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Generalization of the Theta Methods of Convergence for Solving Distillation and Absorber-Type Problems

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Abstract

An extension of the θ methods of convergence wherein it is required that all terminal streams must satisfy simultaneously material balances, energy balances, and equilibrium relationships is presented. By use of this new convergence method, any distillation-type or absorber-type problem may be solved. The procedure has the flexibility of treating any column either as a single unit or a system of any number of subunits. The new procedure permits the direct solution of problems by use of the θ methods which could not be solved by the original method.

Applications of the θ method to problems which differ from those considered previously are presented. First an extension of the original θ method is presented which makes it possible to solve distillation problems in which the reflux ratio and the boilup ratio, or the condenser duty and the reboiler duty, or combinations of these are specified in lieu of the reflux rate and the distillate rate. The technique used to solve these distillation problems is the same as that used to solve absorber problems in which the total flow rates and compositions of the lean gas and rich oil streams are to be determined when the inlet lean oil and rich gas streams are completely specified. A further extension of the new version of the θ method permits any column to be solved as an equivalent system of any number of subunits. The formulations shown herein and the testing of these have thus far been for systems whose mixtures form ideal solutions.

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Application of the Extended Version of the θ Method to Distillation Columns

The original θ method was developed for the case where the specifications for the distillation column (see Fig. 1) are taken to be the number of stages, the location of the feed plate, the type of condenser, the column

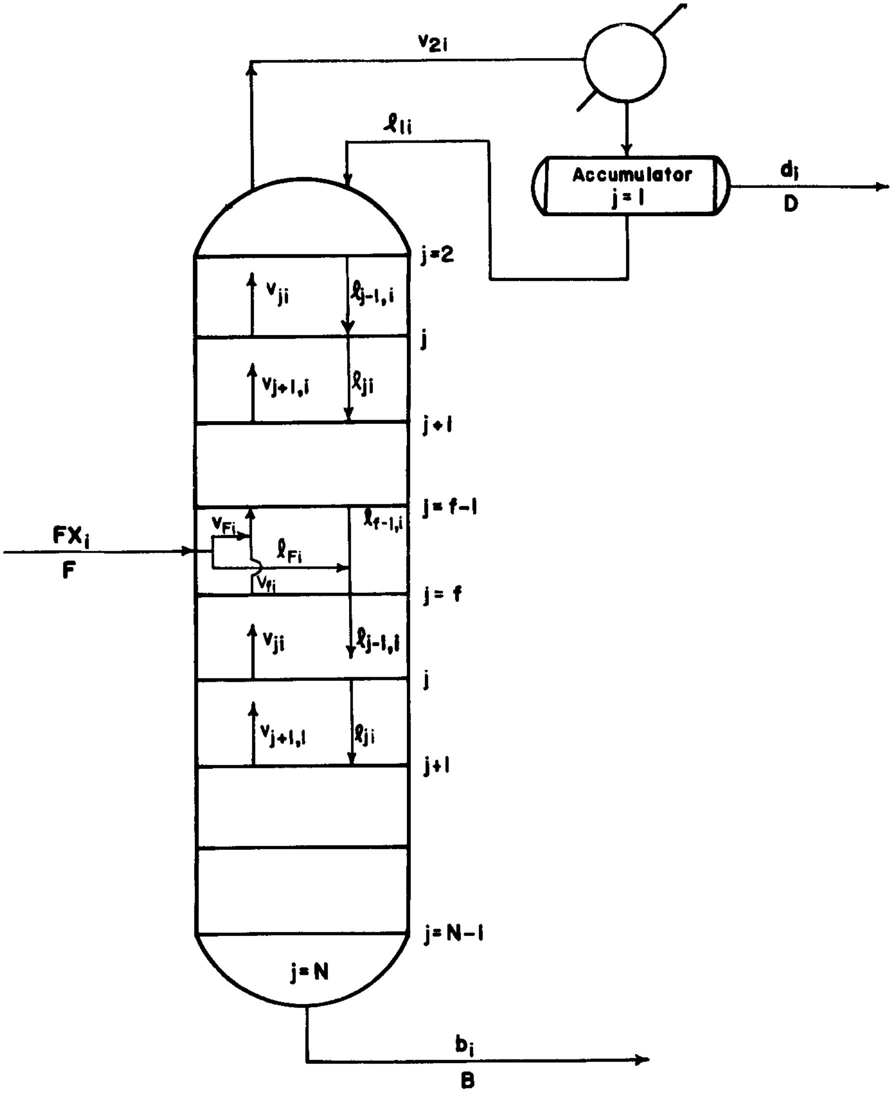

FIG. 1. Sketch of a conventional distillation column.

pressure, the distillate rate D, and the reflux rate L_1. Many times it is desired to make specifications such as the reflux ratio L_1/D and the boilup ratio V_N/B or the top and bottom temperatures T_D and T_B or some combination of these instead of the reflux and distillate rates L_1 and D. Although both the condenser and reboiler duties, Q_C and Q_R, may be specified in lieu of L_1 and D_1, the choosing of two such values for which a solution exists could prove difficult. Consequently, the specification of both of these duties is not generally recommended unless the specified values are known to be realistic.

For definiteness, suppose that the reflux ratio L_1/D and B/V_N are taken to be specified instead of L_1 and D in the above set of specifications for the conventional distillation column shown in Fig. 1. Except for the additional functions and variables involved in the extended version of the θ method, the general calculational procedure is the same as that used with the original θ method (*9*, *10*). In the interest of completeness these equations are presented in Table 1, but in the interest of brevity they are not derived.

On the basis of sets of assumed temperatures $\{T_j\}$ and vapor rates $\{V_j\}$, the component material balances may be solved for the component flow rates. (It is of course supposed that the liquid rates $\{L_j\}$ are first computed by use of the set of assumed vapor rates $\{V_j\}$ and the total material balances.) The component-material balances may be represented by the matrix equation

$$\mathbf{A}_i\mathbf{v}_i = -\mathscr{f}_i \tag{1}$$

where the elements of the square matrix $\mathbf{A}_i$ and the column vectors $\mathbf{v}_i$ and $\mathscr{f}_i$ are presented in Table 1. After Eq. (1) has been solved for the component flow rates (these rates are denoted by the subscript "*ca*") and used in an extended θ method of convergence in the following manner. First the multiplier θ is defined in the usual way.

$$\left[\frac{b_i}{d_i}\right]_{co} = \theta\left[\frac{b_i}{d_i}\right]_{ca} \tag{2}$$

where it is required that the corrected rates, denoted by the subscript "*co*," satisfy the component-material balance enclosing the entire column; namely,

$$FX_i = (d_i)_{co} + (b_i)_{co} \tag{3}$$

Elimination of $(b_i)_{co}$ from Eqs. (2) and (3) gives

$$(d_i)_{co} = \frac{FX_i}{1 + \theta\left[\frac{b_i}{d_i}\right]_{ca}} = \frac{(d_i)_{ca}FX_i}{(d_i)_{ca} + \theta(b_i)_{ca}} \tag{4}$$

TABLE 1

Equations for Conventional Distillation Columns Which Are to Be Used with the θ Method of Convergence

I. Component-Material Balance

$$\mathbf{A}_i\mathbf{v}_i = -\mathbf{f}_i \tag{A}$$

where

$$\mathbf{A}_i = \begin{bmatrix} -\rho_{1i} & 1 & 0 & 0 & 0 & \cdots & 0 \\ A_{1i} & -\rho_{2i} & 1 & 0 & 0 & \cdots & 0 \\ 0 & A_{2i} & -\rho_{3i} & 1 & 0 & \cdots & 0 \\ \cdots & \cdots & \cdots & \cdots & \cdots & \cdots & \cdots \\ 0 & \cdots & \cdots & \cdots & 0 & A_{N-1,i} & -\rho_{Ni} \end{bmatrix}$$

$$\mathbf{v}_i = [d_i v_{2i} v_{3i} \cdots v_{Ni}]^T$$

$$\mathbf{f}_i = [0 \cdots 0 v_{Fi} l_{Fi} 0 \cdots 0]^T$$

$\rho_{ji} = 1 + A_{ji}$, $A_{ji} = L_j/K_{ij}V_j$ for $j \neq 1, N$. $A_{1i} = L_1/K_{1i}D$ for a partial condenser, $A_{1i} = L_1/D$ for a total condenser, $A_{Ni} = B/K_{Ni}V_N$

The flow rates v_{Fi} and l_{Fi} denote the vapor and liquid flow rates of component i in a partially vaporized feed. Equation (1) may be solved for the component-flow rates by use of the Thomas Algorithm (*9*, *10*) or modifications of it proposed by Boston et al. (*3*).

II. Calculation of Corrected Mole Fractions

$$x_{ji} = \frac{(l_{ji})_{ca}p_i}{\sum_{i=1}^{c}(l_{ji})_{ca}p_i}, \qquad y_{ji} = \frac{(v_{ji})_{ca}p_i}{\sum_{i=1}^{c}(v_{ji})_{ca}p_i} \tag{B}$$

where p_i is defined by Eq. (5).

III. Calculation of Temperatures by the K_b Method

$$K_{jb}|_{T_{j,n+1}} = \frac{1}{\sum_{i=1}^{c}\alpha_{ji}|_{T_{jn}}x_{ji}}, \qquad \text{or } K_{jb}|_{T_{j,n+1}} = \sum_{i=1}^{c}\frac{y_{ji}}{\alpha_{ji}|_{T_{jn}}} \tag{C}$$

$$K_{jb} = \frac{b}{T_j} + a \tag{D}$$

where

$\alpha_{ji} = K_{ji}/K_{jb}$

$a, b =$ constants selected such that the values of the K_b at the lower and upper temperature limits of the curve fits are equal to the respective K values of the mid-boiling or those of the component in the mixture which is just lighter

IV. Calculation of Total Flow Rates by Use of Enthalpy Balances and Total Material Balances

1. Energy balances for the rectifying section:

$$L_j = \frac{-D \sum_{i=1}^{c} [H_i(T_{j+1}) - H_{Di}(T_1)]X_{Di} + Q_C}{\sum_{i=1}^{c} [H_i(T_{j+1}) - h_i(T_j)]x_{ji}}, \quad (j = 1, 2, ..., f-2)$$

$$L_{f-1} = \frac{-D \sum_{i=1}^{c} [H_i(T_f) - H_{Di}(T_1)X_{Di} + V_F \sum_{i=1}^{c} [H_i(T_f) - H_i(T_F)]y_{Fi} + Q_C}{\sum_{i=1}^{c} [H_i(T_f) - h_i(T_{f-1})]x_{f-1,i}}$$

2. Energy balances for the stripping section:

$$V_j = \frac{-B \sum_{i=1}^{c} [h_i(T_N) - h_i(T_{j-1})]x_{Bi} + Q_R}{\sum_{i=1}^{c} [H_i(T_j) - h_i(T_{j-1})]y_{ji}} \quad (j = f+1, f+2, ..., N)$$

V. Total Material Balances

$$V_{j+1} = L_j + D \quad (j = 1, 2, ..., f-2)$$
$$V_f + V_F = L_{f-1} + D$$
$$L_j = V_{j+1} + B \quad (j = f+1, f+2, ..., N)$$
$$F = D + B$$

To avoid numerical difficulties which arise when $(d_i)_{ca} = 0$, the new variable p_i is introduced. Its definition is

$$p_i = \frac{FX_i}{(d_i)_{ca} + \theta(b_i)_{ca}} \tag{5}$$

Then

$$(d_i)_{co} = p_i(d_i)_{ca} \tag{6}$$

Next the θ method is applied. The θ method of convergence consists of a procedure for selecting a new set of terminal flow rates such that the terminal streams are in material balance, energy balance, and the equilibrium relationships for these streams are satisfied. In this procedure, the variables $\mathbf{x}$,

$$\mathbf{x} = [\theta T_1 T_2 T_{N-1} T_N Q_C Q_R]^T \tag{7}$$

are to be selected such that the functions **f**,

$$\mathbf{f} = [g_1 g_2 \cdots g_7]^T \tag{8}$$

are satisfied $\mathbf{f} = \mathbf{0}$. The first four functions are based on the equilibrium relationships for the streams D, V_2, L_{N-1}, and B:

$$g_1 = \frac{1}{\sum_{i=1}^{c} d_i}\left[\sum_{i=1}^{c} K_i(T_1)d_i\right] - 1 \tag{9}$$

$$g_2 = \frac{1}{\sum_{i=1}^{c} v_{2i}}\left[\sum_{i=1}^{c} v_{2i}/K_i(T_2)\right] - 1 \tag{10}$$

$$g_3 = \frac{1}{\sum_{i=1}^{c} l_{N-1,i}}\left[\sum_{i=1}^{c} K_i(T_{N-1})l_{N-1,i}\right] - 1 \tag{11}$$

$$g_4 = \frac{1}{\sum_{i=1}^{c} b_i}\left[\sum_{i=1}^{c} K_i(T_N)b_i\right] - 1 \tag{12}$$

The function g_1 applies for the case where the column has a total condenser. If the column is equipped with a partial condenser, the dew point form of the equilibrium relationship is used as in Eq. (10). Also, the subscript "*co*" has been omitted in the above equations as well as those which follow in the interest of simplicity. The flow rates v_{2i} and $l_{N-1,i}$ are expressed in terms of d_i and b_i by use of component-material balances enclosing the condenser-accumulator and the reboiler, respectively:

$$v_{2i} = l_{1i} + d_i = A_{1i}d_i + d_i = \left[\frac{L_1}{K_i(T_1)D} + 1\right]d_i \tag{13}$$

and

$$l_{N-1,i} = v_{Ni} + b_i = S_{Ni}b_i + b_i = \left[\frac{K_i(T_N)V_N}{B} + 1\right]b_i \tag{14}$$

The functions g_5, g_6, and g_7 are based on enthalpy balances enclosing the condenser-accumulator section, the entire column, and the reboiler, respectively:

$$g_5 = \frac{\sum_{i=1}^{c} d_i[H_{Di}(T_1) - h_i(T_1)] + Q_C}{\sum_{i=1}^{c} v_{2i}[H_i(T_2) - h_i(T_1)]} - 1 \tag{15}$$

where $H_{Di}(T_1) = h_i(T_1)$ for a total condenser and $H_{Di}(T_1) = H_i(T_1)$ for a partial condenser.

$$g_6 = \frac{\sum_{i=1}^{c} d_i[H_{Di}(T_1) - h_i(T_N)] + Q_C}{\sum_{i=1}^{c} FX_i[H_i(T_{\text{feed}}) - h_i(T_N)] + Q_R} - 1 \tag{16}$$

$$g_7 = \frac{\sum_{i=1}^{c} v_{Ni}[H_i(T_N) - h_i(T_N)]}{\sum_{i=1}^{c} l_{N-1,i}[h_i(T_{N-1}) - h_i(T_N)] + Q_R} - 1 \tag{17}$$

where the expressions for v_{2i} and $l_{N-1,i}$ are given by Eqs. (13) and (14), respectively. The flow rate v_{Ni} is expressed in terms of b_i by the equilibrium relationship

$$v_{Ni} = S_{Ni}b_i = \left[\frac{K_i(T_N)V_N}{B}\right]b_i \tag{18}$$

Observe that the functions g_1 through g_7 may be stated explicitly in terms of θ by expressing them in terms of p_i since p_i is expressed explicitly in terms of θ. The variables d_i, v_{2i}, b_i, $l_{N-1,i}$, and v_{Ni} which appear in these functions are expressed in terms of p_i as follows. First, observe that Eq. (6) gives d_i in terms of p_i, and that Eqs. (6) and (13) may be combined to give an expression for v_{2i} in terms of p_i,

$$v_{2i} = \left[\frac{L_1}{K_i(T_i)D} + 1\right]p_i(d_i)_{ca} \tag{19}$$

Equations (2) and (6) may be combined to give b_i in terms of θ; namely,

$$b_i = \theta(b_i)_{ca}p_i \tag{20}$$

The flow rate $l_{N-1,i}$ is expressed in terms of p_i by use of Eqs. (14) and (20) as follows:

$$l_{N-1,i} = \left[\frac{K_i(T_N)V_N}{B} + 1\right]\theta(b_i)_{ca}p_i \tag{21}$$

Finally, v_{Ni} is expressed in terms of p_i by use of Eqs. (18) and (20),

$$v_{Ni} = \left[\frac{K_i(T_N)V_N}{B}\right]\theta(b_i)_{ca}p_i \tag{22}$$

The solution set of values of the variables $\mathbf{x} = [\theta_1 T_1 T_2 T_{N-1} T_N Q_C Q_R]^{\mathrm{T}}$ which make $\mathbf{f} = \mathbf{0}$ may be found by use of the Newton-Raphson method or a variation of it such as the one proposed by Broyden (*5*). The Newton-

Raphson method consists of the repeated use of the Newton-Raphson equations

$$\mathbf{J}\Delta\mathbf{X} = -\mathbf{f} \tag{23}$$

until the convergence criteria have been satisfied. The Jacobian matrix **J** and the column vector **ΔX** appearing in the above equation have the following definitions:

$$\mathbf{J} = \begin{bmatrix} \frac{\partial f_1}{\partial \theta} \frac{\partial f_1}{\partial T_1} \frac{\partial f_1}{\partial T_2} \cdots \frac{\partial f_1}{\partial Q_C} \frac{\partial f_1}{\partial Q_R} \\ \frac{\partial f_2}{\partial \theta} \cdots\cdots\cdots\cdots \frac{\partial f_2}{\partial Q_R} \\ \cdots\cdots\cdots\cdots\cdots\cdots \\ \frac{\partial f_7}{\partial \theta} \cdots\cdots\cdots\cdots \frac{\partial f_7}{\partial Q_R} \end{bmatrix}$$

$$\Delta\mathbf{X} = [\Delta\theta \Delta T_1 \Delta T_2 \Delta T_{N-1} \Delta T_N \Delta Q_C \Delta Q_R]^T$$

$$\Delta\theta = \theta_{n+1} - \theta_n$$

where θ_n is the value of θ assumed to make the nth trial. After Eq. (23) has been solved for **ΔX**, the values of the variables to be used for the next trial are found as follows:

$$\begin{aligned} \theta_{n+1} &= \theta_n + \Delta\theta \\ T_{1,n+1} &= T_{1,n} + \Delta T \\ \vdots\quad & \quad\vdots \\ Q_{R,n+1} &= Q_{R,n} + \Delta Q_R \end{aligned} \tag{24}$$

In the the event that the computed value of any variable is unacceptable (either negative or outside the range of curve fits), each of the corrections is reduced successively by factors of 1/2 until an acceptable set of values of the variable for working the next trial is obtained. Prior to solving Eq. (23) for **ΔX**, column scaling followed by scaling is recommended.

Analytical expressions may be used to evaluate the elements of the Jacobian. These expressions are readily obtained by explicit differentiation of the functions **f** with respect to each of the variables in the same manner as shown below for the function g_1:

$$\frac{\partial g_1}{\partial \theta} = \frac{1}{D} \sum_{i=1}^{c} \left[K_i(T_i)(d_i)_{ca} \left(\frac{\partial p_i}{\partial \theta} \right) \right] - \frac{g_1}{D} \frac{\partial D}{\partial \theta} \tag{25}$$

where

$$D = \sum_{i=1}^{c} (d_i)_{ca} p_i, \qquad \frac{\partial D}{\partial \theta} = \sum_{i=1}^{c} (d_i)_{ca} p_i$$

$$\frac{\partial p_i}{\partial \theta} = -\frac{(b_i)_{ca} F X_i}{[(d_i)_{ca} + \theta (b_i)_{ca}]^2}$$

$$\frac{\partial g_1}{\partial T_1} = \frac{1}{D} \sum_{i=1}^{c} (d_i)_{ca} p_i \frac{\partial K_i(T_1)}{\partial T_1} \tag{26}$$

$$\frac{\partial g_1}{\partial T_2} = \frac{\partial g_1}{\partial T_{N-1}} = \frac{\partial g_1}{\partial T_N} = \frac{\partial g_1}{\partial Q_C} = \frac{\partial g_1}{\partial Q_R} = 0 \tag{27}$$

Instead of evaluating the elements of J by use of the analytical expressions for the partial derivatives, the derivatives may be evaluated numerically. In order to avoid the evaluation of the derivatives and the inversion of the Jacobian matrix for each trial, Broyden's method (*5*) may be used. Some reduction of the computer time required by Broyden's method may be achieved through the use of a combination of Broyden's and Bennett's algorithms (*1*, *8*).

After the solution set of variables has been obtained, the compositions are computed by use of the expressions given by Eq. (B) of Table 1. These compositions are used to compute the remaining unknown temperatures (T_3, T_4, ..., T_{N-2}) by use of the K_b method; see Eqs. (C) and (D) of Table 1. The variables $\mathbf{x}$ which make $\mathbf{f} = \mathbf{0}$ as well as the compositions found by Eq. (B) of Table 1 are used in the calculation of a new set of total flow rates by use of the enthalpy and total material balances; see Table 1.

Specification sets other than the reflux ratio and the boilup ratio may be made as mentioned above. For the sets enumerated, the seven g functions listed above are used. However, when the reflux ratio and the distillate rate D are specified as in the orginal θ method (*9*, *10*), only one g function is required; namely,

$$g(\theta) = \sum_{i=1}^{c} (d_i)_{ca} - D \tag{28}$$

After the $\theta > 0$ that makes $g(\theta) = 0$ has been obtained, the temperatures are found by the K_b method and the total flow rates are found by use of enthalpy and total material balances as shown in Table 1.

Illustrative Examples

In order to compare the proposed extension of the θ method with the algorithms based on the Newton-Raphson method, the results obtained by solving several examples are presented. To compare the proposed extension of the θ method with the original θ method, Example 1 (see

Table 2) was solved. The solution value found previously (*9*) for the boilup ratio ($V_N/B = 1.80585$) was used as one of the specifications and a reflux ratio $L_1/D = 2$ was used as the other specification. The variation of the variables θ, T_1, T_2, T_{N-1}, T_N, Q_C, and Q_R of the proposed extension of θ method with trial number is shown in Table 3 and the solution values of the variables are shown in Table 4. This same example was also solved by use of the seven g functions stated above and the specifications of Q_C and Q_R corresponding to the solution values obtained by previous solution. In this case the independent variables were as follows: θ, T_1, T_2, T_{N-1}, T_N, L_1/D, and V_N/B. This same example was also solved by the $2N$ Newton-Raphson method by Hess et al. (*8*) as shown in Table 5. In this

TABLE 2

Statement of Example 1

Component	FX_i	Specifications
CH_4	2.0	$L_1/D = 2$ and $V_N/B = 1.80585$, boiling point liquid feed, partial condenser, column pressure = 300 psia, $N = 12$, and $f = 5$. Equilibrium and enthalpy data for all components are given in Ref. *9*. The initial temperature profile is to be taken linear with plate number between $T_1 = 610°R$ and $T_{12} = 910°R$. Take the initial vapor rate profile to be $V_j = 94.8$ $(1 \leq j \leq 12)$, and the corresponding liquid rate profile is given by material balance. Component i-C_4H_{10} was taken as the base component and a and b in Eq. (D) of Table 1 were determined on the basis of the values for the K of i-C_4H_{10} at 510 and 960°R.
C_2H_6	10.0	
C_3H_6	6.0	
C_3H_8	12.5	
i-C_4H_{10}	3.5	
n-C_4H_{10}	15.0	
n-C_5H_{12}	15.2	
n-C_6H_{14}	11.3	
n-C_7H_{16}	9.0	
n-C_8H_{18}	8.5	
400[a]	7.0	

[a] Commonly referred to as the 400°F normal boiling fraction.

TABLE 3

Convergence Characteristics of the θ Method for Example 1 When the Additional Specifications Are $L_1/D = 2$ and $V_N/B = 1.80585$

Trial no.	θ	T_1	T_2	T_{N-1}	T_N	Q_C	Q_R
	1.0000	610.0	635.0	885.0	910.0	3.0×10^5	2.0×10^6
1	3.5990	582.82	619.01	715.16	790.96	3.5863×10^5	1.1689×10^6
2	2.0270	566.62	595.20	773.53	827.08	3.8713×10^5	1.3081×10^6
3	0.77160	567.13	593.51	768.14	826.54	3.9443×10^5	1.3194×10^6
4	1.0820	567.29	593.89	767.93	826.48	3.9512×10^5	1.3199×10^6
5	0.98006	567.36	594.04	767.87	826.45	3.9542×10^5	1.3201×10^6
6	1.0034	567.36	594.03	767.88	826.45	3.9541×10^5	1.3201×10^6
7	0.99926	567.36	594.04	767.87	826.45	3.9543×10^5	1.3201×10^6
8	1.0002	567.36	594.04	767.87	826.45	3.9543×10^5	1.3201×10^6
9	0.99991	567.36	594.04	767.87	826.45	3.9543×10^5	1.3201×10^6

TABLE 4

Solution of Example 1[a]

Production distribution			Temperature and vapor rate profiles		
Component	d_i	b_i	Stage no.	Temperature (°R)	Vapor rate (lb-mol/h)
CH_4	0.200000×10	0.11163×10^{-8}	1 (distillate)	567.57	—
C_2H_6	0.999990×10	0.11627×10^{-3}	2	594.37	92.80
C_3H_6	0.597230×10	0.27665×10^{-1}	3	611.93	93.29
C_3H_8	0.1234600×10^2	0.15358	4	630.26	89.42
$i\text{-}C_4H_{10}$	0.74216	0.27578×10	5 (feed)	667.41	80.11
$n\text{-}C_4H_{10}$	0.53699	0.14462×10^2	6	688.69	110.80
$n\text{-}C_5H_{12}$	0.20153×10^{-2}	0.15197×10^2	7	703.28	126.27
$n\text{-}C_6H_{12}$	0.94035×10^{-5}	0.11299×10^2	8	714.13	136.86
$n\text{-}C_7H_{14}$	0.94025×10^{-5}	0.89999×10	9	722.90	144.41
$n\text{-}C_8H_{16}$	0.63427×10^{-7}	0.84999×10	10	731.71	148.87
400	0.65162×10^{-12}	0.69999×10	11	744.15	149.47
			12	768.00	143.72
			13 (bottoms)	826.57	123.52

[a] Convergence criterion: $|g(1)| \leq 10^{-5}$

formulation of the Newton-Raphson method, two independent variables per stage are used for a total of $2N$ variables and $2N$ functions. As illustrated in Table 5 by the results obtained for Example 2, the θ method becomes many times faster than the $2N$ Newton-Raphson method as the number of stages is increased.

To compare the $2N$ Newton-Raphson method with another formulation of the Newton-Raphson method called the Almost Band Algorithm (*6*) [which is similar to the formulation of Sandholm et al. (*11*)], the sequence of examples shown in Table 6 was solved by both methods. The Almost Band Algorithm differs from the $2N$ Newton-Raphson method in that the formulation is in terms of $[N(c + 2) + 1]$ independent variables instead of $2N$. For small numbers of components, the $2N$ Newton-Raphson method is faster than the Almost Band Algorithm and, conversely, for large numbers of plates and a small number of components the Almost Band Algorithm is faster than the $2N$ Newton-Raphson Method as shown in Table 7. Since the θ method is 5 to 20 (or more) times faster than the $2N$ Newton-Raphson method, it can be expected to be faster than the Almost Band Algorithm by the same orders of magnitude. The computer memory requirements for the θ method are much less than those of the Newton-Raphson method. For columns with large numbers of plates and components, this advantage of the θ method over the Newton-Raphson method becomes most significant. The $2N$ Newton-Raphson

TABLE 5

Computer Times Required

Example no.	Refs.	No. of stages	No. of components	Specificant ions	Method	No. of trials	Computer time (s)	Compiler
1	*10*	13	11	$\frac{L_1}{D}$ and D	θ method	12	2.6	WATFIV
1	*7*	13	11	$\frac{L_1}{D}$ and $\frac{V_N}{B}$	θ method	13	1.66	FORTRAN H OPT 2
1	*7*	13	11	Q_C and Q_R	θ method	10	1.37	FORTRAN H OPT 2
1	*8*	13	11	$\frac{L_1}{D}$ and $\frac{V_N}{B}$	$2N$ Newton-Raphson	5^a	10.74	WATFIV
2	*8*	104	7	$\frac{L_1}{D}$ and D	θ method	17	3.65	FORTRAN H OPT 2
2	*8*	104	7	$\frac{L_1}{D}$ and $\frac{V_N}{B}$	$2N$ Newton-Raphson	—	90 s per iteration; did not run to convergence	FORTRAN H OPT 2

[a] Five trials were required when the derivatives were evaluated by use of the analytical expression for the partial derivatives; 10 trials and 12.45 s were required by Broyden's method.

TABLE 6

Statement of Examples Used in the Comparison of the 2*N* Newton-Raphson and the Almost Band Matrix Method[a]

Component	Number of components 4	6	8	10	12
C_2H_6				×	×
C_3H_6		×	×	×	×
C_3H_8	×	×	×	×	×
i-C_4H_8					×
i-C_4H_{10}			×	×	×
n-C_4H_{10}	×	×	×	×	×
i-C_5H_{12}	×	×	×	×	×
n-C_5H_{12}	×	×	×	×	×
n-C_6H_{14}			×	×	×
n-C_7H_{16}				×	×
n-C_8H_{18}			×	×	×
400					×

[a] The distillation column had a total condenser and the feed plate was located in the middle of the column, *N*/2, where *N* is equal to the total number of stages. An equimolar feed was used for each example and the total flow rate of the feed was fixed at 100 mol/h. Examples were solved with 4, 6, 8, 10, and 12 components. The identity of the particular set of components used for each example is given in the body of the table. The temperature of the feed for each Example 2 was 100°F, and a column pressure of 300 psia was used for all examples. The reflux ratio was held fixed at 2, and the product rates were set at 50% of the feed rate for all examples. The ideal solution *K* values and enthalpies were taken from Tables A-4 and A-8 of Ref. *9*.

TABLE 7

Comparison of the 2*N* Newton-Raphson and the Almost Band Matrix Methods

Example No. of stages	 No. of components	2*N* Newton-Raphson method[a] No. of trials	 Time (s)	Almost Band Matrix method No. of trials	 Time (s)
12	4	9	1.03	6	0.57
12	6	5	1.32	9	0.92
12	8	5	1.49	9	2.35
12	10	8	1.73	9	3.68
12	12	7	1.87	10	6.11
25	4	6	2.59	10	1.05
25	6	8	4.52	10	1.62
25	8	12	4.32	10	2.47
25	10	16	5.37	12	4.36
25	12	9	7.34	12	6.15
50	4	16	13.13	20	3.08

[a] These results were obtained by use of Procedure 2, Broyden's method, as modified by Bennett.

method is an exact application of the Newton-Raphson method for problems involving mixtures which form ideal solutions, and the Almost Band Algorithm is an exact application of the Newton-Raphson method for problems involving mixtures which form either ideal or nonideal solutions.

Absorber-Type Problems

Problems involving columns which do not have both a condenser and a reboiler, such as absorbers, strippers, and reboiled absorbers, are called absorber-type problems. For illustrative purposes the θ method will be applied to the absorber shown in Fig. 2.

The specifications commonly made on such a column are as follows: the number of stages N, the complete definitions of the lean oil L_0 and rich gas $N + 1$ (temperatures, thermal conditions, compositions, and flow rates), and the column pressure. The calculational procedure is analogous to that described for distillation. The component-material balances are again represented by the matrix equation given by Eq. (1). In this case, however, $\mathbf{v}_i = [v_{1i} v_{2i} \cdots \mathbf{v}_{Ni}]^T$ and the vector f_i contains the lean oil and rich gas rates in the first and last rows; that is, $f_i = [l_{0i} 0 \cdots 0 v_{N+1,i}]$.

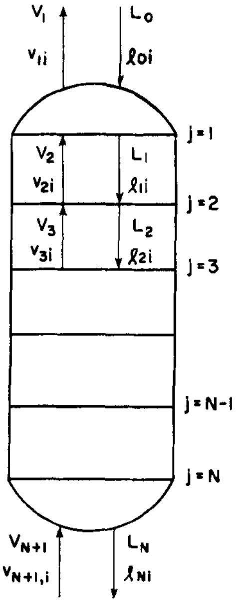

FIG. 2. Absorber and identifying symbols.

After the component-material balances have been solved for the component flow rates, the θ method is applied for the purpose of obtaining improved values for V_1, L_N, T_1, and T_N. The equations for the θ method are developed as follows. First θ is defined in the usual way:

$$\left[\frac{l_{Ni}}{v_{1i}}\right]_{co} = \theta\left[\frac{l_{Ni}}{v_{1i}}\right]_{ca} \tag{29}$$

The formula for $(v_{1i})_{co}$ is found in a manner analogous to that demonstrated above for $(d_i)_{co}$. Use of Eq. (29) to eliminate $(l_{Ni})_{co}$ from a component-material balance yields the following expression upon rearrangement:

$$(v_{1i})_{co} = p_i(v_{1i})_{ca} \tag{30}$$

where

$$p_i = \frac{l_{0i} + v_{N+1,i}}{(v_{1i})_{ca} + \theta(l_{Ni})_{ca}}$$

The multiplier θ is to be selected such that the component-material balances and energy balance enclosing the entire column are satisfied as well as the dew point temperature of V_1 and the bubble point temperature of L_N. In this case the variables and functions of the θ method are as follows:

$$\mathbf{x} = [\theta T_1 T_N]^T \tag{31}$$

$$\mathbf{f} = [g_1 g_2 g_3]^T \tag{32}$$

where g_1 is based on the dew point relationship for the stream V_1, g_2 is based on the bubble point expression for L_N, and g_3 is based on an energy balance enclosing the entire column. These functions are as follows:

$$g_1 = \frac{1}{\sum_{i=1}^{c} v_{1i}}\left[\sum_{i=1}^{c} v_{1i}/K_i(T_1)\right] - 1 \tag{33}$$

$$g_2 = \frac{1}{\sum_{i=1}^{c} l_{Ni}}\left[\sum_{i=1}^{c} K_i(T_N)l_{Ni}\right] - 1 \tag{34}$$

$$g_3 = \frac{\sum_{i=1}^{c} v_{1i}[H_i(T_1) - h_i(T_N)]}{\sum_{i=1}^{c} \{v_{N+1,i}[H_i(T_{N+1}) - h_i(T_N)] + l_{0i}[h_i(T_0) - h_i(T_N)]\}} - 1 \tag{35}$$

The set of variables $\mathbf{x}$ required to make $\mathbf{f} = \mathbf{0}$ is readily found by use of the Newton-Raphson method. After a solution set of values of the variables has been found which satisfy the g functions, the compositions of

Stages 2 through $N - 1$ are computed by use of the expressions given by Eq. (B) of Table 1. Then the K_b method is applied to determine the temperatures $T_2, T_3, \ldots, T_{N-1}$. Next the constant-composition form of the enthalpy balances is used to compute the total flow rates:

$$L_j = \frac{\sum_{i=1}^{c} (H_{j+1,i} - h_{0i})l_{0i} - \sum_{i=1}^{c} (H_{j+1,i} - H_{1i})v_{1i}}{\sum_{i=1}^{c} (H_{j+1,i} - h_{ji})x_{ji}}$$
$$(j = 1, 2, \ldots, N - 1) \tag{36}$$

The corresponding vapor rates are found by use of the total material balances. (Note: the values of V_1 and L_N need not be determined because

TABLE 8

Statement and Solution of Example 3. [taken from Boyum (*4*)]

I. Statement of Example 2[a]

Component	$v_{N+1,i}$ (lb-mol/h)	l_{0i} (lb-mol/h)
n-C$_4$H$_{10}$	14	50
n-C$_5$H$_{12}$	21	30
i-C$_5$H$_{12}$	35	20
	70	100

[a] Other specifications: $N = 15$, $P = 14.7$ psia, $T_0 = 30$°F, and $T_{N+1} = 90$°F. Initial temperature profile: linear between $T_1 = 40$°F and $T_N = 89.6$°F. Initial vapor rate profile: $V_j = 70.29$ ($j = 1, 2, \ldots, N$). Use the vapor–liquid equilibrium and enthalpy data given by Boyum (*4*).

II. Convergence Characteristics

Trial no.	θ	T_1 (°F)	T_N (°F)
1	1.4635	43.96	89.60
2	0.93779	49.33	80.12
3	0.79829	52.98	77.19
4	0.96843	52.30	75.13
5	0.98789	51.72	75.46
6	1.0069	51.33	75.82
7	1.0125	51.13	75.02
8	1.0111	51.06	76.19
9	1.0071	51.08	76.23
10	1.0032	51.11	76.22
11	1.0006	51.15	76.20
12	0.99935	51.18	76.17
13	0.99905	51.19	76.16

(*continued*)

TABLE 8 (Continued)

III. Final Temperature and Vapor Rate Profiles

Plate no.	V_j (lb-mol/h)	T_j (°F)
1	61.376	51.19
2	70.522	51.20
3	70.522	51.20
4	70.521	51.22
5	70.520	51.24
6	70.517	51.29
7	70.511	51.39
8	70.499	51.59
9	70.476	51.99
10	70.431	52.76
11	70.350	54.24
12	70.220	56.92
13	70.055	61.38
14	69.954	67.94
15	70.120	76.15

IV. Final Product Distribution

Component	v_{1i} (lb-mol/h)	l_{Ni} (lb-mol/h)
n-C_4H_{10}	47.395	16.605
n-C_5H_{12}	9.449	41.551
i-C_5H_{12}	4.532	50.468

they will have been determined by the use of the equations for the θ method.)

To illustrate this application of the θ method, Example 3 of Table 8 was solved. The test example proposed by Boyum (*4*) was used because the approximate variations of the Newton-Raphson method such as the one proposed by Sujata (*12*) failed to converge for this example. The convergence characteristics of the θ method for this example are illustrated in Table 8 in which the variation of the variables θ, T_1, and T_N with trial number is shown.

In order to solve certain other absorber examples by this procedure, it was necessary to divide the column into a system of two or more columns and then apply the θ method to each column of the system as described below.

Decomposition of a Column or a System of Columns into a System Containing Any Arbitrary Number of Columns

It may be desirable because of stability, speed, or the size of the computer available to reduce a large problem (a large set of equations) into a set of smaller problems which are solved sequentially by dividing the column into two or more columns as suggested by Fig. 3. In the proposed calculational procedure, one or more complete trials are made on each column of the newly formed system. The Θ method is then applied in order to pick a set of corrected terminal flow rates which satisfy the component-material balances and the energy balances enclosing each column as well as the equilibrium relationships for each of the streams cut by the energy and material balance enclosures.

To illustrate this application of the Θ method, the absorber shown in Fig. 2 is divided into two parts, and these parts are called Columns 1 and 2 as shown in Fig. 3. The solution to a typical absorber problem, Example 3, is to be found by obtaining the solution to the system of two columns shown in Fig. 3.

To initiate the first trial on Column 1, the composition of V_{M+1} is

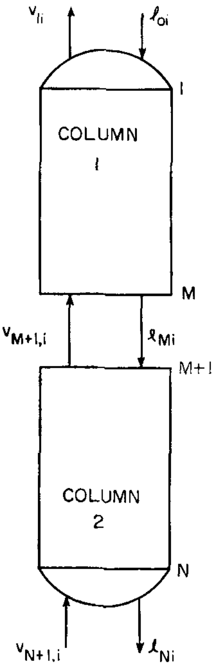

FIG. 3. Division of a single column into a system of two columns.

assumed, and one or more trials are made on this absorber by use of the θ method as described for absorbers. The new sets of temperatures and flow rates so obtained are saved. The values of the l_{Mi}'s obtained by the θ method are used to make one or more trials on the second column, and the temperatures and flow rates so obtained are saved. Prior to making the next set of trials on each column, the Θ method is applied in order to find new sets of terminal flow rates $\{v_{1i}\}$, $\{v_{M+1,i}\}$, $\{l_{Mi}\}$, and $\{l_{Ni}\}$ which satisfy the material and energy balances enclosing each column as well as the equilibrium relationships for each of the terminal streams.

In this application of the Θ method to the system of two columns shown in Fig. 3, two multipliers are defined:

$$\frac{l_{Mi}}{v_{1i}} = \Theta_1\left[\frac{l_{Mi}}{v_{1i}}\right]_{ca} \tag{37}$$

$$\frac{l_{Ni}}{v_{M+1,i}} = \Theta_2\left[\frac{l_{Ni}}{v_{M+1,i}}\right]_{ca} \tag{38}$$

where the subscript "*co*," which was used previously to denote the corrected values on the left-hand sides of these equations, has been omitted in the interest of simplicity.

The Θ's are to be picked such that the corrected component flow rates satisfy the following component-material balances simultaneously:

$$v_{M+1,i} - v_{1i} - l_{Mi} = -l_{0i} \tag{39}$$

$$l_{Mi} - v_{M+1,i} - l_{Ni} = -v_{N+1,i} \tag{40}$$

Use of Eqs. (37) and (38) to restate Eqs. (39) and (40) in terms of v_{1i} and $v_{M+1,i}$ gives the following result when stated as a matrix equation:

$$\begin{bmatrix} -(1 + r_{i,i}) & 1 \\ r_{i,1} & -(1 + r_{i,2}) \end{bmatrix} \begin{bmatrix} v_{1,i} \\ v_{M+1,i} \end{bmatrix} = -\begin{bmatrix} l_{0i} \\ v_{N+1,i} \end{bmatrix} \tag{41}$$

where

$$r_{i,1} = \Theta_1\left(\frac{l_{Mi}}{v_{1i}}\right)_{ca}, \qquad r_{i,2} = \Theta_2\left(\frac{l_{Ni}}{v_{M+1,i}}\right)_{ca}$$

The energy balances enclosing Columns 1 and 2 depend upon Θ_1, Θ_2, and the four temperatures, T_1, T_M, T_{M+1}, and T_N, of the terminal streams. Thus the variables and functions of the Θ method are:

$$\mathbf{x} = [\theta_1 \theta_2 T_1 T_M T_{M+1} T_N]^T$$

$$\mathbf{f} = [g_1 g_2 \cdots g_6]^T \tag{42}$$

Of the six functions, four are based on the equilibrium relationships for the terminal streams, and two are based on the energy balances enclosing the respective columns. They are

$$\begin{aligned}
g_1 &= \frac{1}{\sum_{i=1}^{c} v_{1i}} \left[\sum_{i=1}^{c} \frac{v_{1i}}{K_i(T_1)} \right] - 1 \\
g_2 &= \frac{1}{\sum_{i=1}^{c} l_{Mi}} \left[\sum_{i=1}^{c} K_i(T_M) l_{Mi} \right] - 1 \\
g_3 &= \frac{1}{\sum_{i=1}^{c} v_{M+1,i}} \left[\sum_{i=1}^{c} \frac{v_{M+1,i}}{K_i(T_{M+1})} \right] - 1 \\
g_4 &= \frac{1}{\sum_{i=1}^{c} l_{Ni}} \left[\sum_{i=1}^{c} K_i(T_N) l_{Ni} \right] - 1 \\
g_5 &= \frac{\sum_{i=1}^{c} v_{1i}[H_i(T_1) - h_i(T_M)]}{\sum_{i=1}^{c} \{l_{0i}[h_i(T_0) - h_i(T_M)] + v_{M+1,i}[H_i(T_{M+1}) - h_i(T_M)]\}} - 1 \\
g_6 &= \frac{\sum_{i=1}^{c} v_{M+1,i}[H_i(T_{M+1}) - h_i(T_N)]}{\sum_{i=1}^{c} \{l_{Mi}[h_i(T_M) - h_i(T_N)] + v_{N+1,i}[H_i(T_{N+1}) - h_i(T_N)]\}} - 1
\end{aligned} \tag{43}$$

The solution set of values of the variables **x** may be found by use of the Newton-Raphson method. Then on the basis of the most recent set of values of the variables, the second set of trials on Column 1 is made. The results so obtained are used to initiate the second set of trials on Column 2.

To illustrate the application of the methods described above, a typical absorber example which had been solved by a formulation of the Newton-Raphson method involving $2N$ variables (the T_j's and the L_j/V_j's) is presented as Example 4 in Tables 9 and 10. This example was selected because it was one of the few absorber examples for which the θ method failed to converge. However, when this problem was solved as a system of two columns with each column containing four plates as illustrated in Fig. 3, convergence was obtained by use of the combination of the θ and Θ methods as described above. It was found that four column trials by the θ method per system trial tended to minimize the total computing time. To determine additional characteristics of the θ methods, several variations of Example 4 were solved in which the number of plates was varied from eight to twenty. Convergence was achieved by using from one to five plates per column or unit. Because of the relatively small number of plates,

TABLE 9

Statement of an Absorber Problem, Example 4

Component	Rich gas, $v_{N+1,i}$ (lb-mol/h)	Lean oil, l_{0i} (lb-mol/h)	Other specification
CO_2	0.4703	0.0	$T_0 = 462.9$°R, $T_{N+1} = 460$°R, $N = 8$, and $P = 800$ psia. Initial temperature profile to be constant at $T_j = 485$°R for all j ($1 \leqq j \leqq N$). The initial vapor rate profile is to be constant at $V_j = 90.88$ ($1 \leqq j \leqq 8$), and the liquid rates are $L_j = 6.3092$ ($1 \leqq j \leqq 7$) and $L_8 = 15.42$. Use the K values and enthalpies given in Ref. *10*
N_2	0.1822	0.0	
CH_4	88.7000	0.0	
C_2H_6	6.6747	0.0	
C_3H_8	2.7786	0.0015	
i-C_4H_{10}	0.6375	0.0006	
n-C_4H_{10}	0.3655	0.0013	
i-C_4H_{12}	0.1158	0.0067	
n-C_5H_{12}	0.0505	0.0061	
C_6H_{14}	0.0146	0.1495	
C_7H_{16}	0.0081	0.5736	
C_8H_{18}	0.0020	1.8214	
C_9H_{20}	0.0	1.6866	
$C_{10}H_{22}$	0.0	2.0619	
	100.00	6.3092	

Convergence Characteristics and Solution of Example 4

Trial no.	Θ_1	Θ_2	T_1[a]	T_M	T_{M+1}	T_N
Initial values	—	—	485.00	485.00	485.00	485.00
1	1.1494	1.0660	495.95	426.63	477.00	468.27
2	0.95466	0.97700	487.40	486.77	483.40	477.11
3	0.96293	0.98039	486.09	492.37	487.81	476.85
4	1.0063	1.0029	488.38	488.12	487.02	474.88
5	1.0006	1.0003	488.14	488.40	486.94	475.18
6	0.99535	0.99764	487.79	489.63	487.49	475.46
7	0.99860	0.99925	487.86	489.66	487.64	475.36
8	1.0001	1.0001	487.93	489.53	487.62	475.30

[a] Temperatures are in °R.

no significant speed advantage of the θ methods over the $2N$ Newton-Raphson method was realized in the solution of absorber problems. This is a consequence of the fact that absorbers generally contain a relatively small number of stages.

In conclusion, the θ method may be used to solve a variety of additional problems involving distillation columns in which specifications other than the reflux and distillate rates are made. Furthermore, the θ method is significantly faster than the Newton-Raphson methods for columns which

TABLE 10

Solution of Example 4

I. Product Rates

Component	v_{1i}	l_{Ni}
CO_2	0.34840	0.12190
N_2	0.18037	0.19104×10^{-2}
CH_4	0.82841×10^2	0.58600×10^1
C_2H_6	0.46875×10^1	0.19872×10^1
C_3H_8	0.67786	0.21022×10^1
i-C_4H_{10}	0.90314×10^{-2}	0.62915
n-C_4H_{10}	0.11957×10^{-2}	0.36556
i-C_5H_{12}	0.17761×10^{-2}	0.12069
n-C_5H_{12}	0.11812×10^{-2}	0.55469×10^{-1}
C_6H_{14}	0.11098×10^{-1}	0.15298
C_7H_{16}	0.17115×10^{-1}	0.56458
C_8H_{18}	0.10240×10^{-1}	0.16763×10^1
$C_{10}H_{22}$	0.60846×10^{-2}	0.20558×10^1
Total	88.816	17.494

II. Temperatures and Vapor Rates

Stage no.	Temperature T_j (°R)	Total vapor rate V_j
1	487.93	88.816
2	491.03	93.959
3	490.85	94.351
4	489.54	94.649
5	487.62	94.966
6	485.08	95.366
7	481.45	95.950
8	475.31	97.011

contain large numbers of components and plates. Although the θ methods may be used to solve absorber problems, no significant speed advantage over the $2N$ Newton-Raphson method was realized. It is anticipated that these new applications of the θ methods will prove most useful because of their desirable characteristics of speed and independence of the initial values of the variables.

SYMBOLS

b_i	molar flow of component i leaving in the bottom product stream B
B	total molar flow rate of the bottom product stream
d_i	molar flow rate of component i in the distillate D
D	total molar flow rate of the distillate
F	total molar flow rate of the feed
f	vector of variables
g_k	the kth function of the mesh variables $\mathbf{x}$
$h_i(T)$	enthalpy of pure component i in the liquid phase at the temperature T
$H_i(T)$	enthalpy of pure component i in the vapor phase at the temperature T
K_i	vapor–liquid equilibrium constant; $y_i = K_i x_i$
l_{ji}	molar flow rate of component i in the liquid leaving plate j
L_j	total molar flow rate of the liquid leaving plate j
P_i	ratio of the corrected to the calculated values of the product rates for component i; see Eqs. (5) and (6)
Q_C	condenser duty
Q_R	reboiler duty
r_i	function of the calculated flow rates and the Θ's; defined beneath Eq. (41)
v_{ji}	molar flow rate of component i in the vapor phase leaving plate j
V_j	total molar flow rate of the vapor leaving the j stage
V_F	flow rate of the vapor part of a partially vaporized feed
x_{ji}	mole fraction of component i in the liquid phase leaving stage j
$\mathbf{x}$	vector of the independent variables of the g functions; see Eqs. (7) and (42)
X_i	total mole fraction of component i in the feed
y_{ji}	mole fraction of component i in the vapor phase leaving stage j

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REFERENCES

1. J. M. Bennett, "Triangular Factors of Modified Matrices," *Numer. Math.*, *7*, 217 (1965).
2. J. F. Boston and S. L. Sullivan, Jr., "An Improved Algorithm for Solving Mass Balance Equations in Multistage Separation Processes," *Can. J. Chem. Eng.*, *50*,

633 (1972).

3. J. F. Boston and S. L. Sullivan, Jr., "A New Class of Solution Methods for Multicomponent, Multistage Separation Processes," *Ibid.*, *52*, 52 (1974).
4. A. A. Boyum, PhD Dissertation, Polytechnic Institute of Brooklyn, Brooklyn, New York, 1966.
5. C. G. Broyden, "A Class of Methods for Solving Nonlinear Simultaneous Equations," *Math. Comput.*, *19*, 577 (1965).
6. S. E. Gallum, PhD Dissertation, Texas A & M University, 1977.
7. J. R. Haas, MS Thesis, Texas A & M University, 1980.
8. F. E. Hess, S. E. Gallum, G. W. Bentzen, C. D. Holland, R. McDanial, and N. J. Tetlow, "Solve More Distillation Problems. Part 8. Which Method to Use," *Hydrocarbon Process.*, *56* (6), 181 (1977).
9. C. D. Holland, *Multicomponent Distillation*, Prentice-Hall, Englewood Cliffs, New Jersey, 1963.
10. C. D. Holland, *Fundamentals and Modeling of Separation Processes*, Prentice-Hall, Englewood Cliffs, New Jersey, 1975.
11. D. P. Sandholm and L. M. Naphtali, "Multicomponent Calculations by Linearization," *AIChE J.*, *17*, 148 (1971).
12. A. D. Sujata, "Absorber Stripper Calculations Made Easier," *Hydrocarbon Process. Pet. Refiner*, *40*, 137 (1961).

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