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## Solution of Absorber, Stripper, and Liquid-Liquid Extraction Problems by use of the $\theta$ -Method of Convergence

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### Abstract

This paper demonstrates the application of the  $\theta$ -method of convergence to the solution of absorber, stripper, and liquid-liquid extraction. By the solution of a wide variety of examples, it is demonstrated that the  $\theta$ -method is exceedingly fast and converges for all problems of the type which appear to be of commercial interest.

The  $\theta$ -method of convergence has been successfully employed to solve problems in which the independent product rates such as the distillate rate of a conventional distillation column are specified. However, for columns such as absorbers, strippers and liquid-liquid extractors, the total flow rates of the product streams are seldom specified. Instead, the operating pressure, number of plates, and the flow rates, compositions, and temperatures of all inlet streams are specified. By consideration of an absorber with one plate (an adiabatic flash problem), two plausible extensions of the  $\theta$ -method of convergence for a column with any number of plates are deduced. The first extension of the  $\theta$ -method makes use of a single  $\theta$  and is called the *single- $\theta$ -method* and the second extension makes use of a  $\theta$  for each plate  $j$  and is called the *multi- $\theta$ -method*. In this paper the development and application of the single- $\theta$ -method

of convergence is presented.

In both of these methods, the temperatures are taken to be the independent variables and the compositions and total flow rates as the dependent variables. For each set of assumed temperatures, the  $\theta$ -method is used in the determination of the solution sets of flow rates and compositions required to satisfy the component-material balances and equilibrium relationships. The total flow rates and compositions so obtained are then used in the enthalpy balances in the determination of an improved set of temperatures by use of the Newton-Raphson method. The determination of temperatures from enthalpy balances by use of the Newton-Raphson method was first proposed by Sujata (17) and was later used by Friday *et al.* (7). More recently, Tomich (19) proposed a procedure in which the temperatures and vapor rates are regarded as the independent variables in the

application of the Newton-Raphson method. This procedure as well as the one proposed by Sujata (17) constitute variations of the more general method proposed by Greenstadt *et al.* (8) wherein the temperatures, flow rates, and compositions were all regarded as independent variables. Other variations of the Newton-Raphson method wherein the temperatures and total flow rates were regarded as the independent variables in the solution of the material and energy balances have been successfully applied by Boynton (2), Boyum (3), Newman (14), and Billingsley *et al.* (1).

The single- $\theta$ -method described herein is very fast, and it converges for all absorber, stripper, and liquid-liquid extraction problems which appear to be of commercial interest. Figure 1 shows a typical column of the type under consideration, and a statement of the type of problem to be solved is as follows. For the set of specifications  $P$ ,  $V_{N+1}$ ,  $\{y_{N+1,i}\}$ ,  $L_0$ ,  $\{x_0\}$ ,  $T_0$ ,  $T_{N+1}$ , and  $N$ , it is desired to find the corresponding product distribution, total flow rates  $\{V_j\}$  and  $\{L_j\}$ , and the temperature  $T_j$  of each plate  $j$  ( $1 \leq j \leq N$ ). The formulation of the single- $\theta$ -method and multi- $\theta$ -methods of convergence is suggested by the following analysis.

### Special Case of an Absorber with One Plate

The special case of an absorber with one plate where the specifications are as enumerated above reduces to the adiabatic flash problem (10) which may be described by  $2c+3$  independent equations in  $2c+3$  unknowns. In particular, one set of independent equations consists of  $c$  component material balances,  $c$  equilibrium relationships, one enthalpy balance, and two equations of the form  $\sum_{i=1}^c x_i = 1$  and  $\sum_{i=1}^c y_i = 1$ , where the  $x_i$ 's and  $y_i$ 's denote the mole fractions of the liquid and vapor streams formed by the flash, respectively.

One of the methods for solving the adiabatic flash problem consists of regarding the flash temperature as the independent variable and the total flow rates and compositions of the liquid and vapor streams produced by the flash as the dependent variables. On

the basis of an assumed flash temperature, the component-material balances and equilibrium relationships are solved simultaneously for the corresponding values of the dependent variables. The values of the total flow rates and compositions so obtained are then used to compute an improved temperature by use of the enthalpy balance.

First consider the problem where the temperature of plate 1 (the one and only plate) is regarded as fixed, and a solution to the corresponding component-material balances and equilibrium relationships is to be found. (This problem is commonly called the *isothermal flash* problem.) The component-material balance for each component is given by

$$v_{N+1,i} + l_{0i} = v_{1i} + l_{1i} \quad (1)$$

From the equilibrium  $y_{1i} = K_{1i}x_{1i}$ , it is evident that

$$\frac{l_{1i}}{v_{1i}} = \frac{L_1}{K_{1i}V_1} \quad (2)$$

Thus, on the basis of an assumed value for  $L_1/V_1$ , the corresponding values of  $l_{1i}/v_{1i}$  may be calculated by use of Equation (2). Let the calculated values so obtained be identified by the subscript "ca" and the assumed values by the subscript "a". Then for an assumed value,  $(L_1/V_1)_a$ , the corresponding set of calculated values of  $v_{1i}$  may be found by use of the following expression which is obtained by rearranging Equation (1) to the following form

$$(v_{1i})_{ca} = \frac{v_{N+1,i} + l_{0i}}{1 + \left(\frac{l_{1i}}{v_{1i}}\right)_{ca}} \quad (3)$$

The  $\theta$ -method of convergence is applied to this problem by defining the multiplier  $\theta$  as follows:

$$\left(\frac{l_{1i}}{v_{1i}}\right)_{ca} = \theta \left(\frac{l_{1i}}{v_{1i}}\right)_{ca} \quad (4)$$

By requiring that the corrected flow rates  $\{(v_{1i})_{ca}\}$  and  $\{(l_{1i})_{ca}\}$  be in component-material balance, the following formula for  $(v_{1i})_{ca}$  is obtained.

$$(v_{1i})_{ca} = \frac{v_{N+1,i} + l_{0i}}{1 + \theta \left(\frac{l_{1i}}{v_{1i}}\right)_{ca}} \quad (5)$$

Since  $T_1$  is regarded as fixed (at the assumed value), it is evident that  $\theta$  must be picked such that the corrected ratios  $\{(v_{1i})_{co}\}$  must satisfy the expression for the dew point temperature,

$$\sum_{i=1}^c \frac{(y_{1i})_{co}}{K_{1i}} = 1, \text{ or } \sum_{i=1}^c \frac{(v_{1i})_{co}}{K_{1i}} = \sum_{i=1}^c (v_{1i})_{co}$$

which may be rearranged to the functional form

$$g(\theta) = \sum_{i=1}^c (v_{1i})_{co} \left[ 1 - \frac{1}{K_{1i}} \right] \quad (6)$$

When  $(v_{1i})_{co}$  is eliminated from this expression by use of Equation (5), the following result is obtained.

$$g(\theta) = \sum_{i=1}^c \frac{(v_{N+1, i} + l_{0i}) \left( 1 - \frac{1}{K_{1i}} \right)}{1 + \theta \left( \frac{l_{1i}}{v_{1i}} \right)_{ca}} \quad (7)$$

[Alternately  $g(\theta)$  could have been formulated by requiring that the  $(l_{1i})_{co}$ 's satisfy the bubble point expression.] Thus, the desired value of  $\theta$  is that  $\theta > 0$  which makes  $g(\theta) = 0$ . A solution exists provided the assumed value of  $T_1$  lies between the bubble point and dew point temperatures of the combined feed  $(V_{N+1} + L_0)$ . The value of  $\theta$  so obtained represents the solution to the component-material balances and equilibrium relationships at the fixed value of  $T_1$ . Observe that the particular value of  $(L_1/V_1)_a$  selected to initiate the trial procedure is immaterial because the value found for  $\theta$  compensates for the choice of  $(L_1/V_1)_a$ . The truth of this statement is evident upon examination of the following expression which is obtained by use of Equations (2) and (4).

$$\left( \frac{L_1}{V_1} \right)_{co} \frac{1}{K_{1i}} = \theta \left( \frac{L_1}{V_1} \right)_a \frac{1}{K_{1i}}$$

or

$$\left( \frac{L_1}{V_1} \right)_{co} = \theta \left( \frac{L_1}{V_1} \right)_a \quad (8)$$

To initiate the calculational procedure for solving an adiabatic flash problem, the material balances are solved as described above for each of two choices of

$T_1$ , say  $T_{1,1}$  and  $T_{1,2}$ . The corresponding sets of total flow rates and compositions are used to compute the unbalance  $G(T_1)$  in the overall energy balance for each choice of  $T_1$ ; namely,

$$G(T_1) = (V_1 H_1 + L_1 h_1) - (V_{N+1} H_{N+1} + L_0 h_0) \quad (9)$$

A next trial temperature may be found by interpolation between the points  $[T_{1,1}, G(T_{1,1})]$  and  $[T_{1,2}, G(T_{1,2})]$  by use of interpolation *regula falsi* (5) as follows:

$$T_{1,3} = \frac{T_{1,1} G(T_{1,2}) - T_{1,2} G(T_{1,1})}{G(T_{1,2}) - G(T_{1,1})} \quad (10)$$

Thus, it is seen that this procedure in effect reduces the original set of  $2c+3$  equations in  $2c+3$  unknowns for an adiabatic flash to one equation [Equation (9)] in one unknown, the flash temperature. However, for each choice of the independent variable  $T_1$ , the  $2c+2$  equations for the isothermal flash must be solved simultaneously for the solution sets of compositions and total flow rates.

For  $N > 1$ , the definition given by Equation (3) may be extended by supposing that the ratio pertains to the terminal streams leaving the column to give,

$$\left( \frac{l_{Ni}}{v_{1i}} \right)_{co} = \theta \left( \frac{l_{Ni}}{v_{1i}} \right)_{ca} \quad (11)$$

where  $\theta$  is to be selected such that an overall component-material balance is satisfied and such that the bubble point function for each plate  $j$  is satisfied as discussed below. Alternately, it may be supposed that the ratio given by Equation (4) pertains to the streams leaving each plate  $j$  to obtain,

$$\left( \frac{l_{ji}}{v_{ji}} \right)_{co} = \theta_j \left( \frac{l_{ji}}{v_{ji}} \right)_{ca}, \quad (1 \leq j \leq N) \quad (12)$$

where the set of  $\theta_j$ 's is to be picked such that all of the dew point functions are satisfied simultaneously. The definition given by Equation (11) forms the basis for the *single- $\theta$ -method* of convergence and the definition given by Equation (12) forms the basis for the *multi- $\theta$ -method* of convergence. The remainder of this paper is concerned with the development and description of the *single- $\theta$ -method* of convergence

while the *multi-θ-method* will be the subject of a subsequent paper.

The single-θ-method of convergence is analogous to the procedure described above for the adiabatic flash in that the temperatures are regarded as the dependent variables. For each set of assumed temperatures { $T_j$ }, a solution to the component-material balances and equilibrium relationships is obtained. The total flow rates and compositions so obtained are used to evaluate the enthalpy balance functions which are in turn used in the prediction of an improved set of temperatures.

In particular for each plate  $j$ , the complete set of independent equations are as follows:  $c$  component-material balances,  $c$  equilibrium relationships, two equations of the form  $\sum_{i=1}^c x_{ji}=1$  and  $\sum_{i=1}^c y_{ji}=1$ , and one enthalpy balance. Thus, in a manner analogous to that described for the adiabatic flash for a single plate absorber, the single-θ-method of convergence reduces the original set of  $(2c+3)N$  equations in  $(2c+3)N$  unknowns to  $N$  equations (the enthalpy balances) in  $N$  unknowns (the temperatures). Again, however, as in the case of the adiabatic flash, for any given set of temperatures, it is necessary to solve the combined set of component-material balances and equilibrium relationships [ $(2c+2)N$  equations] simultaneously for the solution sets of compositions and total flow rates.

### Material-Balance Equations

The proposed calculational procedure is initiated by the assumption of a set of vapor rates { $V_j$ } and a set of temperatures { $T_j$ }. After the liquid rates { $L_j$ } corresponding to the set of assumed vapor rates have been computed by use of the total material balances,

$$V_{j+1} + L_{j-1} - V_j - L_j = 0, \quad (1 \leq j \leq N) \quad (13)$$

the component-material balances may be solved for the component flow rates.

The component-material balances enclosing each plate of a typical absorber, stripper, or liquid-liquid extractor (see Figure 1) may be reduced to a set of

equations containing either the set of unknown liquid rates { $l_{ji}$ } or the set of unknown vapor rates { $v_{ji}$ } by use of the equilibrium relationship  $y_{ji} = K_{ji}x_{ji}$ , which may be restated in the following forms:

$$l_{ji} = A_{ji}v_{ji}; \quad v_{ji} = S_{ji}l_{ji} \quad (14)$$

When the first of the two relationships given by Equation (14) is used to eliminate the  $l_{ji}$ 's from the material balances for plates  $j=1$  through  $j=N$ , the following set of equations is obtained for each component  $i$ ,

$$\begin{aligned} - (A_{1i} + 1)v_{1i} + v_{2i} &= -l_{0i} \\ A_{j-1, i}v_{j-1, i} - (A_{ji} + 1)v_{ji} + v_{j+1, i} &= 0, \\ & \quad (2 \leq j \leq N-1) \end{aligned} \quad (15)$$

$$A_{N-1, i}v_{N-1, i} - (A_{Ni} + 1)v_{Ni} = -v_{N+1, i}$$

When this set of equations is stated in the matrix form  $AX=C$ , it will be found that the square matrix  $A$  is of tridiagonal form. For matrices of this type, the solution set of component-flow rates { $v_{ji}$ } may be obtained by use of either Gaussian elimination or the recurrence formulas obtained by Gaussian elimination (5, 7, 10, 11). For each component  $i$ , the corresponding liquid flow rates are computed by use of Equation (14). Let the flow rates so obtained be identified by the subscript "ca"; that is, { $(v_{ji})_{ca}$ } and { $(l_{ji})_{ca}$ }. The single-θ-method of convergence makes use of the sets of calculated rates { $(v_{ji})_{ca}$ } and { $(l_{ji})_{ca}$ } in picking an improved set of total flow rates.

Except for the formulation of the function  $g(\theta)$ , the development of the single-θ-method for the present application is carried out in an analogous manner to that shown previously for conventional distillation columns (10). The multiplier  $\theta$ , defined by Equation (11), is subject to the condition that the corrected rates satisfy the component-material balances enclosing the entire column,

$$v_{N+1, i} + l_{0i} = (l_{Ni})_{co} + (v_{1i})_{co} \quad (16)$$

The following formula for  $(v_{1i})_{co}$  is readily obtained from Equations (11) and (16)

$$(v_{1i})_{co} = \frac{v_{N+1, i} + l_{0i}}{1 + \theta \left( \frac{l_{Ni}}{v_{1i}} \right)_{ca}} \quad (17)$$

For any choice of  $\theta$ , the corresponding value of the total flow rate  $(V_1)_{co}$  is found by summing the component-flow rates given by Equation (17) over all components  $i$ . The corresponding total flow rate  $(L_N)_{co}$  may be computed by solving Equations (11) and (16) for  $(l_{Ni})_{co}$  followed by the summation over all components or by use of  $(V_1)_{co}$  and an overall material balance.

Next, formulas for the calculation of a new set of total flow rates which are consistent with the corrected flow rates  $(V_1)_{co}$  and  $(L_N)_{co}$  are developed as follows. Let the corrected flow rates for all components  $i$  which appear in both phases be defined by:

$$\begin{aligned} (l_{ji})_{co} &= \eta_j \left( \frac{l_{ji}}{v_{1i}} \right)_{ca} (v_{1i})_{co} \\ (v_{ji})_{co} &= \sigma_j \left( \frac{v_{ji}}{v_{1i}} \right)_{ca} (v_{1i})_{co} \end{aligned} \quad (18)$$

where  $\eta_j$  and  $\sigma_j$  are at this point undetermined multipliers. The definitions given by Equation (18) do imply, however, that

$$\begin{aligned} (L_j)_{co} &= \eta_j \mathcal{L}_j \\ (V_j)_{co} &= \sigma_j \mathcal{V}_j \end{aligned} \quad (19)$$

where

$$\begin{aligned} \mathcal{L}_j &= \sum_{i=1}^c \left( \frac{l_{ji}}{v_{1i}} \right)_{ca} (v_{1i})_{co} \\ \mathcal{V}_j &= \sum_{i=1}^c \left( \frac{v_{ji}}{v_{1i}} \right)_{ca} (v_{1i})_{co} \end{aligned}$$

From the definition of a mole fraction and the above relationships, it follows that

$$\begin{aligned} (x_{ji})_{co} &= \frac{(l_{ji})_{co}}{(L_j)_{co}} = \frac{\left( \frac{l_{ji}}{v_{1i}} \right)_{ca} (v_{1i})_{co}}{\mathcal{L}_j} \\ (y_{ji})_{co} &= \frac{(v_{ji})_{co}}{(V_j)_{co}} = \frac{\left( \frac{v_{ji}}{v_{1i}} \right)_{ca} (v_{1i})_{co}}{\mathcal{V}_j} \end{aligned} \quad (20)$$

The multipliers  $\sigma_{j+1}$  and  $\eta_j$  are related by a total material balance enclosing the top of the column and any plate  $j$  as follows.

$$\sigma_{j+1} \mathcal{V}_{j+1} - \eta_j \mathcal{L}_j - [(V_1)_{co} - L_0] = 0 \quad (21)$$

For any choice of  $\theta$ , the values of the quantities  $(V_1)_{co}$ ,  $\mathcal{V}_{j+1}$ , and  $\mathcal{L}_j$  may be computed, and thus Equation (21) reduces to one equation in two unknowns,  $\sigma_{j+1}$  and  $\eta_j$ . Consequently, infinitely many choices of values of these variables exist which will satisfy Equation (21). Of the choice or relationships investigated (13), the following one

$$\sigma_{j+1} = \frac{1}{\eta_j}, \quad (1 \leq j \leq N-1) \quad (22)$$

gave the most satisfactory results for the absorber problems. This relationship is in agreement with the fact that at convergence  $\sigma_{j+1} \times \eta_j = 1$  (also, at convergence  $\sigma_{j+1} = \eta_j = 1$ ). Other characteristics of this relationship are given in Appendix A. When Equations (21) and (22) are solved for  $\eta_j$ , the following formula is obtained.

$$\eta_j = \frac{-\mathcal{B} + \sqrt{\mathcal{B}^2 + 4\mathcal{L}_j \mathcal{V}_{j+1}}}{2\mathcal{L}_j} \quad (23)$$

where

$$\mathcal{B} = (V_1)_{co} - L_0.$$

Also, observe that Equations (11) and (18) require that  $\eta_N = \theta$  and  $\sigma_1 = 1$ . Thus, for each choice of  $\theta$ , corresponding sets of compositions and total flow rates may be computed by use of Equations (17) through (23).

### Formulation of the $g$ Function

The formulation of the function  $g(\theta)$  for the determination of  $\theta$  is analogous to that demonstrated for the isothermal flash problem. However, instead of only one bubble point function, there exist  $N$  bubble point functions to be satisfied by the choice of  $\theta$ ; namely,

$$f_j = \sum_{i=1}^N (K_{ji})_a (x_{ji})_{co} - 1, \quad (1 \leq j \leq N) \quad (24)$$

(Again, as in the case of the flash problem, the dew point functions could have been used instead of the bubble point functions.) By use of the definitions of  $(x_{ji})_{co}$ ,  $(y_{ji})_{co}$ , and the fact that  $(l_{ji})_{ca} = (A_{ji})_a (v_{ji})_{ca}$ , the assumed K-values may be eliminated to give

$$f_j = \left( \frac{L_j}{V_j} \right)_a \left( \frac{Q_j}{L_j} \right) - 1, \quad (1 \leq j \leq N) \quad (25)$$

The expressions given by Equation (25) are more rapidly evaluated than those given by Equation (24). The  $g$  function may be defined as the arithmetic average of the square of the Euclidean norm of the bubble point function,

$$g(\theta) = \frac{1}{N} \sum_{j=1}^N f_j^2 \quad (26)$$

Prior to convergence, it is generally impossible to find a single  $\theta$  such that  $f(\theta) = 0$ , simultaneously, for all  $j$ . Thus, at the end of any given trial prior to convergence, a  $\theta$  is picked such that  $g(\theta)$  is minimized.

The method used to find the  $\theta$  closest to unity for which  $g(\theta)$  is minimized should be regarded as peripheral to the single- $\theta$ -method of convergence. Many suitable methods have been proposed for the minimization of a function of a single variable (20). The methods used by the authors consisted of (a) the successive approximation of the minimum through the use of a parabolic approximation and (b) "The Golden Section" (20).

In order to apply each of these methods, it is first necessary to locate a finite interval that contains the minimum. The parabolic method is initiated by choosing three values of  $\theta$  denoted by  $\theta_{n-1} < \theta_n < \theta_{n+1}$ , where  $\theta_n = 1.0$ . If the corresponding values of the  $g$  functions indicates that a minimum lies between  $\theta_{n-1}$  and  $\theta_{n+1}$ , the minimum is estimated by use of the expression obtained by curve fitting the equation of a parabola. If, however, the  $g$  function increases or decreases monotonically in the interval  $\theta_{n-1}$  to  $\theta_{n+1}$ ,

it is searched in the direction it decreases by varying  $\theta$  by preassigned increments until either an interval containing the minimum has been located or a preassigned number of  $\theta$ 's has been tried. In the solution of the illustrative examples, a maximum of eight values of  $\theta$  lying between 0.97 and 1.03 were tested. The rate of convergence of a given problem did not depend strongly on the size of the increment in  $\theta$  which was employed, but it was necessary to make a sufficient number of trials to find  $\theta$  to the desired accuracy as convergence of the problem was approached.

After the desired value of  $\theta$  has been found, the corresponding set of total flow rates are computed as indicated by Equations (17) through (23). On the basis of the total flow rates so obtained and the assumed temperature profile, the component-material balances [Equation (15)] are solved and the  $\theta$ -method applied again. This procedure is repeated until the convergence criteria for the material balance equations have been satisfied. The compositions and total flow rates so obtained are used in the enthalpy balances in the determination of an improved set of temperatures.

### Determination of an Improved Set of Temperatures

The enthalpy balances,

$$V_{j+1}H_{j+1} + L_{j-1}h_{j-1} - V_jH_j - L_jh_j = 0, \quad (1 \leq j \leq N) \quad (27)$$

are employed to predict an improved set of temperatures by use of the Newton-Raphson method. In the application of this method, the enthalpy balances are restated in functional notation as follows:

$$G_j = V_{j+1}H_{j+1} + L_{j-1}h_{j-1} - V_jH_j - L_jh_j, \quad (1 \leq j \leq N) \quad (28)$$

The Newton-Raphson equation is given by

$$B_n \Delta X_n = C_n \quad (29)$$

where the subscript  $n$  denotes the  $n$ th iteration through the column. The matrix  $B_n$  contains the

partial derivatives of the  $G_j$ 's with respect to the  $T_j$ 's, and it is a tridiagonal matrix which is square and of order  $N$ . The matrices  $C_n$  and  $\Delta X_n$  are conformable column vectors which have the following representation.

$$C_n = [(-G_1) (-G_2) \cdots (-G_N)]^T$$

$$\Delta X_n = [\Delta T_1 \Delta T_2 \cdots \Delta T_N]^T \quad (30)$$

$$\Delta T_j = T_{jn} - T_{j, n-1}$$

In the development of the formulas for the partial derivatives of the  $G_j$ 's with respect to the temperatures, only the dependency of the enthalpies of the pure components was taken into account; that is, the dependency of the total flow rates and compositions on temperature was neglected in the manner as originally suggested by Sujata (17). The functions  $G_j$  which appear in  $C_n$  and their derivations which appear in  $B_n$  are evaluated on the basis of the most recent set of temperatures used to solve the component-material balances and the final sets of compositions and total flow rates so obtained. The set of temperatures found by one application of the Newton-Raphson method becomes the assumed set to be used for the next trial through the column. A summary if the steps of the proposed calculational procedure follows.

1. Assume a set of temperatures  $\{T_j\}$  and a set of vapor rates  $\{(V_j)_a\}$ . Compute the corresponding set of liquid rates  $\{(L_j)_a\}$  by use of the total material balances given by Equation (13). Solve Equation (15) for the component flow rates for each component  $i$  and denote them by  $\{(v_{ji})_{ca}\}$ . Then compute the corresponding flow rates  $\{(l_{ji})_{ca}\}$  for each component  $i$  in the liquid phase by use of relationship:  $(l_{ji})_{ca} = (A_{ji})_a (v_{ji})_{ca}$ .
2. On the basis of the sets of calculated flow rates  $\{(v_{ji})_{ca}\}$  and  $\{(l_{ji})_{ca}\}$  found in Step 1, the set of assumed vapor rates  $\{(V_j)_a\}$  and corresponding liquid rates  $\{(L_j)_a\}$  used in Step 1, find the  $\theta$  closest to unity which minimizes  $g(\theta)$ . Then compute the corresponding corrected values of total flow rates.

3. Repeat Steps 1 through 3 until the convergence criterion for the material balances has been satisfied. (In practice, a total of five iterations were made.)
4. Use the final sets of corrected compositions and total flow rates found in Steps 1 through 4 and the temperature profile assumed in Step 1 through 4 and the temperature profile assumed in Step 1 to evaluate the  $G_j$  functions and an improved set of temperatures by applying the Newton-Raphson method one time.
5. If each of the temperatures found in Step 4 differs by no more than a preassigned amount from the corresponding ones assumed in Step 1, convergence has been achieved. Otherwise, repeat Steps 1 through 4 on the basis of the most recent sets of temperatures and total flow rates until the convergence criteria have been satisfied.

Table 1. Statement of Examples 1 and 2

I. Statement of Example 1:

Component	$v_{N+1,i}$ (lb-moles/hr)	$l_{0i}$ (lb-moles/hr)
CO <sub>2</sub>	14.08154	0.0
N <sub>2</sub>	5.45767	0.0
CH <sub>4</sub>	2655.8245	0.0
C <sub>2</sub> H <sub>6</sub>	199.85249	0.0
C <sub>3</sub> H <sub>8</sub>	83.19560	0.04345
i-C <sub>4</sub> H <sub>10</sub>	19.08945	0.01889
n-C <sub>4</sub> H <sub>10</sub>	10.94352	0.03778
i-C <sub>5</sub> H <sub>12</sub>	3.46664	0.20024
n-C <sub>5</sub> H <sub>12</sub>	1.51297	0.18324
C <sub>6</sub> H <sub>14</sub>	0.43565	4.47708
C <sub>7</sub> H <sub>16</sub>	0.24159	17.17535
C <sub>8</sub> H <sub>18</sub>	0.05973	54.53534
C <sub>9</sub> H <sub>20</sub>	0.00086	50.49841
C <sub>10</sub> H <sub>22</sub>	0.00042	61.73645
	2994.16259	188.9063

Initial temperature profile:

$T_j = 25^\circ F$  ( $1 \leq j \leq N$ ). Initial vapor rates are linear between  $V_1 = 2721$  and  $V_{N+1}$ .  $T_0 = 2.9^\circ F$ ,  $T_{N+1} = 0^\circ F$ ,  $N = 8$ , Column Pressure = 800 psia, and  $E_{ji} = 1$  for all  $i$  and  $j$ . The curve fits for the  $K$ -values and enthalpies given in Tables 1, 2, and 3 of Reference (13) were used.

## II. Statement of Example 2:

Same as Example 1 except that  $N=20$ .

Table 2. Statement of Examples 3 Through 11

Component	Example Number									
	3		4		5		6		7	
	$v_{N+1,i}$	$l_{0i}$	$v_{N+1,i}$	$l_{0i}$	$v_{N+1,i}$	$l_{0i}$	$v_{N+1,i}$	$l_{0i}$	$v_{N+1,i}$	$l_{0i}$
Single-Phase Light	0	0	0	0	70	0	0	0	0	0
CH <sub>4</sub>	70	0	70	0	0	0	1	0	0.1	0
C <sub>2</sub> H <sub>6</sub>	15	0	15	0	15	0	4	0	0.5	0
C <sub>3</sub> H <sub>8</sub>	10	0	10	0	10	0	10	0	2.4	0
<i>n</i> -C <sub>4</sub> H <sub>10</sub>	4	0	4	0	4	0	15	0	7.5	0
<i>n</i> -C <sub>5</sub> H <sub>12</sub>	1	0	1	0	1	0	20	0	44.5	0
C <sub>6</sub> H <sub>14</sub>	0	0	0	0	0	0	0	0	0	0
C <sub>7</sub> H <sub>16</sub>	0	0	0	0	0	0	0	0	0	0
C <sub>8</sub> H <sub>18</sub>	0	20	0	0	0	20	0	70	0	65
500	0	0	0	0	0	0	0	0	0	0
Single-Phase Heavy	0	0	0	20	0	0	0	0	0	0
T <sub>0</sub> , °F	90		90		90		350		415	
T <sub>N+1</sub> , °F	-7.79		-6.34		-5.0		370		425	
N	8		8		8		8		8	
Initial {T <sub>j</sub> } °F	Linear between T <sub>1</sub> =100 and T <sub>N</sub> =80		Linear between T <sub>1</sub> =100 and T <sub>N</sub> =80		Linear between T <sub>1</sub> =100 and T <sub>N</sub> =80		T <sub>j</sub> =350, (1 ≤ j ≤ N)		T <sub>j</sub> =400, (1 ≤ j ≤ N)	
Initial {V <sub>j</sub> }	Linear between V <sub>1</sub> =80 and V <sub>N-1</sub>		Linear between V <sub>1</sub> =80 and V <sub>N+1</sub>		Linear between V <sub>1</sub> =80 and V <sub>N+1</sub>		Linear between V <sub>1</sub> =80 and V <sub>N+1</sub>		Linear between V <sub>1</sub> =80 and V <sub>N+1</sub>	

Table 2. (CONT'D.)

Component	Example Number				Other Specifications
	8, 9, 10		11		
	$v_{N+1,i}$	$l_{0i}$	$v_{N+1,i}$	$l_{0i}$	
Single-Phase Light	0	0	13.47	0	The column pressure for Example 3 through 10 was 300 psia. The equilibrium and enthalpy data in Tables A-4 and A-8 of Reference (10) were used. The enthalpy of the single-phase light of Example 5 was taken to be equal to that of methane. The enthalpy of the single-phase heavy of Example 4 was taken to be equal to that of normal octane. The column pressure for Example 11 was 50 psia. The equilibrium and enthalpy data for this example were taken from Tables A-1 and A-8 of Reference (10). The enthalpy for steam which is given on page 220 of Reference (10) was used. For each of the feed entrance plates 1 and N, it was assumed that the respective feeds L <sub>0</sub> and V <sub>N+1</sub> mixed perfectly with the liquid on the respective plates, and that a state of equilibrium existed between the total vapor and total liquid streams leaving each of these feed plates.
CH <sub>4</sub>	0.1	0	0	0.01	
C <sub>2</sub> H <sub>6</sub>	0.5	0	0	0.17	
C <sub>3</sub> H <sub>8</sub>	2.4	0	0	1.30	
<i>n</i> -C <sub>4</sub> H <sub>10</sub>	7.5	0	0	2.38	
<i>n</i> -C <sub>5</sub> H <sub>12</sub>	54.5	0	0	1.75	
C <sub>6</sub> H <sub>14</sub>	0	0	0	2.35	
C <sub>7</sub> H <sub>16</sub>	0	0	0	2.55	
C <sub>8</sub> H <sub>18</sub>	0	55	0	0	
500	0	0	0	82.24	
Single-Phase Heavy	0.0	0.0	0	0	
T <sub>0</sub> , °F	395		370		
T <sub>N+1</sub> , °F	405		500		
N	N=8 for Ex. 8 N=12 for Ex. 9 N=20 for Ex. 10		8		
Initial {T <sub>j</sub> }	T <sub>j</sub> =400, (1 ≤ j ≤ N)		Linear between T <sub>1</sub> =340, T <sub>8</sub> =375		
Initial {V <sub>j</sub> }	Linear between V <sub>1</sub> =80 and V <sub>N-1</sub>		Linear between V <sub>1</sub> =80 and V <sub>N+1</sub>		

Table 3. Solution Sets of Temperatures and Flow Rates for Selected Examples

Plate No.	Example 1		Example 3		Example 6		Example 11	
	$T_j$ (°F)	$V_j$ (lb./moles/hr)	$T_j$ (°F)	$V_j$ (lb.-moles/hr)	$T_j$ (°F)	$V_j$ (lb.-moles/hr)	$T_j$ (°F)	$V_j$ (lb.-moles/hr)
1	27.929	2721.08	107.636	85.000	364.228	8.282	368.007	23.268
2	31.043	2755.22	111.436	89.813	367.777	27.234	367.294	19.120
3	30.900	2789.35	112.494	90.506	370.966	80.665	366.909	17.762
4	29.597	2823.48	112.131	90.785	374.494	33.420	366.628	17.083
5	27.665	2857.61	110.224	90.999	378.611	36.263	366.361	16.629
6	25.101	2891.74	105.816	91.284	382.796	39.673	365.029	16.235
7	21.468	2925.88	96.433	91.812	384.708	43.981	365.403	15.791
8	15.320	2960.01	74.365	93.156	377.632	49.387	359.832	15.102

Table 4. Comparison of the Computational Procedures for the Determination of Product Distributions

Example No.	$\theta$ -Method		Sujata (17)		Tomich (19)	
	Number of Trials	Time (sec.)	Number of Trials	Time (sec.)	Number of Trials	Time (sec.)
1	7	14.9	10	28.8	(32)	(41)
2	20	67.3	23	126.0	—	—
3	7	9.2	7	12.2	23	(17)
4	7	8.5	6	11.4	23	(18)
5	8	11.1	6	10.8	23	(19)
6	9	14.6	20	21.0	45	(27)
7	17	24.4	Cycling at the end of 50 trials; $T_1$ varied about 16°F every five trials.		(24)	(19)
8	11	16.2	Same as Example 7 except that $T_1$ varied about 4°F every four trials.		(24)	(19)
9	14	27.2	Same as Example 7 except that $T_1$ varied about 50°F every four trials.		(39)	(28)
10	20	48.0	Temperatures on plates 2 through 10 went off of the curve fits at the end of the 25th trial.		—	—
11	3	4.0	4	7.68	—	—

Table 5. Independent Comparison of the Methods of Sujata (17) and Tomich (19)\*

Example No.	Sujata (17) <sup>1,2</sup> (Used curve fits stated in Tables 1 and 2)		Tomich (19) <sup>1,2</sup> (Used curve fits stated in Tables 1 and 2)		Tomich (19) <sup>1,3,4</sup> (Used data of Ref. (6))	
	Number of Trials	Time (sec)	Number of Trials	Time (sec)	Number of Trials	Time (sec)
1	14	1.094	—	—	32	2.770
3	10	0.638	23	0.605	21	1.798
4	9	0.570	23	0.615	21	1.294
5	10	0.602	23	0.626	20	1.140
6	37	2.216	—	—	44	3.878
7	Cycled	—	—	—	24	1.699
8	Cycled	—	—	—	24	1.701
9	Cycled	—	—	—	36	3.950
11	6	0.431	—	—	—	—

Notes: 1. These solutions were obtained on a UNIVAC 708 Computer, and the following convergence criteria were used:  
 $|\Delta T| \leq 0.001^\circ\text{F}$  and  $\left| \frac{\Delta V}{V} \right| \leq 0.0001$  between successive material for both methods.

- One iteration on the material balances and a maximum of five iterations were made on the enthalpy balances per trial.
- K-values which were independent of composition were used to get in the neighborhood of the solution, and then the composition dependent K-values given in Reference (6) were used.
- The program based on the Tomich method did not contain provisions for handling single phase components, and to approximate these,  $n\text{-C}_{12}\text{H}_{26}$  was used in Example 4 and  $\text{H}_2$  was used in Example 5.

\*These results were provided through the courtesy of the ChemShare Corp., 730 Asp Street, Norman, Oklahoma. The program based on the Tomich method was written by Dr. A. D. Epperly.

For typical absorber and stripper problems such as Examples 1 through 5 and 11 (see Tables 1 through 5), the procedure described above converged very rapidly. However, for relatively narrow boiling mixtures such as Examples 6 through 10 (see Tables 1 through 5), it was necessary to modify the procedure in order to prevent over-corrections. In particular, if the corrected total flow rates failed to give an improvement at the end of Step 1, this step was repeated on the basis of the calculated values of the total flow rates. An improvement was said to have been achieved if  $g(\theta)$  at  $\theta=1$  at the end of Step 1 was less than it was for the previous trial.

### Treatment of Single Phase Components

When the system contains single phase components, only minor modifications of the above equations are required. A **single phase light** component is defined as one that appears in the gas phase alone, and a **single heavy component** is defined as one which is miscible in and appears in the liquid phase alone. It will be supposed, of course, that the single phase lights enter in the stream  $V_{N+1}$  and that the single phase heavies enter in the stream  $L_0$ . Let  $v_L$  denote the total flow rate of single phase light components and  $l_H$  the total flow rate of single phase heavy components. Since the flow rates for the single phase components remain fixed throughout the column, it follows that their component-material balances are represented by

$$v_{jL}=v_L, \quad l_{jL}=0 \quad (31)$$

and

$$v_{jH}=0, \quad l_{jH}=l_H$$

In this case the quantities  $L_j$ ,  $\mathcal{V}_j$ ,  $\mathcal{B}$ ,  $\eta_j$ , and  $\sigma_j$  have the following definitions,

$$(L_j)_{co} = \eta_j l_j + l_H; \quad l_j = \sum_{\substack{i=1 \\ i \neq H,L}}^c \left( \frac{l_{ji}}{v_{1i}} \right)_{ca} (v_{1i})_{co}$$

$$(V_j)_{co} = \sigma_j \mathcal{V}_j + v_L; \quad \mathcal{V}_j = \sum_{\substack{i=1 \\ i \neq L}}^c \left( \frac{v_{ji}}{v_{1i}} \right)_{ca} (v_{1i})_{co} \quad (32)$$

$$\mathcal{B} = [(V_1)_{co} - v_L] - [L_0 - l_H]$$

while the bubble point functions given by Equations (24) and (25) become, respectively,

$$f_j = \sum_{\substack{i=1 \\ i \neq H,L}}^c (K_{ji})_a (x_{ji})_{co} - (1 - y_{jL})_{co}$$

$$f_j = \frac{L_j}{V_j a} \frac{\eta_j \mathcal{V}_j}{\eta_j l_j + l_H} - \frac{\sigma_j \mathcal{V}_j}{\sigma_j \mathcal{V}_j + v_L} \quad (33)$$

where

$$(y_{jL})_{co} = v_L / (V_j)_{co}$$

### Solution of Liquid-Liquid Extraction Problems

In the solution of liquid-liquid extraction problems, the temperatures are generally regarded as constant or fixed throughout the column. Problems which involve a typical countercurrent extractor of the type illustrated in Figure 1 may be solved by use of the single- $\theta$ -method in the same manner as described for the solution of the material balances and the equilibrium relationships. One minor modification of this method was made. After  $\theta$  had been determined in Step 2, the corresponding set of corrected compositions were used to compute the corrected set of  $K_{ji}$ 's for use in the next trial through the column,

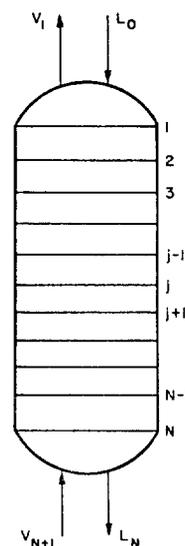


Fig. 1 Graphical Representation of an Absorber, Stripper, or Extractor

where

$$(K_{ji})_{co} = \frac{\gamma^L_{ji}}{\gamma^V_{ji}} \quad (34)$$

and

$$\gamma^L_{ji} = \text{function of } \{(x_{ji})_{co}\};$$

$$\gamma^V_{ji} = \text{function of } \{(y_{ji})_{co}\}.$$

When an additional feed is introduced on an intermediate plate  $f$  as shown in Figure 2, the material balances expressions given by Equation (15) must be altered as required to reflect this additional feed.

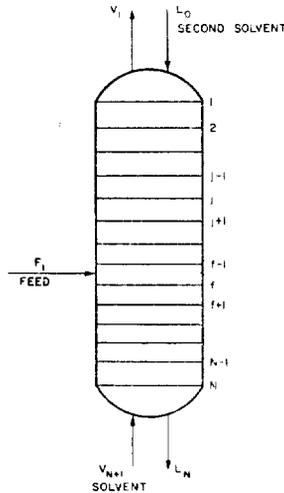


Fig. 2 Sketch of an Extractor with One Feed and Two Solvents

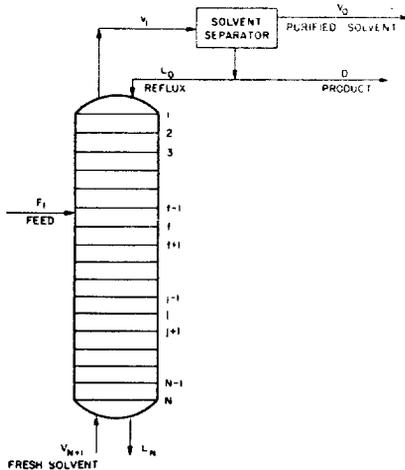


Fig. 3 Sketch of an Extractor with Extract Reflux

For the case where extract reflux is used to aid in effecting a given separation as shown in Figure 3, only minor modifications of the procedure described above are required to represent the addition of the solvent removal stage. Although the solvent removal stage is similar to a condenser on a distillation column, it seldom consists of a single equilibrium-stage. Instead the solvent removal stage generally consists of some other type of separation process, which should be solved simultaneously with the extractor problem. However, in order to focus complete attention on the solution of extractor problems it will be supposed that the separations effected by the solvent removal stage are independent of the flow rate and composition of  $V_1$  to the solvent removal stage. That is, it is supposed that the recovery  $r_i$  for each component  $i$  is constant where  $r_i$  is defined as follows:

$$r_i = \frac{L_0 x_{0i} + D X_{Di}}{V_0 y_{0i}} = \left(\frac{L_0}{D} + 1\right) \frac{d_i}{v_{0i}} \quad (35)$$

The material balance enclosing the solvent removal stage is given by

$$v_{1i} = v_{0i} + l_{0i} + d_i = v_{0i} + \left(\frac{L_0}{D} + 1\right) d_i \quad (36)$$

Elimination of  $d_i$  from Equations (35) and (36) gives

$$-(1+r_i)v_{0i} + v_{1i} = 0 \quad (37)$$

For any component  $i$ , the material balance enclosing plate 1 is given by

$$v_{2i} + l_{0i} - v_{1i} - l_{1i} = -F_1 X_{1i} \quad (38)$$

The ratio  $l_{0i}/v_{0i}$  may be stated in terms of  $r_i$  through the use of Equation (35),

$$\frac{l_{0i}}{v_{0i}} = \left(\frac{L_0/D}{L_0/D+1}\right) r_i \quad (39)$$

By use of this relationship and the equilibrium relationship  $l_{1i} = A_{1i} v_{1i}$ , it is possible to restate Equation (38) in the following form:

$$\left(\frac{L_0/D}{1+L_0/D}\right) r_i v_{0i} - (A_{1i} + 1) v_{1i} + v_{2i} = -F_1 X_{1i} \quad (40)$$

This equation constitutes the first in the set of the component-material balances. The remaining balances of this set are formulated in an analogous manner to that demonstrated for Equation (15).

For an extractor with reflux (see Figure 3), the single- $\theta$ -method differs slightly from the procedure shown above. The multiplier  $\theta$  is defined as follows:

$$\left(\frac{l_{N_i}}{v_{0i}}\right)_{co} = \theta \left(\frac{l_{N_i}}{v_{0i}}\right)_{ca} \quad (41)$$

Again it is required that the corrected rates satisfy the overall component-material balance,

$$F_1 X_{1i} + F_2 X_{2i} + v_{N+1, i} = (v_{0i})_{co} + (d_i)_{co} + (l_{N_i})_{co} \quad (42)$$

Since both  $L_0/D$  and the set of  $r_i$ 's are known and remain fixed for all trials, it follows that  $(d_i/v_{0i})_{co}$  is uniquely determined for all trials by Equation (35). Then by use of Equation (35), the definition of  $\theta$  as given by Equation (41), and Equation (42), the following formula for  $(v_{0i})_{co}$  is obtained.

$$(v_{0i})_{co} = \frac{F_1 X_{1i} + F_2 X_{2i} + v_{N+1, i}}{1 + \left(\frac{r_i}{(L_0/D) + 1}\right) + \theta \left(\frac{l_{N_i}}{v_{0i}}\right)_{ca}} \quad (43)$$

The remaining equations are similar but differ slightly from those stated for columns of the type represented in Figure 1. In particular,  $v_{1i}$  in Equations (18) through (20) should be replaced by  $v_{0i}$ . The calculation of the corrected values of  $D$  and  $L_0$  merits some attention because it differs from the remainder of the calculational procedure described above. Since each member of the set  $\{r_i\}$  as well as  $L_0/D$  remains fixed, it follows that the corrected values of the ratio  $d_i$  to  $v_{0i}$  are given by Equation (25). When Equation (35) is solved for  $(d_i)_{co}$  and summed over all components, one obtains,

$$D_{co} = \left(\frac{1}{\frac{L_0}{D} + 1}\right) \sum_{i=1}^c r_i (v_{0i})_{co} \quad (44)$$

where  $(v_{0i})_{co}$  is given by Equation (43). Likewise, the following expression for  $(L_0)_{co}$  is obtained from Equation (35).

$$(L_0)_{co} = \left(\frac{L_0/D}{\frac{L_0}{D} + 1}\right) \sum_{i=1}^c r_i (v_{0i})_{co} = \left(\frac{L_0}{D}\right) D_{co} \quad (45)$$

Again as in the case of a conventional column, it can be shown that  $\sigma_1=1$  and  $\eta_N=\theta$ . The remaining  $\eta_j$ 's and  $\sigma_j$ 's are calculated in analogous manner to that demonstrated above.

## Discussion and Analysis of the Numerical Results

In order to demonstrate some of the characteristics of the single- $\theta$ -method in the solution of absorber and stripper problems, a wide variety of examples were solved. Statements of Examples 1 through 11 are presented in Tables 1 and 2. Typical solutions are presented in Table 3 while the complete set of solutions for all examples is presented elsewhere (15). Other numerical results for Examples 1 through 11 are summarized in Tables 4 and 5. This array of examples covers a wide range of feed mixtures ( $V_{N+1}$  and  $L_0$ ) as well as a significant variation in the number of plates. To demonstrate the applicability of the  $\theta$ -method of convergence for solving liquid-liquid extraction problems, Examples 12 and 13 were solved; see Tables 6 through 9.

Table 6. Statement of Example 12

Component	Component Number	$l_{0i}$ (Solvent) moles/hr	$v_{N+1, i}$ (Solvent) moles/hr	$FX_i$ (Feed) moles/hr
Acetone	1	0.0	0.0	0.1
Ethanol	2	0.0	0.0	0.1
Chloroform	3	0.8	0.0	0.0
Water	4	0.0	1.0	0.0

### Other Specifications

Total number of plates  $N=15$ , feed plate for  $F$  is  $f=5$ , and feed plate for  $V_{N+1}$  is  $N=15$  (See Figure 2). The activity coefficients are computed by use of the following three-suffix Margules equation for component  $I$  in a mixture of  $L$  components

$$\gamma_1 = \exp \left\{ \left[ 2x_1 \sum_{j=1}^L x_j A_{jI} \right] + \left[ \sum_{j=1}^L (x_j)^2 A_{jI} \right] + \left[ \sum_{j=1}^L \sum_{k=2}^L x_j x_k A^*_{jIk} \right] - \left[ 2 \sum_{i=1}^L (x_i)^2 \sum_{j=1}^L x_j A_{ij} \right] - 2 \left[ \sum_{i=1}^L \sum_{j=2}^L \sum_{k=3}^L x_i x_j x_k A^*_{iJk} \right] \right\}$$

where,

$$A^*_{iJk} = 1/2 (A_{iJ} + A_{jI} + A_{iK} + A_{kI} + A_{jK} + A_{kI})$$

Table 6. (Cont'd.)

Other Specifications (Cont'd.)			
(This equation consists of a corrected form of the expression presented in Reference (9)). The values of $A_{IJ}$ are as follows:			
$A_{11}=0$	$A_{12}=0.5446$	$A_{13}=-0.9417$	$A_{14}=1.872$
$A_{21}=0.599$	$A_{22}=0.0$	$A_{23}=1.61$	$A_{24}=1.46$
$A_{31}=-0.674$	$A_{32}=0.501$	$A_{33}=0.0$	$A_{34}=5.91$
$A_{41}=1.338$	$A_{42}=0.877$	$A_{43}=4.76$	$A_{44}=0.0$

Table 7. Solution of Example 12

I. Initial Assumptions and the Solution Set of Flow Rates  $\{V_j\}$ 

Plate No.	$V_j$ (Initial) lb-moles/hr	$V_j$ (Final) lb-moles/hr	Other Initial Specifications
1	1.4	1.048	All streams $V_j$ were assumed to have the same initial composition as $V_{N+1}$ . All streams $L_j$ were assumed to have the initial composition of the combined streams $L_0$ and $F$ . The initial set of activity coefficients were computed on the basis of these sets of assumed compositions for $V_j$ and $L_j$ .
2	1.4	1.102	
3	1.4	1.142	
4	1.4	1.180	
5	1.4	1.226	
6	1.0	1.307	
7	1.0	1.327	
8	1.0	1.322	
9	1.0	1.313	
10	1.0	1.299	
11	1.0	1.275	
12	1.0	1.293	
13	1.0	1.190	
14	1.0	1.131	
15	1.0	1.069	

Table 7. (Cont'd.)

II. Final Compositions of Streams  $L_N$  and  $V_1$ 

Component No.	$x_{Ni}$	$y_{1i}$
1	0.10506	$0.23973 \times 10^{-6}$
2	0.04531	$0.54253 \times 10^{-1}$
3	0.83613	$0.39686 \times 10^{-2}$
4	0.01350	0.94178

## III. Comparison of the Proposed Computational Procedures for Example 12

Computational Procedure	Number of Trials	Computational Time (min.)*
Bruno et al. (18)	24	6.15
Hanson et al. (9)	43	1.23
Single- $\theta$ -method	17	0.82

\*The convergence criterion used was  $\left| \frac{\Delta V}{V} \right| \leq 10^{-3}$ , where  $\Delta V = V$  correct -  $V$  calculated. The correct set was obtained

by making a large number of trials to converge within the accuracy of the IBM 360/65 computer.

Table 8. Statement of Example 13

Component	Component Number	$F_1 X_{1i}$ (Solvent) lb-moles/hr	$F_2 X_{2i}$ (Feed) lb-moles/hr	$V_{N+1, i}$ (Solvent) lb-moles/hr	Separator Factors*
Acetone	1	0.0	0.1	0.0	200
Ethanol	2	0.0	0.1	0.0	570
Chloroform	3	0.8	0.0	1.0	350
Water	4	0.0	0.0	1.0	$7 \times 10^{-4}$

## Other Specifications

Total number of plates  $N=15$ , solvent  $F_1$  enters on plate 1, feed  $F_2$  enters on plate 5, and solvent  $V_{N+1}$  enters plate 15; see Figure 3. The reflux ratio  $L_0/D$  is fixed at 0.25, and the activity coefficients are to be computed by use of the expressions and constants  $A_{IJ}$  stated for Example 12.

\*The operation of the solvent separator is described by the specification of the separator factors,  $r_i$ , where

$$r_i = \frac{L_0 x_{0i} + D X_{Di}}{V_0 y_{0i}}$$

Table 9. Solution of Example 13

I. Initial Assumptions and the Solution Set of Flow Rates  $\{V_j\}$ 

Plate No.	$V_j$ (Initial) lb-moles/hr	$V_j$ (Final) lb-moles/hr	Other Initial Assumptions
1	1.4	1.060	All streams $V_j$ were assumed to have the same initial composition as $V_{N+1}$ . All streams $L_j$ were assumed to have the initial of the combined streams $F_1$ and $F_2$ . The initial set of activity coefficients were computed on the basis of these sets of assumed compositions for $V_j$ and $L_j$ .
2	1.4	1.111	
3	1.4	1.148	
4	1.4	1.185	
5	1.4	1.231	
6	1.0	1.312	
7	1.0	1.332	
8	1.0	1.328	
9	1.0	1.320	
10	1.0	1.305	
11	1.0	1.281	
12	1.0	1.246	
13	1.0	1.196	
14	1.0	1.136	
15	1.0	1.071	

Table 9. (Cont'd.)

II. Final Compositions\* of Streams  $N_N$ ,  $V_0$ , and  $D$ 

Component No.	$x_{Ni}$	$y_{0i}$	$y_{Di}$
1	0.10479	$0.14034 \times 10^{-8}$	$0.37540 \times 10^{-5}$
2	0.0470	$0.12196 \times 10^{-3}$	0.92976
3	0.83454	$0.13005 \times 10^{-4}$	$0.60879 \times 10^{-1}$
4	0.01359	0.99987	$0.93610 \times 10^{-2}$

### III. Convergence Characteristics of the $\theta$ -Method and Direct Iteration

Calculational Procedure	Number of Trials	Computational Time (min.)*
Single- $\theta$ -method	15	0.82
Direct Iteration	21	0.65

\*The convergence criterion used was  $\frac{\Delta V}{V} \leq 10^{-3}$  (see Item III of Table 7).

In the discussion of Examples 1 through 11, the fraction of the total feed consisting of  $C_3$  and lighter components is used as a measure of the *boiling range* of the total feed mixture. For Example 1 (a *wide boiling mixture*) the fraction of  $C_3$  and lighter components in the total feed is 29.6/31.8 while for Example 8 (a *narrow boiling mixture*), the fraction of  $C_3$  and lighter components is equal to 1/40. Example 11 was included in order to demonstrate the characteristics of the proposed procedures in the solution of separation problems involving the use of steam strippers. Although separations of the type described by Examples 6 through 10 would seldom be of commercial interest, they were included in order to demonstrate the characteristics exhibited by the proposed procedure in the solution of such problems.

The results for the procedure by Tomich (19) were obtained with a different type of computer than were those presented in Table 4 for the single- $\theta$ -method and Sujata's method (17). The time requirements given in Table 4 for the Tomich method were estimated by use of the results presented in Table 5.

A comparison of the results appearing in Table 4 shows that the single- $\theta$ -method and the Tomich method converged for all examples; whereas, Sujata's method failed for Examples 7 through 10. The possibility of the failure of Sujata's method for narrow boiling mixtures such as Examples 6 through 10 has been demonstrated by Friday *et al.* (7). Also, Friday *et al.* demonstrated that the tendency toward failure to converge increased as the number of plates was increased.

The proposed combination of the single- $\theta$ -method and the Newton-Raphson method is seen to extend the range of convergence to include all absorber

problems which appear to be of commercial interest (Examples 1 through 5) as well as problems outside the range of commercial interest (see Examples 6 through 11). Although the combination of the single- $\theta$ -method and the Newton-Raphson method for the determination of temperatures will converge for problems having somewhat lighter lean oils relative to the rich gas streams than those shown for Examples 6 through 10, these problems are approaching the outer bounds of convergence of this method. For example, for problems in which the lean oil is lighter than the rich gas such as Example 3 proposed by Boyum (3), the proposed combination of the single- $\theta$ -method and the Newton-Raphson failed to converge.

To demonstrate the convergence characteristics of the single- $\theta$ -method in the solution of liquid-liquid extraction problems, Examples 12 and 13 were selected. For all liquid-liquid extraction problems attempted by the single- $\theta$ -method, convergence was obtained. Actually, an example which more dramatically demonstrates the speed of convergence of the single- $\theta$ -method relative to direct-iteration than does Examples 12 and 13 has been presented as Example 5-4 by Hutton (12). Hutton's Example 5-4 converged in 20 trials when the single- $\theta$ -method was employed, but it had not converged to the correct solution at the end of 160 trials when direct-iteration was used.

In summary, the proposed combination of the single- $\theta$ -method and the Newton-Raphson procedure for the determination of temperatures provides a very rapid procedure for solving absorber, stripper, and liquid-liquid extraction problems of the type which appear to be of commercial interest.

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### Notation

- $A_{ji}$ =Absorption factor for component  $i$  on plate  $j$ ;  
 $A_{ji}=L_j/K_{ji}V_j$ .  
 $\mathcal{B}$ =A constant appearing in Equations (23) and (32).  
 $\mathbf{B}_n$ =Tridiagonal matrix that contains the partial derivatives of  $G_j$  functions with respect to the temperatures.  
 $\mathbf{C}_n$ =Column matrix; defined by Equation (30).  
 $f_j$ =Bubble point function for plate  $j$ ; see Equations (24) and (25).  
 $g(\theta)$ =Arithmetic average of the Euclidean norm of the bubble point functions [Equation (26)].  
 $G_j$ =Enthalpy functions; defined by Equations (28).  
 $h_{ji}$ =Enthalpy of one mole of pure component  $i$  in the liquid phase at the temperature of plate  $j$ .  
 $h_j$ =Enthalpy of mole of liquid leaving plate  $j$ .  
 $H_{ji}$ =Enthalpy of one mole of pure component  $i$  in the vapor phase at the temperature of plate  $j$ .  
 $K_{ji}$ =The K-value for component  $i$ ; evaluated at the temperature and pressure of plate  $j$ .  
 $l_{ji}$ =Molal flow rate at which component  $i$  in the liquid phase leaves plates  $j$ .  
 $\rho_j$ =A total molal flow rate that approaches  $L_j$  as convergence to the problem is approached; defined below Equation (19).  
 $L_j$ =Total molal flow rate at which the liquid leaves plate  $j$ .  
 $N$ =Total number of plates; also,  $N$  is the number of the bottom plate, since the plates are numbered down from the top of the column.  
 $P$ =Column pressure.  
 $S_{ji}$ =Stripping factor for component  $i$  and plate  $j$ ;  $S_{ji}=K_{ji}V_j/L_j$ .  
 $T_j$ =Temperature of plate  $j$ .  
 $v_{ji}$ =Molal flow rate at which component  $i$  leaves plate  $j$  in the vapor phase.  
 $\mathcal{V}_j$ =A total molal flow rate that approaches  $V_j$  as convergence to the problem is approached; defined below Equation (19).  
 $V_j$ =Total molal flow rate at which the vapor leaves plate  $j$ .  
 $\Delta \mathbf{X}_n$ =Column matrix; defined by Equation (30).

### Subscripts

- $a$ =Assumed value.  
 $ca$ =Calculated value.  
 $co$ =Corrected value.

### Greek Letters

- $\eta_j$ =A multiplier; defined by the first expression given by Equation (32).  
 $\theta$ =A multiplier; defined by Equations (11) and (41).  
 $\sigma_j$ =A multiplier; defined by the second expression given by Equation (32).

### Mathematical Symbols

- $\sum_{\substack{c \\ i=H,L}}^c$  =Sum over all components from 1 to  $c$  except  $H$  and  $L$ .  
 $\{T_j\}$ =Set of all  $T_j$ 's for plates  $j=1$  through  $j=N$ .

### Appendix A

The relationship given by Equation (22) has additional significant characteristics which may be demonstrated by first restating Equation (21) in the form

$$\left( \mathcal{V}_{j+1} - \frac{\eta_j \rho_j}{\sigma_{j+1}} \right) \sigma_{j+1} = \mathcal{B}, \quad (1 \leq j \leq N-1) \quad (\text{A-1})$$

and then in matrix notation,

$$\mathbf{M}\sigma = \mathcal{B}\mathbf{U} \quad (\text{A-2})$$

where  $\mathbf{M}$  is a square diagonal matrix of order  $N-1$ ,  $\mathbf{U}$  is a conformable unit vector, and

$$\sigma = [\sigma_2 \sigma_3 \cdots \sigma_{N-1} \sigma_N]^T \quad (\text{A-3})$$

If

$$\eta = [\eta_1 \eta_2 \cdots \eta_{N-2} \eta_{N-1}]^T \quad (\text{A-4})$$

and if each side of Equation (A-2) is premultiplied first by  $\mathbf{M}^{-1}$  and then by  $\eta^T$ , one obtains

$$\eta^T \sigma = \eta^T \mathbf{M}^{-1} \mathbf{U} \quad (\text{A-5})$$

When the condition given by Equation (22) is imposed on Equation (A-5), the left-hand side

reduces to the square of the Euclidean norm of the unit vector  $U$ ; that is,

$$\eta^T \sigma = U^T U = N-1 = B \eta^T M^{-1} U \quad (A-6)$$

Thus, Equation (22) consists of that unique relationship for which the value of the product  $\eta^T \sigma$  at any trial prior to convergence is equal to its value  $U^T U$  at convergence. The relationship given by Equation (22) further requires that each element of  $\eta^T \sigma$  at any trial prior to convergence be equal to the corresponding element of  $U^T U$ . Furthermore at any trial prior to convergence, each element of the right-hand side of Equation (A-6) takes on that value which it possesses at convergence. For example, for the case of any element  $j$  ( $1 \leq j \leq N-1$ ), it follows that

$$1 = \frac{(V_1)_{co} - L_0}{(1/\tau_j) \sigma_{j+1} - \eta_j \rho_j} = \left( \frac{V_1 - L_0}{V_{j+1} - L_j} \right) \Big|_{\text{At convergence}} \quad (A-7)$$

Although the resulting condition of restraint on the intermediate flow rates represented by Equation (22) does not assure convergence, it does suggest, however, that convergence may be promoted by the reciprocal relationship between  $\sigma_{j+1}$  and  $\eta_j$ , Equation (22).

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