On the Numerical Solution of Problems in Multicomponent Distillation at the Steady State

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A part of the empirical and generally effective θ method of Holland for the numerical solution of steady state multicomponent distillation problems is placed on a sound mathematical basis. Additional analysis of two other aspects of the numerical procedure is also presented. Finally, some numerical Jacobian types of matrices are discussed for two test problems. This discussion provides a numerical comparison between the strength of convergence of Holland's approach and direct iteration.

FLOW AND EQUILIBRIUM EQUATIONS

The unit to be discussed is the complex distillation column at steady state. For purposes of analysis the column is considered to be perfectly insulated, heat being supplied only through the reboiler and in the feed streams. Heat is regarded as leaving the unit only through the condenser and withdrawal streams. Figure 1 is a schematic diagram of such a system.

The method most widely successful in solving for the internal flow rates of each of the components is perhaps that proposed by Holland (*4*). The reader is referred to the indicated reference for an exhaustive treatment of this method, certain aspects of which constitute the subject of this paper. It is to be assumed that a fraction $1 - e_{Vj}$ of the vapor entering the j^{th} plate comes into intimate contact with liquid on that plate and that a fraction $1 - e_{Lj}$ of the liquid entering the j^{th} plate comes into intimate contact with vapor at that plate. The liquid and vapor in intimate contact are assumed to come to equilibrium at the bubble or dew point of this equilibrium mixture. This will in general be different from the bubble or dew point which would be obtained if the entire vapor flow and the entire liquid flow came to equilibrium with each other. It will be assumed, however, that the liquid and vapor leaving a plate are at the temperature of the bubble or dew point just mentioned. Thus, if $e_{Lj} \neq 0$ or $e_{Vj} \neq 0$, the vapor or liquid will be somewhat subcooled or superheated. Relations similar to those presented by Holland (*4*) will be given and will be placed in the form described by Ball (*1*) and solved by Gaussian elimination as indicated by Peaceman and Rachford (*7*). Some comments on the numerical accuracy of this solution will then be made. In all this work the index indicating the component will normally be suppressed. Thus, define

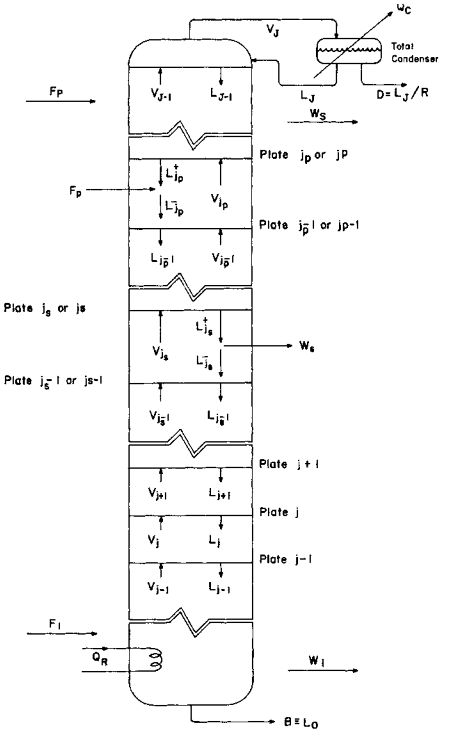

Fig. 1. Complex distillation column.

$$A_j = A_{ij} = \frac{L_j - e_{Lj}L_{j+1}}{K_{ij}(V_{j+1} - e_{Vj}V_j)} \tag{1}$$

Note that e_{Lj} and e_{Vj} are not functions of the component index *i*. Then from the preceding discussion

$$l_j - e_{Lj}l_{j+1} = A_j(v_{j+1} - e_{Vj}v_j) \tag{2}$$

Of course e_{Lj} and e_{Vj} each lie in the closed interval [0, 1]. If both are zero, all material is in equilibrium. If e_{Lj} is 1 and $0 < e_{Vj} < 1$, differential partial condensation occurs alone, whereas if e_{Vj} is 1 and $0 < e_{Lj} < 1$, differential partial vaporization occurs alone. For other values of e_{Lj} and e_{Vj} both phenomena occur to various extents. The relations lose all meaning if any of the differences become negative.

From Figure 1 it is seen that in the absence of external streams

$$v_{j+1} + l_j = l_{j+1} + v_j \tag{3}$$

so that from (2) and (3)

$$(1 - e_{Lj})l_j = (A_j + e_{Lj})v_{j+1} - (A_je_{Vj} + e_{Lj})v_j \tag{4}$$

and from (3) and (4)

$$-\frac{1 - e_{Lj-1}}{1 - e_{Lj}}(A_j + e_{Lj})v_{j+1} + \left[\frac{1 - e_{Lj-1}}{1 - e_{Lj}}(A_je_{Vj} + e_{Lj}) + A_{j-1} + 1\right]v_j - (A_{j-1}e_{Vj-1} + 1)v_{j-1} = 0 \tag{5}$$

For notational convenience it will be assumed henceforth that

$$e_{Lj} = e_{Lj-1} = e_{Lj+1} \text{ and } e_{Vj} = e_{Vj-1} = e_{Vj+1}$$

Subsequent developments could have been carried out without these restrictions, but the equations would have been more difficult to read and would have displayed no additional ideas. Thus (5) becomes

$$-(A_j + e_L)v_{j+1} + (A_j e_V + A_{j-1} + e_L + 1)v_j - (A_{j-1}e_V + 1)v_{j-1} = 0 \quad (6)$$

Applying (6) to successive values of j one gets

$$\begin{gathered}
-(A_1 + e_L)v_2 + (A_1 e_V + A_o + e_L + 1)v_1 = (A_o e_V + 1)v_o \\
-(A_2 + e_L)v_3 + (A_2 e_V + A_1 + e_L + 1)v_2 - (A_1 e_V + 1)v_1 = 0 \\
-(A_3 + e_L)v_4 + (A_3 e_V + A_2 + e_L + 1)v_3 - (A_2 e_V + 1)v_2 = 0 \\
\cdots \qquad (7) \\
-(A_{J-1} + e_L)v_J + (A_{J-1}e_V + A_{J-2} + e_L + 1)v_{J-1} - (A_{J-2}e_V + 1)v_{J-2} = 0 \\
(A_{J-1} + 1 - R_D)v_J - (A_{J-1}e_V + 1)v_{J-1} = 0
\end{gathered}$$

At a liquid feed location as depicted in Figure 1 define

$$A_{ijp-1} = A_{jp-1} = \frac{L_{jp-1} - e_L L^-_{jp}}{K_{ijp-1}(V_{jp} - e_V V_{jp-1})} = \frac{l_{jp-1} - e_L\, l^-_{jp}}{v_{jp} - e_V v_{jp-1}} \quad (8)$$

$$A_{ijp} = A_{jp} = \frac{L^+_{jp} - e_L\, L_{jp+1}}{K_{ijp}\,(V_{jp+1} - e_V V_{jp})} = \frac{l^+_{jp} - e_L\, l_{jp+1}}{v_{jp+1} - e_V v_{jp}} \quad (9)$$

where the subscripts $j_p - 1$ and j_p have been written as the compound subscripts $jp - 1$ and jp, respectively. Furthermore

$$l^+_{jp} + f_p = l^-_{jp} = v_{jp} + l_{jp-1} - v_{jp-1} \quad (10)$$

and

$$L^+_{jp} + F_p = L^-_{jp} \quad (11)$$

From (8) and (10)

$$(1 - e_L)\, l^-_{jp} = (A_{jp-1} + 1)v_{jp} - (A_{jp-1}e_V + 1)v_{jp-1} \quad (12)$$

while from (4)

$$(1 - e_L)\, l^+_{jp} = (A_{jp} + e_L)v_{jp+1} - (A_{jp}e_V + e_L)v_{jp} \quad (13)$$

so that from (10), (12), and (13)

$$-(A_{jp} + e_L)v_{jp+1} + (A_{jp}e_V + A_{jp-1} + e_L + 1)v_{jp} - (A_{jp-1}e_V + 1)v_{jp-1} = (1 - e_L)f_p \quad (14)$$

Equations (8) to (11) describe the conditions which distinguish a liquid feed. The equation corresponding to (14) but for vapor feed may be developed in a manner similar to that just employed.

At a liquid withdrawal as shown in Figure 1 define

$$A_{ijs-1} = A_{js-1} = \frac{L_{js-1} - e_L L^-_{js}}{K_{ijs-1}(V_{js} - e_V V_{js-1})} = \frac{l_{js-1} - e_L\, l^-_{js}}{v_{js} - e_V v_{js-1}} \quad (15)$$

$$A_{ijs} = A_{js} = \frac{L^+_{js} - e_L L_{js+1}}{K_{ijs}(V_{js+1} - e_V V_{js})} = \frac{l^+_{js} - e_L\, l_{js+1}}{v_{js+1} - e_V v_{js}} \quad (16)$$

where

$$l^+_{js} - w_s = l^-_{js} = v_{js} + l_{js-1} - v_{js-1} \quad (17)$$

$$w_s/W_s = l^+_{js}/L^+_{js} = l^-_{js}/L^-_{js} \quad (18)$$

and

$$L^+_{js} - W_s = L^-_{js} \quad (19)$$

Here again subscripts have been written as compounds. From (17) and (18) there is

$$l^-_{js} = [1 - (W_s/L^+_{js})]\, l^+_{js} \quad (20)$$

and from (4) there is

$$(1 - e_L)\, l^+_{js} = (A_{js} + e_L)v_{js+1} - (A_{js}e_V + e_L)v_{js} \quad (21)$$

so that from (4), (17), (20), and (21)

$$[1 - (W_s/L^+_{js})]\,[(A_{js} + e_L)v_{js+1} - (A_{js}e_V + e_L)v_{js}] = (1 - e_L)(v_{js} - v_{js-1}) + (A_{js-1} + e_L)v_{js} - (A_{js-1}e_V + e_L)v_{js-1}$$

which may be rearranged to

$$-[1 - (W_s/L^+_{js})](A_{js} + e_L)v_{js+1} + \{[1 - (W_s/L^+_{js})](A_{js}e_V + e_L) + A_{js-1} + 1\}v_{js} - (A_{js-1}e_V + 1)v_{js-1} = 0 \quad (22)$$

Equations (15) to (19) express the conditions which distinguish a liquid side draw.

Equations corresponding to (14) and (22) and valid for the situation in which e_L and e_V may vary from plate to plate may be derived in a manner analogous to that just employed.

A matrix representation follows for the case of $J = 6$, $j_p = 3$, and $j_s = 4$. For notational convenience e_L and e_V have been taken to be zero. Even without this restriction the matrix would be tridiagonal:

$$\begin{pmatrix}
A_5 + 1 & -1 & 0 & 0 & 0 & 0 \\
-A_5 & A_4 + 1 & -1 & 0 & 0 & 0 \\
0 & -\left[1 - \dfrac{W_1}{L^+_4}\right] A_4 & A_3 + 1 & -1 & 0 & 0 \\
0 & 0 & -A_3 & A_2 + 1 & -1 & 0 \\
0 & 0 & 0 & -A_2 & A_1 + 1 & -1 \\
0 & 0 & 0 & 0 & -A_1 & A_o + 1
\end{pmatrix}
\begin{pmatrix} v_6 \\ v_5 \\ v_4 \\ v_3 \\ v_2 \\ v_1 \end{pmatrix}
\quad
\begin{pmatrix} l_6 \\ 0 \\ 0 \\ f \\ 0 \\ v_o \end{pmatrix}$$

After v_{j+1} has been found, l_j may be determined by (4).

The general forms of (7), (14), and (22) are

$$\left.\begin{aligned}
(A_{J-1} + 1)v_J - v_{J-1} &= l_J \\
-c_j v_{j+1} + (A_{j-1} + 1)v_j - v_{j-1} &= \omega_j \\
-c_1 v_2 + (A_o + 1)v_1 &= v_o
\end{aligned}\right\} \quad (23)$$

This form of the equations representing equilibrium conditions and flow rates is due to Ball (1). The following identifications are to be made:

$$\left.\begin{aligned}
&c_j = A_j, && j \neq js \\
&c_j = [1 - (W_s/L^+_{js})]A_j, && j = js \\
&\omega_j = 0 && j \neq 1, J, jp \\
&\omega_{jp} = f_p,\ \omega_1 = v_o,\ \omega_J = l_J
\end{aligned}\right\} \quad (24)$$

so that when (24) is applied to (23) Gaussian elimination [see for example Peaceman and Rachford (7)] becomes

$$\left.\begin{aligned} r_J &= A_{J-1} + 1 \\ g_J &= \omega_J/r_J = \omega_J/(A_{J-1} + 1) \\ r_j &= A_{j-1} + 1 - (c_j/r_{j+1}) \\ g_j &= (\omega_j + c_j g_{j+1})/r_j \\ v_1 &= g_1 \\ v_j &= g_j + v_{j-1}/r_j \end{aligned}\right\} \qquad (25)$$

The question of numerical accuracy arises next. Equations (24) and (25) show that subtraction occurs only in the computation of r_j; the effect of this will be scrutinized, since it is the subtraction step which has in the past been primarily responsible for introducing intolerable error into the solution of certain problems. More specifically, in problems other than absorber ones this intolerable error has been seen to arise from the fact that the order of magnitude of the result of the subtraction step was less than that of the larger of the numbers differenced, all quantities involved being positive. Holland (4) discusses this point.

An extended discussion of the numerical accuracy of Gaussian elimination is given by Rall (9). Albasiny (9) shows that Gaussian elimination applied to equations of the type expressing the material and equilibrium relations for a column, that is Equation (25) applied to Equations (23) and (24), produces a solution in which the computational error is not significant, provided the equations to be solved are not mathematically ill conditioned.

Fortunately, the relative magnitudes of the result of the subtraction step in Equation (25) and the numbers differenced there may be investigated without recourse to the more powerful and esoteric methods employed by Albasiny. To this end recall

$$r_J = A_{J-1} + 1 > A_{J-1} > 0$$

$$\therefore 0 < A_{J-1}/r_J < 1$$

Suppose

$$0 < A_{j-1}/r_j < 1 \ \left[\text{or } 0 < \left(1 - \frac{W_s}{L^+{}_{js}}\right) A_{js}/r_{js+1} < 1\right]$$

Then since $A_{j-1} > 0$, there is from Equations (24) and (25)

$$r_{j-1} = A_{j-2} + 1 - (A_{j-1}/r_j) > A_{j-2} > 0$$

Hence by mathematical induction

$$r_j > A_{j-1} \text{ or } 0 < A_{j-1}/r_j < 1$$

for all values of j. It will now be shown that if either $A_{j-1} > 1$ or $A_j < A_{j-1}$, r_j will have the same order of magnitude as $A_{j-1} + 1$ or A_{j-1}. These restrictions on the A_j insure that if any $A_j > 1$, then each A (for the same component) between this A_j and the hot end of the unit also exceeds 1.

Suppose a section of the column exists where $A_j < 1$. Then by assumption $A_j < A_{j-1}$. Assume $r_{j+1} > 1$. Then $0 < A_{j-1} - (A_j/r_{j+1}) < A_{j-1} < 1$, so that in this case the computation of r_j involves differencing two positive numbers each less than 1 to obtain a positive remainder and adding this difference to 1. Thus the result will have the same order of magnitude as $A_{j-1} + 1.0$. Furthermore, the result r_j exceeds 1. When one recalls $r_J = A_{J-1} + 1 > 1$, there is then by mathematical induction: $r_j > 1$ throughout this section, and r_j will have the same order of magnitude as $A_{j-1} + 1$ throughout this section of the column.

Suppose next that there is a section of the column in which $A_{j-1} > 1$. Thus $A_{j-1} + 1 > 2$, and the computation of r_j reduces to taking the difference between a number exceeding 2 and a number less than 1. The result is a number which is more than 1 and has the same number of meaningful digits as did A_{j-1}.

In the event that neither of the stated restrictions on the A_j holds, the analysis just completed may be performed upon the following formulation. One sees this by dividing the i^{th} scalar equation represented in the following matrix equation by A_i, thus producing a system mathematically similar to the one just considered:

$$\begin{bmatrix} A_o + 1 & -A_1 & 0 & 0 & \dots \\ -1 & A_1 + 1 & -A_2 & 0 & \dots \\ 0 & -1 & A_2 + 1 & -A_3 & \dots \\ 0 & 0 & -1 & A_3 + 1 & \dots \\ \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot \end{bmatrix} \begin{bmatrix} v_1 \\ v_2 \\ v_3 \\ v_4 \\ \cdot \\ \cdot \\ \cdot \end{bmatrix} = \begin{bmatrix} v_o \\ 0 \\ f \\ 0 \\ \cdot \\ \cdot \\ \cdot \end{bmatrix}$$

CORRECTION EQUATIONS

Attention is next to be focused on the equations developed by Holland (4) for correcting the flows of individual components in product and internal streams. In this development two different types of sums are required. The first is the sum over components on a plate and will be denoted by Σ. The second is a sum on one component over feed or side-draw streams from the hot end of the unit to plate j. This latter type of sum will be indicated by $\boldsymbol{\Sigma}$. $\triangleq$ will denote: is defined as equal to.

Define the corrected value of d_i/b_i or w_{is}/b_i for the s^{th} side draw, respectively, to be

$$\left.\begin{aligned} \frac{d_i}{b_i} &= \theta_o \left(\frac{d_i}{b_i}\right)_c \\ \frac{w_{is}}{b_i} &= \theta_s \left(\frac{w_{is}}{b_i}\right)_c \end{aligned}\right\} \qquad (26)$$

where the subscript c denotes the last previously computed value for the quantity to which it applies. For any component over the entire unit

$$d + b + \sum_{s=1}^{S} w_s = \sum_{p=1}^{P} f_p \triangleq F^o$$

so that

$$b = \frac{F^o}{1 + \dfrac{d}{b} + \displaystyle\sum_{s=1}^{S} \frac{w_s}{b}}$$

$$= \frac{F^o}{1 + \theta_o \left(\dfrac{d}{b}\right)_c + \displaystyle\sum_{s=1}^{S} \theta_s \left(\dfrac{w_s}{b}\right)_c} \qquad (27)$$

Substitution of (27) into (26) yields

$$w_{is} = w_s = \theta_s \left(\frac{w_s}{b}\right)_c b$$

$$= \frac{\theta_s \left(\dfrac{w_s}{b}\right) F^o}{1 + \theta_o \left(\dfrac{d}{b}\right)_c + \displaystyle\sum_{s=1}^{S} \theta_s \left(\dfrac{w_s}{b}\right)_c} \qquad (28)$$

If B and each W_s are specified, then, since

$$\sum_i w_{is} = W_s$$

use (27) and (28) to obtain

$$\left.\begin{aligned} G_o &\triangleq B-\sum_i \frac{F^o}{1+\theta_o\left(\dfrac{d}{b}\right)_c+\displaystyle\sum_{s=1}^{S}\theta_s\left(\dfrac{w_s}{b}\right)_c} \\ G_s &\triangleq W_s-\sum_i \frac{\theta_s\left(\dfrac{w_s}{b}\right)_c F^o}{1+\theta_o\left(\dfrac{d}{b}\right)_c+\displaystyle\sum_{s=1}^{S}\theta_s\left(\dfrac{w_s}{b}\right)} \end{aligned}\right\} \quad (29)$$

There are S equations G_s giving a total of $S + 1$ equations in the $S + 1$ unknown θs. If a solution composed entirely of positive θ's exists for the set of Equations (29), then the w_{is}/b_i obtained by using this solution in (26) will be such that Σw_{is} equals the specified value of W_s for each s. Also in this case Σb_i will equal the specified value of B. Holland (*4*) outlines proofs for the existence of such a solution for the cases $S = 0$ and $S = 1$. In the case $S = 1$ the system (29) reduces to

$$G_o = B-\sum_i \frac{F^o}{1+\theta_o\left(\dfrac{d}{b}\right)_c+\theta_1\left(\dfrac{w_1}{b}\right)_c}=0$$

$$G_1 = W_1-\sum_i \frac{\theta_1\left(\dfrac{w_1}{b}\right)_c F^o}{1+\theta_o\left(\dfrac{d}{b}\right)_c+\theta_1\left(\dfrac{w_1}{b}\right)_c}=0$$

The existence proof outlined by Holland requires a demonstration that for $\theta_o = 0$ the value of θ_1 required for $G_o(0, \theta_1) = 0$ is larger than the value of θ_1 required for $G_1(0, \theta_1) = 0$. The method employed below displays more clearly the effect of the physical flows than does the method employed in (*4*).

Let $\theta_1{}^o$ and $\theta_1{}^1$ denote the values of θ_1 required for $G_o(0, \theta_1{}^o) = 0$ and $G_1(0, \theta_1{}^1) = 0$, respectively, in the case of only one side draw (that is, $S = 1$). Now for any component in the case of one side draw

$$b=\frac{F^o}{1+\theta_o\,(d/b)_c+\theta_1\,(w_1/b)_c}$$

$$w_1=\frac{\theta_1\,(w_1/b)_c\,F^o}{1+\theta_o\,(d/b)_c+\theta_1\,(w_1/b)_c}$$

$$d+b+w_1=F^o \therefore b+w_1=F^o-d<F^o$$

Thus for $\theta_o = 0$ there is

$$b=\frac{F^o}{1+\theta_1{}^o\,(w_1/b)_c}$$

$$w_1=\frac{\theta_1{}^1\,(w_1/b)_c\,F^o}{1+\theta_1{}^1\,(w_1/b)_c}$$

and finally

$$\frac{F^o}{1+\theta_1{}^o\,(w_1/b)_c}+\frac{\theta_1{}^1\,(w_1/b)_c\,F^o}{1+\theta_1{}^1\,(w_1/b)_c}<F^o$$

The following algebraic acrobatics yield the desired result. From the last previous equation

$$\frac{\theta_1{}^1\,(w_1/b)_c}{1+\theta_1{}^1\,(w_1/b)_c}<1-\frac{1}{1+\theta_1{}^o\,(w_1/b)_c}=\frac{\theta_1{}^o\,(w_1/b)_c}{1+\theta_1{}^o\,(w_1/b)_c}$$

or

$$\theta_1{}^1\,[1+\theta_1{}^o\,(w_1/b)_c]<\theta_1{}^o\,[1+\theta_1{}^1\,(w_1/b)_c]$$

so that $\theta_1{}^1 < \theta_1{}^o$.

Since the relations of the previous paragraph hold for each component, it follows that $\theta_1{}^1 = \theta_1{}^o$ if and only if $D\ (= \Sigma d) = 0$.

The equations given in (*4*) for correcting internal flows deserve a more penetrating analysis. In this analysis e_V, e_L, and the values of the A_{ij} are considered to be fixed; v_o is taken as zero; and the identification $l_o \equiv b$ is made. To satisfy the condition on the A_{ij} it might be assumed that the temperature and L_{j-1}/V_j profiles do not change when the l_{ij} and v_{ij} are corrected. From Equation (4) there is

$$(1-e_L)b=(A_o+e_L)v_1$$

so that

$$dv_1/db=(1-e_L)/(A_o+e_L)=v_1/b \qquad (30)$$

which is constant. Similarly, since

$$\left.\begin{aligned} l_1 &= v_1+b \\ dl_1/db &= 1+dv_1/db=l_1/b \end{aligned}\right. \qquad (31)$$

which is constant. Again from (4), (30), and (31)

$$\frac{dv_2}{db}=\left(\frac{1-e_L}{A_1+e_L}\right)\frac{dl_1}{db}+\left(\frac{A_1e_V+e_L}{A_1+e_L}\right)\frac{dv_1}{db}=\frac{v_2}{b} \qquad (32)$$

which is constant. Also from (3), (30), (31), and (32)

$$\frac{dl_2}{db}=\frac{dv_2}{db}+\frac{dl_1}{db}-\frac{dv_1}{db}=\frac{l_2}{b} \qquad (33)$$

which again is constant. From (3), (4), (18), (32), and (33) it follows by mathematical induction that

$$\left.\begin{aligned} dl_j/db &= l_j/b \\ dv_j/db &= v_j/b \end{aligned}\right. \qquad (34)$$

so long as there are no feeds between l_j or v_j and the hot end of the unit. Furthermore, these derivatives are constant.

Now the change (or correction) in v_j resulting from a change in b is given by

$$v_j-(v_j)_c=\frac{d(v_j)_c}{db}\Delta b+\frac{1}{2}\,\frac{d^2(v_j)_c}{db^2}(\Delta b)^2+\ldots$$

so that in view of (34)

$$v_j=(v_j)_c+(v_j/b)_c\,\Delta b \qquad (35)$$

or

$$\begin{aligned} v_j &= (v_j)_c+(v_j/b)_c\,(b-b_c) \\ &= (v_j)_c+(v_j/b)_c\,b-(v_j)_c \\ &= (v_j/b)_c\,b \end{aligned} \qquad (36)$$

Equation (36) is the result stated by Holland.

A similar analysis working from the cool end of the unit shows that

$$v_j=(v_j/v_J)_c\ v_J \qquad (37)$$

so long as there are no feed streams between v_j and v_J. The results given by (36) and (37) do not hold in regions between feed streams; consequently their use in these areas cannot be rigorously justified. Furthermore, if both b and v_J are changed, the change in v_j will be some combination of the changes indicated by (36) and (37). For v_j near the hot end of the unit the change given by (36) must predominate, while for v_j near the cool end of the unit that indicated by (37) must predominate. The corrections indicated by (36) and (37) become progressively less desirable toward the middle of the unit. This may account for the observed fact that numerical convergence is most rapid at the ends of the unit and slowest near the middle of the unit.

Table 2. Minimized Maximum Sum of Scaled Absolute Values of Scalar Elements in a Row of Matrix (43) for Example 1

	Holland iteration				Direct iteration			
Iteration No.	Row No.	Scale factor	Maximum sum scaled	Unscaled sum	Row No.	Scale factor	Maximum sum scaled	Unscaled sum
1	1	0.309576	1.027	2.980	1	0.584962	15.793	24.277
2	1	0.182680	1.358	6.509	1	0.583171	15.807	24.741
3	1	0.180606	1.370	6.582	1	0.155185	5.256	20.111
4	1	0.180171	1.374	6.599	1	0.067926	3.385	18.580
5	1	0.180286	1.379	6.610	1	0.083710	3.541	18.146
6	1	0.179015	1.372	6.616	1	0.095864	3.614	17.042
7	1	0.178733	1.373	6.622	1	0.095967	3.708	18.025
12	1	0.209925	1.573	6.626	1	0.096108	3.712	18.030

The fundamental theoretical shortcomings of the derivation just presented and consequently of the correction method given by Holland lie in the assumptions that the values of the A_{ij} remain constant while the b, l_j, and v_j undergo changes. These assumptions are not necessary; if they are not made, Equation (30) for instance becomes with constant e_L:

$$\frac{dv_1}{db} = \frac{\partial v_1}{\partial b} + \frac{\partial v_1}{\partial (A_o + e_L)^{-1}} \frac{d(A_o + e_L)^{-1}}{db}$$

$$= \frac{1 - e_L}{A_o + e_L} - \frac{(1 - e_L)b}{(A_o + e_L)^2} \frac{dA_o}{db} \tag{38}$$

Comparison of Equations (30) and (38) shows that taking cognizance of the changes in plate temperature and L_o/V_1 introduces the last term in Equation (38). The corresponding term for arbitrary j is difficult to evaluate. After considerable manipulation with heat effects still neglected, there results for each plate the following set of simultaneous equations linear in the unknown values of dv_{ij+1}/db_i:

$$\sum_i \left[A_{nj}\,\delta_{in} - \frac{l_{nj}}{V_{j+1}} \frac{db_i}{db_n} \right] \frac{dv_{ij+1}}{db_i}$$

$$= \sum_i \left[1 + \frac{dv_{ij}}{db_i} + \sum_{j_s \leqq j} \theta_s \left(\frac{w_{is}}{b_i} \right)_c \right] \left\{ \delta_{in} \right.$$

$$\left. + l_{nj} \left[\frac{\dfrac{dK_{nj}}{dT_j}(1 - K_{ij})}{K_{nj} \displaystyle\sum_i l_{ij} \frac{dK_{ij}}{dT_j}} - \frac{1}{L_j} \right] \frac{db_i}{db_n} \right\}$$

$$n = 1, 2, \ldots, I \tag{39}$$

The quantities db_i/db_n are evaluated as

$$\frac{db_i}{db_n} = \frac{\dfrac{db_i}{d\theta_o}}{\dfrac{db_n}{d\theta_o}} = \left[\frac{1 + \theta_o \left(\dfrac{d_n}{b_n} \right)_c + \displaystyle\sum_{s=1}^{S} \theta_s \left(\frac{w_{ns}}{b_n} \right)_c}{1 + \theta_o \left(\dfrac{d_i}{b_i} \right)_c + \displaystyle\sum_{s=1}^{S} \theta_s \left(\frac{w_{ns}}{b_i} \right)_c} \right]^2$$

$$\left[\frac{\left(\dfrac{d_i}{b_i} \right)_c + \displaystyle\sum_{s=1}^{S} \left(\frac{w_{is}}{b_i} \right)_c \frac{d\theta_s}{d\theta_o}}{\left(\dfrac{d_n}{b_n} \right)_c + \displaystyle\sum_{s=1}^{S} \left(\frac{w_{ns}}{b_n} \right)_c \frac{d\theta_s}{d\theta_o}} \right] \frac{F_i{}^o}{F_n{}^o} \tag{40}$$

The quantities $d\theta_s/d\theta_o$ are the components of a vector in the space spanned by $\theta_o, \theta_1, \theta_2, \ldots, \theta_S$. The direction of this vector has so far not been fixed and may, for instance, be taken as parallel to the θ_o axis so that $d\theta_s/d\theta_o = 0$ $s = 1, 2, \ldots, S$ and

$$\frac{db_i}{db_n} = \left(\frac{b_i}{F_i{}^o} \right)^2 \left(\frac{F_n{}^o}{b_n} \right)^2 \left(\frac{d_i}{b_i} \right)_c \left(\frac{b_n}{d_n} \right)_c . \tag{41}$$

Equations (39) and (41) provide a basis on which to assess the corrections given by Equation (36). The use of (39) and (41) in normal computation is not suggested for two reasons. First, the additional computation required to solve the set of simultaneous Equations (39) at each plate would be likely to require more time than might be saved by having to perform fewer iterations. Second, each set of Equations (39) requires the solutions of Equations (39) for the previous plate. In principle there is no objection to this; however, it is a particularly objectionable feature for the actual numerical solution of distillation problems. It is to be noted that Equation (36) does not suffer from this drawback.

CONVERGENCE

Friday and Smith (3) have treated the asymptotic convergence of iterative methods presently in general use for the solution of multicomponent distillation problems. By asymptotic convergence is meant the convergence of the method at the actual solution. Certainly if an iterative procedure is divergent at the solution to the problem, it cannot in general yield that solution; however, a study of the asymptotic convergence does not show whether or not a method convergent at the solution can ever yield that solution if the initial estimate of the solution is not extremely good.

Consider the multicomponent distillation problem as an iteration of the form

$$\begin{bmatrix} \overline{V} \\ \\ \overline{T} \end{bmatrix}_{n+1} = \begin{bmatrix} \overline{\Lambda}(\overline{V}_n, \overline{T}_n) \\ \\ \overline{\Phi}(\overline{V}_n, \overline{T}_n) \end{bmatrix} \tag{42}$$

where $\overline{V} = (B, V_1, \ldots, V_j, \ldots, V_{J-1}, V_J)^T$ and $\overline{T} = (T_B, T_1, \ldots, T_j, \ldots, T_{J-1}, T_J)^T$. The superscript T denotes the transpose. $\overline{\Lambda}$ and $\overline{\Phi}$ are the vector valued functions or sequences of computations by which the next approximations to the true values of $\overline{V}$ and $\overline{T}$, respec-

Table 1. Feed Used in Example 1

Component	Moles/hr.	
Myristic acid	0.744	Bubble point 332.1°F.
Stearic acid	3.120	Dew point
Abietic acid	5.166	440.3°F.
Methyl ester	1.140	Feed temperature
Total	10.17	325.0°F.

Table 3. Feed Used in Example 2

Component	Moles/hr.	
Methane	4.00	Bubble point 41.7°F.
Ethane	14.22	Dew point
n-Pentane	6.80	459.9°F.
Octane	15.83	Feed temperature
Total	40.85	41.7°F.

tively, are determined from the last previous estimates of these quantities. It is well known that the system (42) will converge if the sum of the magnitudes of the scalar elements of each row of the following matrix is less than 1:

$$\begin{bmatrix} \dfrac{\partial\bar{\Lambda}}{\partial\bar{V}} & \dfrac{\partial\bar{\Lambda}}{\partial\bar{T}} \\[2ex] \dfrac{\partial\bar{\Phi}}{\partial\bar{V}} & \dfrac{\partial\bar{\Phi}}{\partial\bar{T}} \end{bmatrix} \tag{43}$$

The k^{th} elements in the j^{th} rows of the matrix elements of (43) are, respectively, $\partial(V_j)_{n+1}/\partial(V_k)_n$, $\partial(V_j)_{n+1}/\partial(T_k)_n$, $\partial(T_j)_{n+1}/\partial(V_k)_n$, and $\partial(T_j)_{n+1}/\partial(T_k)_n$, where n is the iteration number. It should be noted that a linear change of scale for temperature or flow rates will not affect the elements of $\partial\bar{\Lambda}/\partial\bar{V}$ or $\partial\bar{\Phi}/\partial\bar{T}$ and will multiply the elements of $\partial\bar{\Lambda}/\partial\bar{T}$ and divide those of $\partial\bar{\Phi}/\partial\bar{V}$ by the same factor. Thus when the sum of the magnitudes of the elements in one or more rows of (43) exceeds 1, it is instructive to see if there exists a linear change of scale which will decrease the largest of these sums. Convergence may always be achieved provided only that such a linear change of scale exists for which in the scaled units the sum of the magnitudes of the elements in each row of (43) is less than 1. This situation will be termed *condition A*. Condition A is a sufficient but not a necessary condition for convergence.

Two numerical examples will next be discussed. The method of Holland (*4*), including temperature averaging and a limit on the permissible change in total flow rates, was applied to each of these examples. At each iteration the matrix elements of (43) were computed numerically both for an iteration in accordance with Holland and a direct iteration as the term is employed in reference *4*. Direct iteration essentially implies the absence of equations similar to (26), (29), or (35) and use of the specified values of B and W_s wherever these items appear. Owing to the rather frightening amount of computer time required to work examples in this fashion (example 1 required almost ½ hr. on an IBM-7094), this type of numerical experience is decidedly limited. The elements of the matrices (43) were computed by successively perturbing the elements of $\bar{V}$and $\bar{T}$ by unity as indicated in reference 3. The first example converged; the second did not. Enthalpy data for the first example were taken from references *2* and *6*, while equilibrium data were obtained from reference *8*. All data for the second example were determined from reference *4* by generating curves from coefficients given therein and subsequently least squares curve fitting the curves so obtained with the polynomials used in this paper. In each example the forms used to express the liquid enthalpy h, the vapor enthalpy H, and the equilibrium constant K are

$$\sqrt{h} = \alpha_0 + \alpha_1 T + \alpha_2 T^2$$
$$\sqrt{H} = \beta_0 + \beta_1 T + \beta_2 T^2$$
$$\sqrt[4]{K} = \gamma_0 + \gamma_1 T + \gamma_2 T^2 + \gamma_3 T^3 + \gamma_4 T^4$$

The temperature range of the curve fits is 140° to 430°F. in example 1 and 40° to 500°F. in example 2. Example 1 is at 0.35 mm. Hg abs., and example 2 is at 1 atm.

Some explanation of Tables 2 and 4 is required. The matrix (43) was examined for each iteration of each problem to determine if condition A existed, or, if not, how closely it was approached. In each case the scale factor s was computed which minimized the maximum sum of absolute values of scalar elements in a row of the matrix (43). In applying the scale factor it was immaterial whether the temperatures were divided by s or the internal flow rates multiplied by s. Since any such scaling decreased the sum of the magnitudes of the scalar elements of any row in the top half of (43) and increased this sum for each row in the bottom half of (43), a quadratic equation in s is obtained by equating any scaled row in the top half of (43) to any scaled row in the bottom half of (43). The basis for choosing among the values thus calculated has already been stated.

In no case did condition A actually exist, but startling differences in the approach to condition A were manifested.

The first example, for which a solution was obtained after twelve iterations, used seven theoretical stages in a partially insulated unit having heat supplied to the lower four stages. The feed, which is described in Table 1, entered on the fourth stage.

It was specified that 7.5 moles/hr. of liquid should be withdrawn at the hot end of the unit and that the remainder of the feed would leave the cool end of the unit as vapor. In view of the small members of moles involved, better estimates of the partial derivatives would probably have been obtained had the elements of $\bar{V}$ been perturbed by 0.1 rather than 1.0 in this example. The fractions of surface insulated and uninsulated as well as relevent heat transfer coefficients were specified. The ambient temperature was taken to be 100°F. and the pressure within the unit low enough for the vapor to be considered a perfect gas. Radiation from the uninsulated part of the unit was found to account for about one-third to one-half of the heat leaving the unit other than by way of the product streams. Before we proceed further, it should be empha-

TABLE 4. MINIMIZED MAXIMUM SUM OF SCALED ABSOLUTE VALUES OF SCALAR ELEMENTS IN A ROW OF MATRIX (43) FOR EXAMPLE 2

	Holland iteration				Direct iteration			
Iteration No.	Row No.	Scale factor	Maximum sum scaled	Unscaled sum	Row No.	Scale factor	Maximum sum scaled	Unscaled sum
1	1	0.519399	2.083	2.835	1	0.982155	428.410	434.811
2	1	0.228417	1.016	4.448	4	0.964118	28.625	29.669
3	4	0.035016	10.195	197.786	4	0.681420	337.231	479.376
4	4	0.019079	19.010	382.937	7	0.828634	424.201	505.847
5	2	0.065920	4.078	21.260	1	0.866041	149.184	169.696
6	4	0.036782	5.775	113.370	7	0.920866	212.582	229.650
7	4	0.013594	30.657	602.639	4	0.311408	234.263	668.777
8	1	0.294202	1.184	3.783	6	0.996771	169.970	170.473
9	4	0.104539	4.427	36.718	1	0.971962	303.730	311.716
10	4	0.028169	8.277	166.979	7	0.888361	364.495	407.545
11	5	0.047359	11.673	167.310	5	0.693226	223.930	314.656
12	4	0.027769	1.311	43.710	7	0.961963	200.137	207.580
13	5	0.008126	52.983	53.348	4	0.522955	348.073	629.842

sized that this problem was chosen because data were available from other work and not to indicate that conventional equipment would be effective.

The first item to notice from Table 2 is that although the starting point for each direct iteration was the result of previous Holland iterations only, the maximum sum of absolute values of elements on a row of (43) was always about three times as large for the direct iteration as for the Holland iteration. This will be observed both for the scaled and unscaled sums. The second point to notice is that in each iteration, Holland or direct, it was the first row of (43) which produced the largest scaled sum of magnitudes of scalar elements on a row. It would be desirable to know if this happens often when convergence occurs.

In comparing Tables 2 and 4 it will be noted that only in the case of Holland iteration for the first sample problem were the scaled sums of absolute values consistently close to 1. This was the only case where convergence was obtained, and, as mentioned previously, the choice of the magnitude of the perturbation used to calculate (43) was probably not good. It seems reasonable that a better choice might have altered the scaled sums by ± 30%.

The second example, for which a solution was not obtained within forty iterations, used the same hypothetical unit that was employed in example 1. The feed for example 2 is described in Table 3. It was specified that 24 moles/hr. of liquid should be withdrawn at the hot end of the unit and that the remainder of the feed would leave the cool end of the unit as vapor. The ambient temperature was taken to be 60°F. and the pressure within the unit 1 atm.

More extreme forcing procedures would perhaps have brought about convergence; the object of this example was to indicate the character of the matrices $\partial\overline{\Lambda}/\partial\overline{V}$, $\partial\overline{\Lambda}/\partial\overline{T}$, $\partial\overline{\Phi}/\partial\overline{V}$, and $\partial\overline{\Phi}/\partial\overline{T}$ when convergence was not obtained. It will be noted that, even for Holland iterations, in this second problem the sums of scaled absolute values are usually larger than those for even direct iterations in the first sample problem. The sums of scaled absolute values for the direct iterations on the second sample problem are seen to be roughly an order of magnitude larger than in other cases. Furthermore, in this case the scale factors are often close to 1, indicating that the sums of unscaled absolute values give a rather good idea of how bad things really are.

The writer will here exercise considerable self-control and forgo discussing several interesting ideas connected with Tables 2 and 4. Such a discussion would require the display of all elements in the matrices (43) and a repetition of that display for a number of successive iterations.

CONCLUSIONS

Equations representing the flow of individual components within a distillation unit have been given for the situation where equilibrium is not attained by all the fluid. These relations have the same matrix form as that given by Ball (*1*) for the case where complete equilibrium is achieved. It is not within the scope of this paper to propose methods for computing the extent to which equilibrium is attained.

An improvement in one of the existence proofs in (*4*) has been made.

Equation (36) states the method assumed by Holland (*4*) for modifying internal flow rates of individual components as a result of each new estimate of the composition of the liquid leaving the hot end of the unit. A derivation has been given for this equation and the assumptions delineated. A corresponding result is then presented wherein the most objectionable of these assumptions have been omitted.

In addition, a well-known criterion for the convergence of an iterative process has been applied to the multicomponent distillation problem. This criterion involves certain matrices which have been computed for two examples. The character of these matrices has been illustrated by Tables 2 and 4.

NOTATION

A_j, A_{ij} = absorption factor, $L_j/(K_{ij}V_{j+1})$ or $(L_j - e_L L_{j+1})/[K_{ij}(V_{j+1} - e_V V_j)]$
b_i, b = rate of flow of the i^{th} component in the liquid stream leaving the hot end of the unit
B = total liquid rate of flow leaving the hot end of the unit, $B = \Sigma b$
d, d_i = rate of flow of the i^{th} component in the stream leaving the cool end of the unit
e_{Lj} = fraction of liquid on plate j which does not contact vapor at plate j
e_{Vj} = fraction of vapor at plate j which does not contact liquid on plate j
f_i, f_p = rate of flow of the i^{th} component in the p^{th} feed
F_p, F = total feed rate for the p^{th} feed
F_i^o, F^o = total rate of feed of the i^{th} component in all feeds
G_o, G_s = functions defined by Equation (29)
h_i, h_{ij} = enthalpy of one mole of component i in the liquid at the temperature of plate j
H_i, H_{ij} = enthalpy of one mole of component i in the vapor at the temperature of plate j
K, K_j, K_i, K_{ij} = equilibrium constant for the i^{th} component on plate j
l_i, l, l_j = rate of flow of the i^{th} component in the liquid stream on plate j
L_j = total rate of liquid flow on plate j; $L_j = \Sigma\, l_{ij}$
T_j, T = temperature of liquid being distilled on plate j
v_i, v_{ij}, v, v_j = rate of vapor flow of the i^{th} component to plate j
V_j = total rate of vapor flow to plate j; $V_j = \Sigma v_i$
w_s, w_{is} = rate of flow of the i^{th} component in the s^{th} side draw
W_s = total rate of flow constituting the s^{th} side draw, $W_s = \Sigma w_{is}$

Greek Letters

α_{ki} = k^{th} constant in the power series for $\sqrt{h_i}$, $\sqrt{h_i} = \alpha_{oi} + \alpha_{1i}\,T + \alpha_{2i}\,T^2$
β_{ki} = k^{th} constant in the power series for $\sqrt{H_i}$, $\sqrt{H_i} = \beta_{oi} + \beta_{1i}\,T + \beta_{2i}\,T^2$
γ_{ki} = k^{th} constant in the power series of $\sqrt[4]{K_i}$, $\sqrt[4]{K_i} = \gamma_{oi} + \gamma_{1i}T + \gamma_{2i}T^2 + \gamma_{3i}T^3 + \gamma_{4i}T^4$
δ_{in} = Kronecker delta; = 1 if $i = n$, = 0 otherwise
θ_o, θ_s = correction factors defined by Equation (26)

Superscripts

$+$ = quantity measured at a point slightly nearer the cool end of the unit than the entry or exit point of an adjacent feed or side-draw stream, respectively
$-$ = quantity measured at a point slightly nearer the hot end of the unit than the entry or exit point of an adjacent feed or side-draw stream, respectively

Subscripts

The absence of a subscript for a quantity measured along the unit indicates that quantity is to be evaluated at whatever plate is in question.

c = last previously calculated value
i = component number
I = total number of components

j = plate number; $j = 0$ denotes the hot end of the unit
J = number of the plate at the cool end of the unit
p = feed stream number; $p = 1$ denotes the feed nearest the hot end of the unit
P = number of the feed nearest the cool end of the unit; this is the total number of feeds to the unit
s = side-draw number; $s = 1$ denotes the side draw nearest the hot end of the unit
S = number of the side draw nearest the cool end of the unit; this is the total number of side draws

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APPENDIX

1. Double subscripts or subscripted subscripts are written as compound subscripts. Thus, $\nu_{w,j+1}$ becomes ν_{wj+1} and l_{j_s-1} becomes l_{js-1}. $l_{j_{s-1}}$ does not occur

2. Σ without indices denotes a sum over all components at plate j

3. $\mathrlap{-}\Sigma$ without indices denotes a sum over one component or quantity entering or leaving the unit from the hot end to and including plate j

4. $\overset{\Delta}{=}$ denotes that the quantity on one side is defined as equal to the quantity on the other

Manuscript received September 30, 1965; revision received March 31, 1966; paper accepted April 15, 1966.

Reverse Osmosis in Annuli

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The nonlinear problem of reverse osmosis in annular conduits is solved by a series expansion method which is very accurate in the diffusion entrance region near the inlet of the membrane section. It is found that polarization at the outer membrane surface is significantly greater than at the inner wall.

In the diffusion entrance region, for the problem considered, the degree of polarization depends on the three parameters σ, η_k, and B_2, which are known once the operating conditions and the physical properties of the system are specified. The quantities $\theta_i(0)$ are tabulated for a wide range of η_k and B_2. With these quantities known one can apply Equation (17) at $\beta = 0$ to calculate the wall concentration distribution and, with Equation (4), the flux distribution along the system. Then, by using Equation (26), the water produced by the system can be determined explicitly in terms of prescribed operating conditions.

Reverse osmosis is currently being studied from various points of view because of its potential as a process for sea and brackish water desalination. Interest in reverse osmosis was sparked by the report of Bretton and Reid (*1*) in 1957 that cellulose acetate films yielded salt rejection of 97 to 98% at an operating pressure of 850 lb./sq.in. with a throughput of some 0.15 gal./(sq.ft.)(day). This membrane was improved very substantially by Loeb (5) to the point where water fluxes up to 20 gal./(sq.ft.)(day) are currently feasible.

Basic research in reverse osmosis is directed along at least two lines. For obvious reasons, there is considerable interest in developing a better understanding of the fundamental transport processes which occur within the membrane structure. Another area of interest relates to the nonlinear diffusional effects on the brine side of the system. A good discussion of the kinetics of water and salt transport in cellulose acetate membranes was given very recently by Michaels, Bixler, and Hodges (*7*). Several discussions of brine side diffusional effects, concentration polarization in particular, are available (*2* to *4*, *6*, *8*, *9*). Sherwood, Brian, Fisher, and Dresner (*8*) studied the linear problem of constant water flux along the membrane in fully developed flow between parallel plates. Gill, Tien, and Zeh (*2*) considered the nonlinear problem wherein the salt concentration at the membrane surface increases along the direction of flow, and therefore the water flux through the membrane decreases with axial distance. Since the Schmidt number for salt water is about 560, the diffusion boundary layer is much thinner than the momentum boundary layer, and, therefore, the velocity components can be represented by expressions which are accurate only in the region near the wall. The method of analysis which will be employed here does not require