_{j+1} H_{j+1} &= \sum_{i=1}^{c} H_{j+1,i}\, v_{j+1,i} \\ &= \sum_{i=1}^{c} H_{j+1,i} \Big[l_{ji} + d_i + \sigma\, (l^{\circ}_{ji} \\ &\quad + d_i^{\circ} - v^{\circ}_{j+1,i}) + \frac{1}{\mu\, \Delta t} \sum_{k=0}^{j} (u_{ki} - u^{\circ}_{ki}) \Big] \end{aligned}$$

the expression so obtained may be solved for L_j $(1 \leqq j \leqq f-2)$ to give

$$\begin{aligned} L_j = &\frac{-D[H(X_D)_{j+1} - H_D] + Q_c + \sigma[V^{\circ}_{j+1}[H(y^{\circ}_{j+1})_{j+1} - H^{\circ}_{j+1}]}{[H(x_j)_{j+1} - h_j]} \\ &\frac{-L_j^{\circ}[H(x_j^{\circ})_{j+1} - h_j^{\circ}] - D^{\circ}[H(X_D^{\circ})_{j+1} - H_D^{\circ}] + Q_c^{\circ}]}{[H(x_j)_{j+1} - h_j]} \\ &\frac{-\left(\frac{1}{\mu\, \Delta t}\right) \sum_{k=0}^{j} U_k[H(x_k)_{j+1} - h_k] + \left(\frac{1}{\mu\, \Delta t}\right) \sum_{k=0}^{j} U_k^{\circ}[H(x_k^{\circ})_{j+1} - h_k^{\circ}]}{[H(x_j)_{j+1} - h_j]} \end{aligned} \qquad (27)$$

Continuation of this procedure yields the remaining liquid rates. The balance that encloses the condenser and the accumulator is used to compute the condenser duty Q_c, and the balance that encloses the entire column is used to compute the reboiler duty. After each liquid rate L_j has been computed, the corresponding vapor rate V_{j+1} is found by use of a total-material balance expression:

$$V_{j+1} - L_j - D + \sigma[V^{\circ}_{j+1} - L_j^{\circ} - D^{\circ}]$$

$$= \left(\frac{1}{\mu\, \Delta t}\right) \sum_{k=0}^{j} (U_k - U_k^{\circ}),\ 1 \leqq j \leqq f-2 \qquad (28)$$

For columns at steady state operation, the advantages of the constant-composition method over the conventional method for making enthalpy balances have been demonstrated (7), and these same advantages exist for columns at unsteady state operation.

The Q method (7) was used in conjunction with Equations (27) and (28) in the determination of the flow rates. The Q method makes use of intercoolers (or heaters) as required to maintain the flow rates throughout the column within specified limits.

COMPLEX COLUMNS

Except for a few relatively minor modifications that follow, the treatment of complex columns is analogous to that presented for conventional columns.

When each component-material balance encloses only one plate, the equations for a complex column are of the same form as those given by Equation (13), provided that no pump-around [a stream withdrawn from some plate, heated (or cooled), and returned to either the same or some other plate of the column] is returned to the column more than two plates above or more than two plates below the one from which it was withdrawn. When a pump-around is returned more than two plates above or below the one from which it was withdrawn, a corresponding element is obtained that lies on a diagonal above or below the three diagonals that contain the coefficients of the v_{ji}'s. These equations may be solved by use of Crout's method.

When the component-material balances enclose the top (or bottom) of the column and each plate, expressions of the general form given by Equation (15) are obtained. Each pump-around stream returned to a plate lower than the one from which it was withdrawn leads to an element that lies on a diagonal above those of the supertriangular part of the matrix $\overline{A}$ of Equation (15). However, the presence of such elements requires no modification of Crout's method.

When the molal holdups $(0 \leqq j \leqq N+1)$ are specified, the expressions given by Equations (16) through (19) and (22) of the θ method of convergence are applicable, provided the formula given by Equation (30) is used for $(d_i)_{co}$. That these equations apply is shown in the following manner. Consider the general case of a complex column with any number of feeds and with a liquid (W_j^L) and vapor side stream (W_j^V) withdrawn from each plate $(1 \leqq j \leqq N)$. For convenience, let the total molal flow rate of component i in all feeds be denoted by FX_i; that is $FX_i = F_1X_{1i} + F_2X_{2i} + \ldots$.

Since the composition of the liquid in each withdrawal stream W_j^L is the same as that on and leaving plate j, it follows that

$$(w_{ji}^L)_{co} = \left(\frac{W_j^L}{U_j}\right)(u_{ji})_{co} = \left(\frac{\theta_j W_j^L}{U_j}\right)\left(\frac{u_{ji}}{d_i}\right)_{ca} (d_i)_{co} \qquad (29)$$

Thus, the additional specifications, the W_j^L's, do not lead to any θ's in addition to those required for the U_j's, namely $\theta_{-1}, \theta_0, \ldots, \theta_N$. However, the specification of the W_j^V's does lead to an independent set of θ's, denoted by θ_1^V,

$\theta_2^V, \theta_3^V, \ldots, \theta_N^V$. When a procedure similar to that described for Equation (21) is followed, the formula

$$(d_i)_{co} = \frac{FX_i + \sigma[F^o X_i^o - d_i^o - b_i^o] - \sum_{j=0}^{N} (w^V{}_{ji} + w^L{}_{ji})^o + \frac{1}{\mu\,\Delta t} \sum_{j=0}^{N+1} u^o{}_{ji}}{1 + \theta_{-1}\left(\frac{b_i}{d_i}\right)_{ca} \left[1 + \frac{U_{N+1}/B}{\mu\,\Delta t}\right] + \sum_{j=0}^{N} \left[\frac{W_j^L}{U_j} + \frac{1}{\mu\,\Delta t}\right] \theta_j \left(\frac{u_{ji}}{d_i}\right)_{ca} + \sum_{j=1}^{N} \theta_j^V \left(\frac{w_{ji}^V}{d_i}\right)_{ca}} \tag{30}$$

is obtained.

Suppose that for the previous case, the $\mathcal{M}_j$'s (mass or volume) are specified instead of the U_j's. For this set of specifications the θ mehod of convergence consists of Equations (18), (19), and (23), where the formula for $(d_i)_{co}$ is obtained by replacing the denominator of the formula given by Equation (30) by

$$1 + \theta_{-1}\left(\frac{b_i}{d_i}\right)_{ca} + \sum_{j=0}^{N+1} \left[\frac{W_j^L}{U_j} + \frac{1}{\mu\,\Delta t}\right] \theta_j \left(\frac{u_{ji}}{d_i}\right)_{ca} + \sum_{j=1}^{N} \theta_j^V \left(\frac{w_{ji}^V}{d_i}\right)_{ca} \tag{31}$$

TRUNCATION AND INHERITED ERROR

The error associated with the approximation of the integral for any given time period is called the *truncation error*. As a consequence of the truncation error for any one time period, the values of v_{ji} for the beginning of the next time period are in error. The error that carried over in this fashion from one time period to the next is called *inherited error* (*14*). In certain numerical methods (*14*), convergence to the desired solution depends upon the choice of the size of Δt. However, as shown by Waggoner (*28*) for $0.5 < \mu < 1$ the inherited error is bounded as the number of time periods approaches infinity. Ball (*3*) was the first to observe instability of the implicit method for $\mu = 0.5$. Furthermore, any finite Δt consistent with the number of digits available may be employed. From the standpoint of application, the only limitation encountered in the choice of Δt was that a Δt greater than 10^{-6} should be used in the expressions for $(d_i)_{co}$. Thus, any scheme may be employed for the selection of the size of each Δt as steady state is approached. In fact if a Δt of the order of 10^{10} is selected, the steady state solution for problems such as Example 1 is obtained at the end of the first time increment.

Selection of the Size of the Time Increments

In order to obtain accurate transient values of the variables, small Δt's should be selected for the first few time intervals after the upset has occurred. As steady state is approached, larger Δt's may be used without significant loss of accuracy in the transient values of the variables. The following scheme appeared to give reliable results for all problems considered. The Δt to be used for a preselected number of time periods is computed such that $\tau = 5$, where

$$\tau = \frac{U_f}{\Delta t\, L_0}$$

At the end of every ten time periods thereafter the value of τ is reduced by one half or Δt is doubled. In order to obtain some idea of the accuracy of this procedure, problems were solved in which the time periods were decreased in size until round-off error became apparent. Relative to the most accurate of these results, the maximum error in composition given by the proposed procedure for any time period was 1% for a column with as many as one hundred plates.

CALCULATIONAL PROCEDURE

In proceding from one time increment to the next, one could choose to predict the values of such intermediate variables as the x_{ji}'s from which the corresponding values of the T_j's and V_j's could be calculated. However, since the direct prediction of the T_j's and V_j's requires less effort, this approach was elected. The point-slope predictor (*14*) stated for T_j

$$T_j \Big|_{t_n+\Delta t} = T_j \Big|_{t_n-\Delta t} + 2\Delta t \frac{dT_j}{dt} \Big|_{t_n} \tag{32}$$

was used to predict the values of T_j and V_j at the end of the time period $(t_n+\Delta t)$. The derivatives of T_j and V_j were evaluated numerically. After each V_j had been predicted by the point-slope predictor, the corresponding value of L_j was computed by a material-balance equation.

In the following calculational procedure, it is supposed that initially the column is at steady state, and that at zero time an upset in the composition of the feed occurs. (Note that other initial conditions and upsets may be selected.)

The calculational procedure for the case where the molal holdups are specified is presented in detail, and the procedures for the other cases are obtained by modification of this one.

Specification of the Holdups in Molal Units

1. Take $\mu = 0.6$ and choose the size of the first increment of time as described in the next section.
2. Assume values for the temperatures and L/V's at $t_n+\Delta t$. For the first two trials, the values at time t_n are satisfactory. For the second and all subsequent time increments, the values for T_j and V_j are predicted by use of the point-slope predictor, see Equation (32).
3. On the basis of the specified Murphree efficiencies, compute the E_{ji}'s. In the event a negative number is obtained, use the positive value computed as described in reference (*7*).
4. Compute d_i, b_i, u_{ji}, l_{ji}, and v_{ji} at the end of each increment of time by use of the material-balance equations.
5. Find the θ's such that $g_{-1} = g_0 = g_1 = \ldots = g_N = 0$ [see Equation (22)] by use of the Newton-Raphson method.
6. Compute the temperatures by use of the K_b method (*7, 26*). Note that after the corrected u_{ji}'s have been found in step 5, the corrected liquid mole fractions may be computed directly from these.
7. Compute the L/V's for the next trial by use of enthalpy and total-material balances.
8. For each time increment repeat steps 3 through 7 until $|\theta_j - 1|$ is equal to or less than a preselected number of order of 10^{-3} or 10^{-4}. In practice, steps 3 through 7 were repeated a minimum of five times and a maximum of ten times.

It is to be observed that the only trial and error involved within a trial calculation for each Δt is the determination of the θ_j's. For the case where the mass holdups are specified, the following procedure is employed.

TABLE 1. STATEMENT OF EXAMPLE 1

Initial conditions, steady state operation

Component	$F°X°$	Specifications *Other conditions*
C_3H_8	60	$D = 50$, $V_1 = 150$, boiling point liquid feed, total condenser, column pressure = 300 lb./sq. in. abs., three rectifying plates, three stripping plates including the reboiler. The K data and enthalpy data are given in Tables A-4 and A-8 of reference (7).
n-C_4H_{10}	20	
n-C_6H_{14}	20	

Steady state solution

Plate No.	Temp., °F.	Vapor rates, moles/min.
0 (condenser)	137.98	50.00
1	142.00	150.00
2	148.43	146.32
3	158.49	141.10
4 (feed)	179.33	130.98
5	199.78	123.73
6 (reboiler)	248.58	109.10

Component	d_i	b_i
C_3H_8	48.3711	11.6289
n-C_4H_{10}	16.2849×10^{-1}	18.3715
n-C_6H_{14}	43.6069×10^{-5}	19.9996

Upsets for Example 1

Component	Upset 1 (at zero time) FX	Upset 2 (at 4 min.) FX	Upset 3 (at 19 min.) FX
C_3H_8	50	30	10
n-C_4H_{10}	10	5	0
i-C_4-H_{10}	10	20	40
n-C_6H_{14}	30	45	50

Other conditions

All specifications and the molal holdups are the same as those stated above.

Specification of the Holdups in Mass or Volumetric Units

For the first trial for the first increment of time (where the initial condition is steady state), the variation of the molal holdup is neglected. At the end of the first and all subsequent trials, the molal holdups at time $t_n+\Delta t$ are computed by use of Equation (23) and are employed for the determination of the θ_j's.

When the volumetric holdups are specified, an analogous procedure is employed.

ILLUSTRATIVE EXAMPLE AND TEST PROBLEMS

Example 1 (Table 1, Figures 1 and 2) was selected for illustrative purposes. In this example, upsets in the feed composition occur at times 0, 4, and 19 min. Also, note that in the first upset the feed contains a component which was not present initially. Each time an upset occurs, the procedure for selecting the size of the Δt's is, of course, initialized.

To test the calculational procedures presented, a wide variety of problems was solved and recorded by Waggoner (28). Problems involving complex columns with side streams and pump-arounds were solved. Problems were solved to show that a different holdup could be specified for each plate or stage in terms of mass, volume, or molal units. A set of modified Murphree efficiencies was specified for an entire run, and the instantaneous vaporization efficiencies were calculated therefrom by use of Equation (7). Feeds having wide boiling ranges with thermal conditions ranging from subcooled liquid to dew-point vapor were used. Problems were solved in which the following upsets as well as combinations of these upsets were specified: step change in the feed composition, step change in the feed rate, and step change in the reflux ratio.

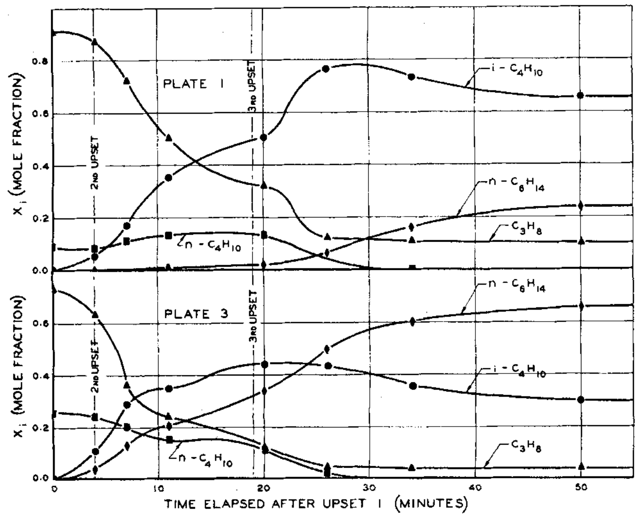

Fig. 1. Transient values of the mole fractions on plates 1 and 3 after upsets 1, 2, and 3.

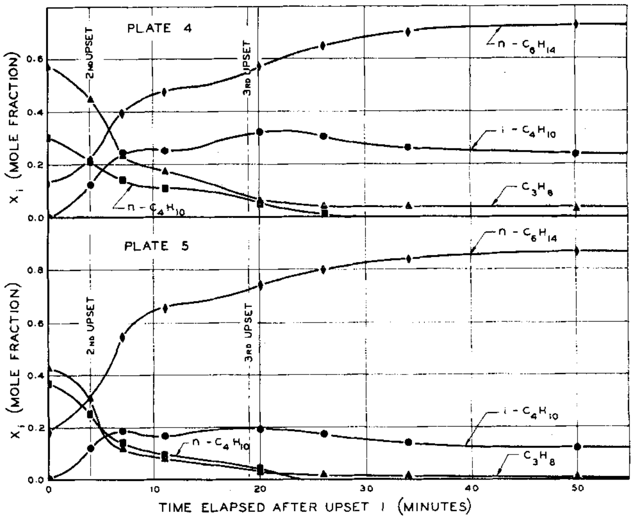

Fig. 2. Transient values of the mole fractions on plates 4 and 5 after upsets 1, 2, and 3.

To demonstrate the validity of the proposed procedures, problems were formulated on the basis of experimental observations of columns at unsteady state operation. In particular, Waggoner (*28*) solved problems corresponding to Runs 1 and 3 of Huckaba et al. (*8*), Runs 318,408-1, and 408-2 of Huckaba et al. (*9*), and Runs F-10:1 and F-18:2 of Armstrong and Wilkinson (*1*). The agreement between the calculated and experimental results was good.

Use of a Modified θ Method to Reduce Computing Time

In the interest of increasing the speed of performing the calculations for each time period, a procedure involving only one θ for a conventional column was investigated and found to give satisfactory results for all problems considered. For any one Δt, the number of trials required to obtain convergence by use of a single θ was about the same as that required when all of the θ's were employed. Also, all problems considered converged to the correct steady state solution where either one or all of the θ's were employed, provided a sufficiently large number of time periods was used. In the procedure that employs a single θ, each θ_j that appears in the formulas for $(d_i)_{co}$ is replaced by θ_{-1}. Thus, the g functions given by Equations (22) and (24) reduce to the function g_{-1}, which was solved for θ_{-1} by use of Newton's method (*16, 25*). An analogous procedure for complex columns was not investigated, but it is anticipated that any scheme for reducing the number of θ's should make use of θ_{-1} for the distillate and a θ for each side stream withdrawn. This choice of θ's corresponds to the number of θ's required to describe complex columns at steady state operation (*7*).

ACKNOWLEDGMENT

The support given by the Esso Research and Engineering Company and by the Data Processing Center of Texas A&M University is gratefully acknowledged. The helpful suggestions of C. S. Hwa, R. E. Bollinger, F. W. Pasterczyk, and G. H. Wolfang of Esso Research and Engineering Company and those of Professor H. A. Luther of Texas A&M University are appreciated.

NOTATION

A_{ji} = absorption factor for component i and plate j; $A_{ji} = L_j/(E_{ji}K_{ji}V_j)$

b_i = molal flow rate of component i in the bottoms; also denoted by $l_{N+1,i}$

c = total number of components

d_i = molal flow rate of component i in the distillate; also denoted by v_{0i}

D = total molal flow rate of the distillate

E_{ji} = instantaneous vaporization efficiency

E^M_{ji} = instantaneous value of the modified Murphree efficiency

$f(T_j)$ = temperature function for plate j

F = total molal flow rate of the feed or feeds

h_{ji}, H_{ji} = enthalpies (molal) of pure component i in the liquid and vapor states, respectively, at the temperature of plate j; these are expressed as polynomials in temperature

$$H(x_j)_{j+1} = \sum_{i=1}^{c} H_{j+1,i}\, x_{ji}$$

K_{ji} = equilibrium constant for component i at the temperature of plate j; these functions are expressed as polynomials in temperature

K_{jb} = equilibrium constant for the base component at the temperature of plate j; see references (*7, 26*)

l_{ji} = molal flow rate at which component i in the liquid phase leaves plate j

l_{Fi} = molal flow rate of component i in the liquid part of a partially vaporized feed; for a bubble-point liquid and subcooled feeds, $l_{Fi} = FX_i$; for dew-point vapor and superheated feeds, $l_{Fi} = 0$

m_{ji} = liquid holdup (mass or volume) of component i on plate j

$\mathcal{M}_j$ = total liquid holdup (mass or volume) on plate j

M_i = molecular weight of component i; also used to denote the volume per mole for component i in the liquid phase on each plate

P_{ji} = constant appearing in the component-material balance enclosing plate j; definition follows Equation (13)

Q_c = condenser duty

S_{ji} = stripping factor for component i and plate j; $S_{ji} = (E_{ji}K_{ji}V_j)/L_j$

t = time in consistent units; t_n = particular time

T_j = temperature of plate j

u_{ji} = liquid holdup (moles) of component i on plate j

U_j = total liquid holdup (moles) on plate j

v_{ji} = molal flow rate at which component i in the vapor phase leaves plate j; also $v_{0i} = d_i$

v_{Fi} = molal flow rate of component i in the vapor part of a partially vaporized feed; for a bubble-point liquid feed, $v_{Fi} = 0$; for bubble-point liquid and subcooled feeds, $v_{Fi} = 0$; and for dew-point vapor and superheated feeds, $v_{Fi} = FX_i$

V_j = total molal flow rate at which vapor leaves plate j

$w^L{}_{ji}$ = liquid withdrawal rate (molal) of component i from plate j

$w^V{}_{ji}$ = vapor withdrawal rate (molal) of component i from plate j

$W_j{}^L$ = total liquid withdrawal rate (molal) from plate j $(1 \leqq j \leqq N)$

$W_j{}^V$ = total vapor withdrawal rate (molal) from plate j $(1 \leqq j \leqq N)$

x_{ji} = mole fraction of component i in the liquid leaving plate j

X_i = total mole fraction of component i in the feed (regardless of state)

X_{Di} = total mole fraction of component i in the distillate (regardless of state)

y_{ji} = mole fraction of component i in the vapor phase leaving plate j

Y_{ji} = variable appearing in the efficiency relationships

Greek Letters

α = relative volatility of component i at the temperature plate j; $\alpha_{ji} = K_{ji}/K_{jb}$

θ_{-1} = multiplier associated with the distillate and bottoms

θ_j = multiplier associated with plate j

λ_j = multiplier for plate j used in the development of the θ method for columns at unsteady state operation

μ = weighting factor used in the evaluation of an integral in terms of the values of a function at times t_n and $t_n + \Delta t$

ρ_{ji} = constant appearing in the component-material balances; definition follows Equation (13)

σ = constant appearing in the component-material balance and in the enthalpy balances; $\sigma = (1 - \mu)/\mu$

τ_j = dimensionless-time factor for plate j; $\tau_j = (U_j/L_j)/\Delta t$; $\tau_j{}^o = (U_j{}^o/L_j{}^o)/\Delta t$, where Δt is the time increment under consideration and not the previous one

$\overline{\tau}_j$ = multiplier in the expression for $(l_{ji})_{co}$

χ_{ji} = factor whose definition follows Equation (30)

Subscripts

ca = calculated value

co = corrected value

i = component number; $i=1$ through $i=c$

j = plate number; the plates are numbered down from the top of the colum; the condenser (total or partial) is assigned the number 0, the top plate the number 1, the feed plate the number represented by f, the bottom plate the number N, the reboiler the number $N+1$.

k = integer used for counting

m = mean value of a function

n = trial number

LITERATURE CITED

1. Acrivos, A., and N. R. Amundson, *Ind Eng. Chem.*, **47**, 1533 (1955).
2. Armstrong, W. D., and W. L. Wilkinson, *Trans. Instn. Chem. Engrs.*, **35**, 352 (1957).
3. Ball, W. E., Paper presented at the 44th National Meeting of the A.I.Ch.E., New Orleans (Feb. 27, 1961).
4. Ceaglske, N. H., *A.I.Ch.E. Journal*, **7**, 653 (1961).
5. Gilliland, E. R., and C. M. Mohr, *Chem. Eng. Progr.*, **58**, No. 9, p. 59 (1962).
6. Grabbe, E. M., S. Ramo, and D. E. Wooldridge, "Handbook of Automation Computation and Control," Vol. 1, pp. 14-28, Wiley, New York (1958).
7. Holland, C. D., "Multicomponent Distillation," Prentice-Hall, Englewood Cliffs, New Jersey (1963).
8. Huckaba, C. E., F. R. Franke, and R. P. May, Paper presented at the 55th Annual Meeting of the A.I.Ch.E., Chicago (Dec. 2-6, 1962).
9. ——————, *Chem. Eng. Progr. Symposium Ser. No. 46*, **59**, 38 (1963).
10. Lapidus, Leon, "Digital Computation for Chemical Engineers," McGraw-Hill, New York (1962).
11. Lyster, W. N., S. L. Sullivan, Jr., D. S. Billingsley, and C. D. Holland, *Petrol. Refiner*, 38, 221, 139 (1959).
12. Mah, T. H. S., S. Michaelson, and R. W. H. Sargent, *Chem. Eng. Sci.*, **17**, 619 (1962).
13. Marshall, W. R., and R. L. Pigford, "The Application of Differential Equations to Chemical Engineering Problems," p. 146, University of Delaware, Newark, Delaware (1947).
14. Milne, W. E., "Numerical Solution of Differential Equations," pp. 19-30, Wiley, New York (1960).
15. Murphree, E. V., *Ind. Eng. Chem.*, **17**, 747 (1925).
16. Nielsen, K. L., "Methods in Numerical Analysis," Macmillan, New York (1960).
17. Peiser, A. M., and S. S. Grover, *Chem. Eng. Progr.*, **58**, No. 9, p. 65, (1962).
18. Pigford, R. L., J. B. Tepe, and C. J. Garrahan, *Ind. Eng. Chem.*, 43, 2592 (1951).
19. Richtmyer, R. D., "Difference Methods for Initial-Value Problems," Interscience, New York (1957).
20. Rose, A., C. L. Johnson, and T. J. Williams, *Ind. Eng. Chem.*, 48, No. 7, p. 1773 (1956).
21. ———, R. F. Sweeney, and V. N. Schrodt, *ibid.*, **50**, 737 (1958).
22. Rosenbrock, H. H., *Trans. Instn. Chem. Engrs.*, **35**, 347 (1957).
23. ———, *Chem. Eng. Progr.*, **58**, No. 9, p. 43 (1962).
24. Sargent, R. W. H., *Trans. Instn. Chem. Engrs.*, **41**, 51 (1963).
25. Sokolnikoff, I. S., and E. S. Sokolnikoff, "Higher Mathematics for Engineers and Physicists," McGraw-Hill, New York (1941).
26. Taylor, D. L., Parke Davis, and C. D. Holland, *A.I.Ch.E. Journal*, ——————.
27. Thiele, E. W., and R. L. Geddes, *Ind. Eng. Chem.*, **25**, 289 (1933).
28. Waggoner, R. C., Dissertation, Texas A&M University, College Station, Texas (1964).
29. Yesberg, D., and A. I. Johnson, *Can. J. Chem. Eng.*, 38, 49 (April, 1960).

Manuscript received March 23, 1964; revision received July 27, 1964; paper accepted July 29, 1964. Paper presented at A.I.Ch.E. Houston meeting.

APPENDIX

Development of Equations (16), (18), and (22)

Let the multiplier $\overline{\tau}_j$ be defined by

$$(l_{ji})_{co} = \overline{\tau}_j \left(\frac{l_{ji}}{b_i} \right)_{ca} (b_i)_{co} \qquad \text{(A-1)}$$

where $(b_i)_{co}$ is one of the set of values for $(d_i)_{co}$ and $(u_{ji})_{co}$ that are both in component-material balance and in agreement with the specified values of D and the U_j's. Equation (A-1) implies

$$L_j = \sum_{i=1}^{c} (l_{ji})_{co} \qquad \text{(A-2)}$$

If after leaving the condenser it is supposed that the vapor distillate is condensed on plate $j = -1$, Equation (A-1) becomes

$$(d_i)_{co} = \overline{\tau}_{-1} \left(\frac{d_i}{b_i} \right)_{ca} (b_i)_{co} \qquad \text{(A-3)}$$

Taking $\theta_{-1} = 1/\overline{\tau}_{-1}$ Equation (A-3) becomes

$$\left(\frac{b_i}{d_i} \right)_{co} = \theta_{-1} \left(\frac{b_i}{d_i} \right)_{ca} \qquad \text{(A-4)}$$

From the definition of the mole fraction, Equations (A-1) and (A-2), it follows that

$$x_{ji} = \frac{(l_{ji})_{co}}{L_j} = \frac{\left(\frac{l_{ji}}{b_i} \right)_{ca} (b_i)_{co}}{\sum_{i=1}^{c} \left(\frac{l_{ji}}{b_i} \right)_{ca} (b_i)_{oo}} \qquad \text{(A-5)}$$

By use of Equation (A-4), this epression may be stated in the form given by Equation (18). Thus, the correct molal holdup of component i on plate j is given by

$$(u_{ji})_{co} = U_j x_{ji} = \left\{ \frac{U_j}{\sum_{i=1}^{c} \left(\frac{l_{ji}}{d_i} \right)_{ca} (d_i)_{co}} \right\} \left(\frac{l_{ji}}{d_i} \right)_{ca} (d_i)_{co} \qquad \text{(A-6)}$$

Observe that the expression enclosed by brackets is independent of i. Then, let

$$\lambda_j = \frac{U_j}{\sum_{i=1}^{c} \left(\frac{l_{ji}}{d_i} \right)_{ca} (d_i)_{co}} \qquad \text{(A-7)}$$

When convergence is obtained, each multiplier λ_j converges to U_j/L_j. In order to retain the symmetry of the θ method, a corresponding θ_j is defined for each λ_j. First, note that

$$(u_{ji})_{co} = \lambda_j \left(\frac{l_{ji}}{u_{ji}} \right)_{ca} \left(\frac{u_{ji}}{d_i} \right)_{ca} (d_i)_{co} \qquad \text{(A-8)}$$

Since the calculated values of u_{ji} and l_{ji} are based on the same set of mole fractions, it follows that

$$(u_{ji})_{co} = \left(\frac{\lambda_j L_j}{U_j} \right) \left(\frac{u_{ji}}{d_i} \right)_{ca} (d_i)_{co} = \theta_j \left(\frac{u_{ji}}{d_i} \right)_{ca} (d_i)_{co} \qquad \text{(A-9)}$$

Multiplication of both sides of Equation (A-7) by L_j/U_j yields

$$\theta_j = \frac{U_j}{\sum_{i=1}^{c} \left(\frac{u_{ji}}{d_i} \right)_{ca} (d_i)_{co}} \qquad \text{(A-10)}$$

Thus, where it is understood that the formula for $(u_{ji})_{co}$ is given by Equation (A-9), Equation (A-10) may be restated in the functional form given by Equation (22) for $0 \leqq j \leqq N$.