Equilibrium Stage Calculations

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Iterative methods for the determination of stage temperatures and interstage flow rates in the equilibrium stage problem are discussed, and the use of the Newton-Raphson method for solution of the systems of simultaneous equations is proposed. It is shown that the complete correction process can be divided into four independent parts, two of which are treated in the paper. The first is equivalent to the constant molal overflow problem in distillation and the second to the constant temperature extraction problem. For each of these cases the necessary partial derivatives describing the effects of temperature and flow rate changes on all material balance equations are developed. Sample problems are briefly discussed to demonstrate the feasibility of the calculations and the fact that quadratic convergence is obtained. Equation derivation is simplified by using matrix notation, which also has the advantage that any interstage flow pattern is allowed.

The equilibrium stage problem can be considered as the determination of a set of stage temperatures, interstage flow rates, and phase compositions which will satisfy all material balances, equilibrium relations, and energy balances. For this paper it will be assumed that the statement of the problem fixes the following:

1. Number of stages
2. Amount, composition, and enthalpy of each feed and the stage into which it enters.
3. Amount of each product stream and the stage from which it is withdrawn.
4. The flow pattern or interstage flow map.

It will also be assumed that the equilibrium ratios and enthalpies are known functions of temperature and composition, that the system is at steady state, and that a two-phase multicomponent system is being used. For convenience the two phases will be called liquid and vapor, although results obviously apply to any two phases. There are n stages and m components.

The above form of the equilibrium stage problem is most convenient for digital calculation. Friday and Smith (*1*) have discussed the general formulation of the problem and list six steps or decisions necessary for solution. They point out (first and second decisions) that all modern computing methods group the equations by components rather than by stages and then use the following sequence: (1) assume a set of flow rates and temperatures; (2) calculate phase compositions; (3) correct flow rates and temperatures; and (4) return to step 2. It is with step 3 that this paper is concerned—the correction of the flow rates and temperatures.

AN ITERATIVE CORRECTION PROCESS

If there are n equilibrium stages, then the correction procedure can be considered as the correction of n stage temperatures and n flow rates with the use of n measures of error in material balances and n measures of error in the energy balances. This is basically the solution of $2n$ nonlinear equations in $2n$ unknowns. An iterative solution can be outlined as follows: Let the n measures of material balance error be λ_1 to λ_n and the n measures of energy balance error be λ_{n+1} to λ_{2n}. At the solution all λ will be zero. A set of temperature corrections (δ_1 to δ_n) and flow rate corrections (δ_{n+1} to δ_{2n}) can then be calculated by

$$\Phi\Delta = -\Lambda \tag{1}$$

where

$$\Delta = (\delta_i)$$

$$\Lambda = (\lambda_i)$$

$$\Phi = (\phi_{ij})$$

Φ is a $2n$ by $2n$ matrix, which will be called the correction matrix. For a given set of errors Equation (1) is used to calculate corrections in temperatures and flow rates. A new set of errors is determined, and if necessary the process is repeated. Whether this sequence will converge and the speed of convergence depend on such factors as the size of the errors in the assumed original temperatures and flows, the properties of Φ, and the kind of problem being solved. Any process in which the corrections are linear in the errors can be put in the form of Equation (1). Each method will be characterized by its own Φ and will have its own convergence properties. It is shown in standard texts (*2*) that when Φ is the Jacobian matrix of the error measures, called here Ψ and defined by

$$\Psi = (\psi_{ij}) \qquad \psi_{ij} = \frac{\partial\lambda_i}{\partial\delta_j} \tag{2}$$

quadratic convergence is obtained in the region of the solution. For another Φ less than quadratic convergence will usually be obtained, although the region of convergence may be larger. With Φ defined as the Jacobian matrix Ψ, the correction procedure is the multivariable form of the Newton-Raphson method. In the later sections of this paper methods for calculation of some of the elements of Ψ will be discussed, but it is useful first of all to consider in more detail the implications of the iterative process described above.

Let Φ, Δ, and Λ be partitioned as follows:

$$\begin{bmatrix} \mathbf{E}_t & \mathbf{E}_v \\ \mathbf{J}_t & \mathbf{J}_v \end{bmatrix} \begin{bmatrix} C_t \\ C_v \end{bmatrix} = -\begin{bmatrix} D_m \\ D_e \end{bmatrix} \tag{3}$$

which can be written as two equations

$$\mathbf{E}_t\, C_t + \mathbf{E}_v\, C_v = -D_m \tag{4}$$

$$\mathbf{J}_t\, C_t + \mathbf{J}_v\, C_v = -D_e \tag{5}$$

Equation (4) is based on errors in the material balances about each stage and Equation (5) on errors in the energy balances about each stage. These equations can be simplified by assuming that one or more of the submatrices of Φ are zero. This permits the determination of the corrections by two sets of n simultaneous equations rather than one set of $2n$ equations. All commonly used correction methods are of this type. For example the temperature correction can be found from Equation (4) if $\mathbf{E}_v = 0$ or from Equation (5) if $\mathbf{J}_v = 0$. The former has been called the *bubble point method* and the latter the *sum rate method* (*1*). The main differences in the various correction methods in use today are in the definitions of the error measure and of the correction matrices Φ. As indicated previously, the most rapid convergence should be obtained when $\Phi = \Psi$, and this is the problem treated in this paper: the determination of suitable expressions for $\mathbf{E}_t$ and $\mathbf{E}_v$ which will provide quadratic convergence. Friday and Smith (*1*) proposed equations identical to Equations (4) and (5) in which the Jacobian matrix would be used. They suggested that the various partial derivatives can be evaluated by finite-difference approximations but they did not develop the method further. In this work a different approach will be used. Error criteria will be defined and then the necessary derivatives obtained by analytic differentiation of the errors. Because of the large number of equations involved, the expressions can become very complicated, and a matrix notation has been developed to simplify the equations. This will be seen to have the added advantage that any interstage flow arrangement is permitted. The main contributions of this paper may be summarized as:

1. The development of a temperature correction procedure in which the effect of a change in temperature in any stage on the compositions in all stages (at constant flow rate) is taken into account, $\mathbf{E}_t$.
2. The development of a flow rate correction procedure in which the effect of a change in any flow rate on the compositions in all stages (at constant temperature) is taken into account, $\mathbf{E}_v$.
3. The development of a matrix notation for the material balance equations which permits the use of any interstage flow connection arrangement.

In the remainder of this work it will be assumed that $\mathbf{E}_t$ and $\mathbf{E}_v$ are the Jacobian forms, but it should be emphasized that convergence of Equation (1) does not depend on this, and it is certainly not the intent here to infer that simpler forms may not be preferable for many problems. In fact, in some problems it might be adequate to use the same Φ matrix for several iterations. However, the fact that the Jacobian form can be calculated puts at the disposal of the system designer a powerful tool not only for use in solving problems, but also for studying the structure of the equilibrium stage problem.

Finally it should be noted that the present work does not treat the formation of $\mathbf{J}_t$ and $\mathbf{J}_v$ and hence the complete correction process indicated by Equation (1) cannot be tested at this time. However, $\mathbf{E}_t$ and $\mathbf{E}_v$ are useful in themselves. The former is the only correction needed in a constant flow process where energy balancing is not required; the well-known constant molal overflow problem is a good example of this. $\mathbf{E}_v$ is the only correction needed in a constant temperature process where energy balancing is not required; here, the extraction problem is a good example. This will be discussed at greater length later.

DEFINITIONS

Preliminary to writing the equations that describe the material balances for the equilibrium stage system, it is necessary to define certain matrices. These are considered in four groups below.

1. Flow connection matrices. In the two-phase system, there are two flow connection matrices called the *liquid flow connection matrix* and the *vapor flow connection matrix*. Each is of size $n \times n$. On the main diagonal of each are negative numbers representing the total flow of liquid or vapor phase leaving each stage, while the off-diagonal elements are positive numbers, the v_{ij} or l_{ij} element representing the flow of vapor or liquid from stage j to stage i.

2. Composition matrices. For each phase there is a phase composition matrix, $\mathbf{X}$ for the liquid phase and $\mathbf{Y}$ for the vapor phase, with the ij element representing the composition of component j in stage i.

The composition matrices are of size $n \times m$, and it is convenient to partition them into m column vectors as follows:

$$\mathbf{X} = (X^{(1)}, X^{(2)}, \ldots X^{(m)})$$

$$\mathbf{Y} = (Y^{(1)}, Y^{(2)}, \ldots Y^{(m)})$$

Each column represents the composition of one component.

3. Feed matrix. $\mathbf{F}$ is an $n \times m$ matrix and is used to represent the feeds or flows entering the system from sources outside the system.

$$\mathbf{F} = (f_{ij}) = (F^{(1)}, F^{(2)}, \ldots F^{(m)})$$

where f_{ij} = the *total* flow of component j to stage i from sources outside the system of equilibrium stages. As with $\mathbf{X}$ and $\mathbf{Y}$, $\mathbf{F}$ is partitioned into m column vectors, each representing a component feed rate.

4. Equilibrium ratio matrices. The equilibrium conditions are given in the form of equilibrium ratios. A diagonal matrix, of size $n \times n$, is defined for each component with the i^{th} diagonal element representing the equilibrium ratio of the component in the i^{th} stage.

BASIC MATERIAL BALANCE EQUATIONS

A matrix formulation of the equilibrium stage problem was first proposed by Amundson (*3, 4*). He demonstrated that by grouping the material balance and equilibrium relations for one component only, it is possible to write

$$\mathbf{Z}^j X^{(j)} = -F^{(j)} \tag{6}$$

where $X^{(j)}$ and $F^{(j)}$ are defined as in the previous section. He presented equations for calculation of the elements of $\mathbf{Z}^j$ for a system with multiple feeds and multiple product streams. His equations were specifically derived for the case of countercurrent flow but could be modified for other flows. This is inconvenient, however, and it will be seen below that $\mathbf{Z}^j$ can be expressed in terms of the matrices defined in the previous section, thus permitting any interstage flow arrangement. More important, it will be seen that by using these definitions, it is possible to separate the equilibrium ratios from the flow rates. This greatly facilitates later developments.

Using the definitions from the previous section, we can write the material balance for component j as

$$\mathbf{L}\, X^{(j)} + \mathbf{V}\, Y^{(j)} = -F^{(j)} \tag{7}$$

and the equilibrium relations for component j are

$$Y^{(j)} = \mathbf{K}^{(j)}\, X^{(j)} \tag{8}$$

Combination of these two equations gives

$$\mathbf{L}\, X^{(j)} + \mathbf{V}\, \mathbf{K}^j\, X^{(j)} = -F^{(j)} \tag{9}$$

and comparison with Equation (6)

$$\mathbf{Z}^j = \mathbf{L} + \mathbf{V}\, \mathbf{K}^j \tag{10}$$

Equations (6) through (10) are fundamental for all that follows. They are presented without proof but can be verified by performing the indicated multiplications. Examination of the resulting set of simultaneous equations will demonstrate that each equation represents a material balance for component j for one stage.

Once a set of flow rates and temperatures has been assumed, the only unknown in Equation (6) is $X^{(j)}$, which is given by

$$X^{(j)} = -(\mathbf{Z}^j)^{-1} F^{(j)} \tag{11}$$

The set of m equations, one for each component, of this form is sufficient to determine all the liquid compositions. Use of Equation (8) will then give the vapor compositions.

THE CONSTANT MOLAL OVERFLOW PROBLEM

If changes in the stage temperatures and the phase compositions have no effect on the energy balance equations, then a unique set of flow rates can be determined which satisfies the energy balances and which is not dependent on stage temperatures or compositions. The problem solution has been greatly simplified since only the stage temperatures must be corrected. Equations (4) and (5) then simplify to

$$\mathbf{E}_t \; C_t = -D_m \tag{12}$$

where

$$\mathbf{E}_t = (e_{t,ik})$$

$$e_{t,ik} = \frac{\partial d_i}{\partial c_{t,k}} = \frac{\partial d_i}{\partial t_k}$$

This last equation follows because c_t and t are linearly related. It is now necessary to determine how a change in temperature at constant flow rate affects the error. The error criterion to be used is that the sum of the mole fractions in each phase must be one. This will be discussed in more detail later. First, an expression will be developed for the effect of a change in any temperature on the composition of any component in any stage.

Differentiating Equation (9) with respect to the temperature in stage k, holding the flow rates constant, we get

$$\mathbf{Z}^j \frac{\partial X^{(j)}}{\partial t_k} + \mathbf{V} \frac{\partial \mathbf{K}^j}{\partial t_k} X^{(j)} = 0 \tag{13}$$

and solving for the desired rate of change of composition, we obtain

$$\frac{\partial X^{(j)}}{\partial t_k} = -(\mathbf{Z}^j)^{-1} \mathbf{V} \frac{\partial \mathbf{K}^j}{\partial t_k} X^{(j)} \tag{14}$$

Equation (14) defines a vector which gives the rate of change of composition of component j on each stage with respect to a change in t_k. If this process is repeated for each value of k from 1 to n, a series of vectors will be formed which when assembled into a matrix will be called $\mathbf{X}_t^{(j)}$, the subscript implying that the elements are derivatives with respect to temperature.

The matrix $\mathbf{X}_t^{(j)}$ can be equated to another matrix whose columns are obtained by varying k from 1 to n in the right-hand side of Equation (14). Obviously $\mathbf{Z}^j$ and $\mathbf{V}$ do not involve the parameter k and can be factored out. Equation (14) can now be written as

$$\mathbf{X}_t^{(j)} = -(\mathbf{Z}^j)^{-1} \mathbf{V} \; \mathbf{M}^j \tag{15}$$

where $\mathbf{M}^j$ is defined as the matrix whose k^{th} column is given by

$$\frac{\partial \mathbf{K}^j}{\partial t_k} X^{(j)}$$

But $(\partial \mathbf{K}^j / \partial t_k)$ has only one nonzero element—at the k^{th} row on the main diagonal—because only the equilibrium ratio on the k^{th} stage will be affected by changing t_k. Therefore, each column of $\mathbf{M}^j$ has only one nonzero element at the k^{th} row, and $\mathbf{M}^j$ must be diagonal.

$$\mathbf{M}^j = \text{diag}\,(m_1^j, \; m_2^j, \; . \; . \; . \; m_n^j) \tag{16}$$

$$m_i^j = \left(\frac{\partial k_i^j}{\partial t_k}\right) \; (x_{ij})$$

The variation of $Y^{(j)}$ with temperature is obtained by differentiating Equation (8):

$$\frac{\partial Y^{(j)}}{\partial t_k} = \left(\frac{\partial \mathbf{K}^j}{\partial t_k}\right) X^{(j)} + \mathbf{K}^j \left(\frac{\partial X^{(j)}}{\partial t_k}\right) \tag{17}$$

and it follows by using the same arguments as above that

$$\mathbf{Y}_t^{(j)} = \mathbf{M}^j + \mathbf{K}^j \, \mathbf{X}_t^{(j)} \tag{18}$$

It is now necessary to define the error function to be used. It is known that at the solution the sums of the mole fractions in each phase must be one. If the compositions are given in mole fraction units, then at the solution

$$\mathbf{X} \; U - U = 0 \tag{19}$$

$$\mathbf{Y} \; U - U = 0 \tag{20}$$

where U is a vector, each element of which is equal to unity. The derivative of Equation (19) with respect to temperature is nothing more than the derivative of the sum of mole fractions in the liquid with respect to temperature and can be obtained by summing Equation (15) over all components. This latter would be the desired Jacobian matrix for the error measure defined by Equation (19), and Equation (12) could be written as

$$\{\sum_j (\mathbf{X}_t^{(j)})\} \, C_t = -(\mathbf{X} \; U - U) \tag{21}$$

Similarly, if Equation (20) were used to define the error vector, then

$$\{\sum_j (\mathbf{Y}_t^{(j)})\} \, C_t = -(\mathbf{Y} \; U - U) \tag{22}$$

Either Equation (21) or (22) could be used by itself. Previous experience with the bubble point correction method (3) has indicated that it is preferable to use the difference in the sums of the mole fractions in the liquid and vapor phases rather than the error in either. This can be done by subtracting Equation (22) from (21):

$$\sum_j \{(\mathbf{X}_t^{(j)} - \mathbf{Y}_t^{(j)})\} \, C_t = -(\mathbf{X} - \mathbf{Y}) U \tag{23}$$

and then

$$D_m = (\mathbf{X} - \mathbf{Y}) \; U \tag{24}$$

$$\mathbf{E}_t = \sum_j (\mathbf{X}_t^{(j)} - \mathbf{Y}_t^{(j)}) \tag{25}$$

By using Equations (15) and (18), we obtain

$$\mathbf{E}_t = \sum_j \{[(\mathbf{K}^j - \mathbf{I}) \; (\mathbf{Z}^j)^{-1} \mathbf{V} - \mathbf{I}] \, \mathbf{M}^j\} \tag{26}$$

Equation (26) is the desired expression for $\mathbf{E}_t$ based on the error measure defined by Equation (24). In spite of its apparent complexity $\mathbf{E}_t$ is calculated without great difficulty. All the terms except $\mathbf{M}^j$ are already available from the determination of $X^{(j)}$, and it is merely necessary to combine them in the proper order and then multiply by the diagonal matrix $\mathbf{M}^j$, which must be calculated. $\mathbf{E}_t$ can then be determined and Equation (23) solved for C_t.

One further modification of Equation (26) is useful. It will be noted that $\mathbf{M}^j$ requires a knowledge of the solution vector $X^{(j)}$, and only an estimate of $X^{(j)}$ is available. It is known that the sum of the compositions in any phase will not be one, and to avoid bias in the calculation of $\mathbf{M}^j$ the compositions can be normalized by forming the product $\mathbf{M}^j \, \mathbf{N}$, where $\mathbf{N}$ is a diagonal normalizing matrix containing as elements

$$N = \text{diag}\ (n_1,\ n_2,\ .\ .\ .\ n_n)$$

where

$$n_i = \{1/\sum_j (x_{ij})\}$$

Since N is the same for each component, it can be factored out of the summation in $\mathbf{E}_t$ to give

$$\mathbf{E}_t = \sum_j \{[(\mathbf{K}^j - \mathbf{I})\ (\mathbf{Z}^j)^{-1}\ \mathbf{V}]\ \mathbf{M}^j\}\ \mathbf{N} \qquad (27)$$

Since N is diagonal, $\mathbf{N}^{-1}$ is also diagonal, and the elements of $\mathbf{N}^{-1}$ are identical with the elements of the vector *XU*.

Application of $\mathbf{E}_t$

Many constant molal overflow problems have been solved with $\mathbf{E}_t$ used. Convergence in general has been rapid. Some typical results are summarized in Table 1 where a comparison is made between the use of $\mathbf{E}_t$ and a bubble point method for a small sample problem with eight stages and three components. For each iteration the quantity listed is the maximum error in either the sum of the liquid mole fractions or the sum of the vapor mole fractions. In comparing the first and second row, not much difference is observed for the first few iterations. However, when close to the solution, the method based on $\mathbf{E}_t$ converges much more rapidly than the bubble point method and shows typical quadratic convergence, the error roughly squaring for each iteration. This same trend is shown even more clearly in rows 3 and 4 where results are presented for the same problem, except that the equilibrium ratios have been made linear functions of the temperature. The method based on $\mathbf{E}_t$ converges very rapidly in this latter case because the derivative of $\mathbf{K}^j$ with respect to temperature is constant. The bubble point method converges at about the same rate as for the nonlinear case. These results indicate that, in the region close to the solution where the equilibrium ratios are almost linear, the use of $\mathbf{E}_t$ provides a much better temperature correction. When not near the solution, there is not much difference, the added refinements included in $\mathbf{E}_t$ being outweighed by the fact that a linear approximation to the equilibrium ratios is too crude. One application of these results could be the use of different correction methods in the same problem—a simpler method such as the bubble point being used for the first few iterations and then more complicated method such as $\mathbf{E}_t$ for rapid convergence near the solution. A detailed description of the sample problem and the computer programs used can be found in reference 5.

THE EXTRACTION PROBLEM

In this section the development of the elements of $\mathbf{E}_v$ will be considered. As indicated previously the extraction problem is an example of the direct use of $\mathbf{E}_v$. As usually practiced, each stage in an extraction battery is operated at a known and fixed temperature (often the temperature of the surroundings). The constant temperature is maintained by exchanging energy in each stage with the surroundings. In this case Equation (5) no longer applies, since there will be no error in the energy balances, and there will be no correction necessary in the stage temperatures. Hence, the correction process for a process with fixed stage temperatures and automatically satisfied energy balances is given by

$$\mathbf{E}_v\ C_v = -D_m \qquad (28)$$

$$\mathbf{E}_v = (e_{v,ik})$$

$$e_{v,ik} = \frac{\partial d_i}{\partial c_{v,k}}$$

In the next section the definition of the flow variable vector C_v will be considered. In the following section the material balance will be developed; then $\mathbf{E}_v$ will be evaluated and some sample problems discussed.

Definition of Flow Variables

For an *n* stage process the vector C_v will have *n* elements, one per stage; yet it will be recalled that the equilibrium stage problem, as considered here, includes the provision for flow between any two stages. Hence, there could be as many as $n - 1$ flows leaving a stage and $n - 1$ flows entering a stage. Only one of these can truly be independent, and there must be enough subsidiary restrictions given to fix all the remaining flows. The flow variables must then be defined in such a way that one independent flow variable can be identified per stage, and there must be some simple mechanism for indicating how all other flows vary as the independent variable changes.

The flow variables are first grouped by stage. This is done by identifying each flow with its stage of origin. Then the flows for each stage can be put into two groups: those that are maintained in some constant ratio to one another and those that are held constant. The first group is called the *variable flows* for the stage and the second group the *fixed flows* for that stage. The distinction can be illustrated by considering a condenser on a distillation column which has two liquid streams leaving, one as product and the other as reflux. First of all it is evident that the relative size of these two streams is not fixed by any fundamental property of the process but is determined by the column designer or operator, and the split is an additional restriction which must be put somehow into the equations. If the product stream is to remain constant as flow rates are varied, then the product stream would be designated as a fixed flow and the reflux as a variable flow. If the ratio of reflux to product is to be constant, then both must be treated as variable flows and the additional restriction as to the relative amounts of the two streams be introduced into the equations.

Any one of the variable flows could be selected as the independent variable, but it is more convenient to use the sum of all the variable flows as the independent variable.

TABLE 1. COMPARISON OF MAXIMUM ERRORS IN SUCCESSIVE ITERATIONS OF A CONSTANT MOLAL OVERFLOW PROBLEM

	Iteration No.						
	0	1	2	3	4	5	6
Nonlinear equilibrium ratios							
$\mathbf{E}_t$ used:	0.92	0.42	0.031	0.00039	10^{-6}		
Bubble point method used:	0.92	0.39	0.33	0.0096	0.0023	0.0004	0.0001
Linear equilibrium ratios							
$\mathbf{E}_t$ used:	0.27	0.002	10^{-6}				
Bubble point method used:	0.27	0.014	0.0021	0.0006	0.0001		

Thus, the n quantities which will be varied in the iterative process will be the n sums of the variable phase flows leaving each stage. If more than two variable phase flows leave a stage, a restriction matrix will be used to indicate how the total flow is divided. This is best illustrated by considering the vapor phase, where the vapor flow matrix is written as

$$\mathbf{V} = \mathbf{A}\,\mathbf{V}^* + \mathbf{V}' \tag{29}$$

The independent vapor flow variable is the matrix $\mathbf{V}^*$, which is diagonal and contains as its i^{th} element the total amount of vapor leaving stage i in variable flow. The matrix $\mathbf{A}$ is the vapor flow restriction matrix. The diagonal elements are -1, and the ij^{th} element is the fraction of the total vapor flow leaving stage j in variable flows which goes to stage i. $\mathbf{V}'$ is the fixed flow matrix and contains all the vapor phase flows which are not to be changed in the iterative process. It should be noted that there must be at least one variable phase flow per stage, so that a fixed flow cannot be identified with a stage unless there are at least two streams leaving the stage with vapor in them. Furthermore, if a stage does not have any stream leaving it with vapor, as would be the case in a total condenser, it is necessary to add a vapor flow, which can be considered as a product stream. This is necessary because it may not be possible to solve the given set of equations, holding all the temperatures constant, without providing for some vapor product from the stage.

Similarly the liquid flow matrix can be written as

$$\mathbf{L} = \mathbf{B}\,\mathbf{L}^* + \mathbf{L}' \tag{30}$$

where $\mathbf{L}'$ is the matrix of fixed liquid flows, $\mathbf{L}^*$ is the variable liquid flow matrix, and $\mathbf{B}$ is the liquid flow restriction matrix. All are defined in a manner exactly analogous to that used above for the vapor flows. It appears that there are two phase flow variables for each stage, one for the liquid flows and one for the vapor flows. However, one of these can be eliminated by the use of the overall material balance for the stage, so that there will only be one flow variable remaining per stage. It was arbitrarily decided to make the vapor flow rates $\mathbf{V}^*$ the independent variable.

Material Balance Equations

The overall material balance can be written as

$$(\mathbf{L} + \mathbf{V})U + \mathbf{F}U = 0 \tag{31}$$

$$(\mathbf{B}\mathbf{L}^* + \mathbf{L}' + \mathbf{A}\,\mathbf{V}^* + \mathbf{V}')U = -\mathbf{F}\,U \tag{32}$$

If a change occurs in one of the independent vapor flow variables, then a compensating change must occur in the liquid flow variables to satisfy Equation (32). Differentiating with respect to one of the independent variables v_k^* and realizing that $\mathbf{B}$, $\mathbf{A}$, $\mathbf{L}'$ and $\mathbf{V}'$ are constant, we get

$$\mathbf{B}\left(\frac{\partial \mathbf{L}^*}{\partial v_k^*}\right) U = -\mathbf{A}\left(\frac{\partial \mathbf{V}^*}{\partial v_k^*}\right) U \tag{33}$$

$$\left(\frac{\partial \mathbf{L}^*}{\partial v_k^*}\right) U = -\mathbf{B}^{-1}\mathbf{A}\left(\frac{\partial \mathbf{V}^*}{\partial v_k^*}\right) U \tag{34}$$

The partial derivative on the right-hand side of Equation (34) is a matrix of which every element is zero except the diagonal element in the k^{th} row, which is $+1$. After defining

$$\mathbf{R} = \mathbf{B}^{-1}\mathbf{A} \tag{35}$$

it is then evident that the product of $\mathbf{R}$ and the partial derivative will be a matrix which is all zeros except for the k^{th} column, which is the same as the k^{th} column in $\mathbf{R}$. This matrix when multiplied by U will produce a vector which is the k^{th} column in $\mathbf{R}$, or $R^{(k)}$. Finally, when we recall that $\mathbf{L}^*$ is a diagonal matrix, it follows that the derivative with respect to v_k^* must also be diagonal, and furthermore the elements of this diagonal matrix must be nothing more than the elements of the vector $R^{(k)}$. Defining a new diagonal matrix $\mathbf{R}^k$ which has the same elements as the vector $R^{(k)}$, it follows that

$$\frac{\partial \mathbf{L}^*}{\partial v_k^*} = -\mathbf{R}^k \tag{36}$$

Equation (36) is useful in that it can be used to eliminate $\mathbf{L}^*$ from the equations which follow.

The component material balance for component j can be written as

$$(\mathbf{L} + \mathbf{V}\,\mathbf{K}^j)\,X^{(j)} = -F^{(j)} \tag{9}$$

or

$$\mathbf{Z}^j X^{(j)} = -F^{(j)} \tag{6}$$

Differentiating with respect to v_k^*, we get

$$\mathbf{Z}^j \frac{\partial X^{(j)}}{\partial v_k^*} + \left[\mathbf{B}\,\frac{\partial \mathbf{L}^*}{\partial v_k^*} + \mathbf{A}\,\frac{\partial \mathbf{V}^*}{\partial v_k^*}\,\mathbf{K}^j\right] X^{(j)} = 0 \tag{37}$$

To simplify Equation (37), Equation (36) can be used to eliminate the derivative of $\mathbf{L}^*$, and it can be noted that the derivative of $\mathbf{V}^*$ with respect to v_k^* is a matrix with only one nonzero element, a $+1$ in the diagonal element in the k^{th} row. The symbol $\mathbf{I}^k$ will be used to represent this matrix, where $\mathbf{I}^k$ is a matrix which is all zeros except for the diagonal element on the k^{th} row which is a $+1$. Then Equation (37) can be written as

$$\frac{\partial X^{(j)}}{\partial v_k^*} = (\mathbf{Z}^j)^{-1}\,(\mathbf{B}\,\mathbf{R}^k - \mathbf{A}\,\mathbf{I}^k\,\mathbf{K}^j)\,X^{(j)} \tag{38}$$

This gives the desired effect of a change in the flow rate v_k^* on the composition of component j in each stage. Equation (38) is a vector equation, and the computation can be done directly. The inverse of $\mathbf{Z}^j$ is available from the composition calculation; $\mathbf{R}^k$ is obtained from $\mathbf{R}$, which can be determined once for an entire problem; $\mathbf{B}$ and $\mathbf{A}$ are constant and known; $\mathbf{I}^k$ has only one nonzero element; and $\mathbf{K}^j$ and $X^{(j)}$ are known.

Formation of $\mathbf{E}_v$

To be consistent with the definition of $\mathbf{E}_t$, the same error criterion must be used:

$$D_m = (\mathbf{X} - \mathbf{Y})\,U \tag{24}$$

Each element in $\mathbf{E}_v$ must be the rate of change of the sum of the mole fractions in the liquid minus the sum of the mole fractions in the vapor with respect to the flow variable. Equation (38) gives the rate of change of the composition of one component in each stage with respect to one flow rate change. If k is varied from 1 to n in Equation (38), a set of n column vectors will be obtained. These can be assembled into a matrix, called here $\mathbf{X}_v^{(j)}$, which is very similar to the matrix $\mathbf{X}_t^{(j)}$ defined in Equation (15). The ik^{th} element of this matrix gives the rate of change of composition of component j in stage i with respect to a change in flow of v_k^*. Finally by repeating the calculation for each component and then summing the matrices, the ik^{th} element of this summation will give the rate of change of the sum of the liquid compositions in stage i with respect to a change in flow v_k^*.

It only remains then to find the rate of change of the vapor phase compositions with respect to the flow rate changes. Recalling that

$$\mathbf{Y}^{(j)} = \mathbf{K}^{(j)} X^{(j)} \tag{8}$$

and since $\mathbf{K}^j$ is constant, we get

$$\frac{\partial \mathbf{Y}^{(j)}}{\partial v_k^*} = \mathbf{K}^j \left(\frac{\partial X^{(j)}}{\partial v_k^*} \right) \tag{39}$$

Defining $\mathbf{Y}_v^{(j)}$ analogously to $\mathbf{X}_v^{(j)}$ it follows that

$$\mathbf{Y}_v^{(j)} = \mathbf{K}^j \mathbf{X}_v^{(j)} \tag{40}$$

Next, by summing over all components, the desired rate of change of the sum of the vapor compositions can be found and $\mathbf{E}_v$ defined as

$$\begin{aligned} \mathbf{E}_v &= \sum_j \{\mathbf{X}_v^{(j)} - \mathbf{Y}_v^{(j)}\} \\ &= \sum_j \{(\mathbf{I} - \mathbf{K}^j)\, \mathbf{X}_v^{(j)}\} \end{aligned} \tag{41}$$

Finally, the normalization matrices can be introduced, as was done in calculating $\mathbf{E}_t$, to give

$$\mathbf{E}_v = \sum_j \{(\mathbf{I} - \mathbf{K}^j)\, \mathbf{X}_v^j\}\, \mathbf{N} \tag{42}$$

and the correction process is given by

$$\sum_j \{(\mathbf{I} - \mathbf{K}^j)\, \mathbf{X}_v^{(j)}\}\, \mathbf{N}\, C_v = -\, (\mathbf{X} - \mathbf{Y})\, U \tag{43}$$

Application of E_v

Many problems have been solved with the equations developed in the last section. Some results are given in this section. The first problem is the same one described for the constant molal overflow case: an eight-stage system divided into two columns, with stage by-passing and entrainment. It is interesting because it provides a test of the method of defining the independent variables. The temperatures were assumed constant, and hence the equilibrium ratios were constant. Various initial flow rate distributions were used and the rate of convergence to the known solution observed. Some typical results are given in the first row of Table 2. The errors in initial assumed flow rates in this case were approximately 10% of the correct values. The convergence is observed to be rapid. This was generally true for errors varying from +90% to −90% of the correct values. Normalization seemed to make little difference (5).

A second problem was the 15-stage, four-component extraction problem described in detail by Hanson (6). Using the same initial assumptions as Hanson, we obtained the results shown in the second row of the table. After six iterations the maximum error is 9×10^{-4}. This compares with a maximum error of 8×10^{-4} reported by Hanson after nineteen iterations. Although there is a significant improvement, the rate of convergence is relatively slow beyond the second or third iteration and is certainly not quadratic. The cause for this is readily found in the fact that the equilibrium ratios for this system (water, ethanol, acetone, and chloroform) change rapidly with composition. That this caused the slow convergence was verified by repeating the problem exactly except that the equilibrium ratios were computed only once, for the first calculation, and then kept constant. The last row in Table 2 gives the results, and it can be seen that convergence is again rapid. Failure to achieve rapid convergence when composition effects are important arises from the fact that the equilibrium ratios were assumed constants in the derivation of Equation (37), where the partial derivative with respect to flow rate changes was taken. The change in flow rate affects the composition and this in turn affects the equilibrium ratio. This could be taken into account by including an additional term in Equation (37), one with $(\partial \mathbf{K}^j / \partial v_k^*)$, and this in turn can be related to the composition changes in a straightforward manner. Additional calculations would of course be required, but it should be possible, if desired, to achieve quadratic convergence in problems with strong composition effects by application of the techniques described in this paper. It should be obvious also that this same sort of problem could arise in the temperature correction process described previously. It did not in that problem because equilibrium ratios were assumed functions of temperature only. One of the advantages in obtaining analytical expressions for the derivatives is that as many effects can be included as are considered important.

DISCUSSION

In the work to date it has been found most convenient to store all variables as matrices and vectors and then to use matrix handling subroutines for manipulation as indicated by the equations. In this way the programs are kept simple. The size of the problem that can be handled in this way is limited by the memory available in the computer to be used. With 32,000 words of rapid-access storage, a fifty-stage problem can be easily handled with no auxiliary storage for $\mathbf{E}_t$ used. $\mathbf{E}_v$ requires more storage and about forty stages is the most that can conveniently be handled without using auxiliary storage. For larger problems or if both are to be included in one program, it is necessary to use tapes, disks, or other secondary storage. The amount of storage for large problems varies as the square of the number of stages. The number of components has relatively little effect on the storage requirements because computations can be done serially for each component; that is, all calculations for one component can be completed before those for the next compo-

TABLE 2. MAXIMUM ERROR IN SUMS OF MOLE FRACTIONS FOR SAMPLE EXTRACTION PROBLEMS

	Iteration No.						
	0	1	2	3	4	5	6
Problem 1 8 Stages *k* Constant	3×10^{-2}	1×10^{-2}	1×10^{-4}	1×10^{-7}			
Problem 2 (Hanson) 15 Stages *k* Composition dependent	2×10^{-1}	5×10^{-2}	1×10^{-2}	4×10^{-3}	3×10^{-3}	2×10^{-3}	9×10^{-4}
Problem 3 15 Stages *k* Constant	2×10^{-1}	5×10^{-2}	2×10^{-3}	7×10^{-6}			

nent are started. This can be seen by examining Equations (26) and (42). While the storage for the **X**, **Y**, and **F** matrices and for equilibrium ratios does vary with the number of components, the effect is slight since the number of components is usually much smaller than the number of stages.

The problems solved to date have included both multiple column operation and stage bypassing. No special problems were encountered in obtaining the inverse of $\mathbf{Z}^j$ for use in Equation (26) even for the largest problem tested, forty-five stages. A standard inversion routine was used, one based on the Gauss-Jordan reduction. This point is mentioned here since there have been statements in the literature that it is impractical to invert large matrices such as encountered in equilibrium stage problems. It should also be noted that an inverse is not required for the solution of Equation (23). A direct reduction method is more rapid. For the same reason the inverse of $\mathbf{Z}^j$ is not required unless Equation (26) is to be used. If only Equation (6) is to be solved and then a bubble point or other method used to correct the temperatures, an equation solving routine can be used. If $\mathbf{Z}^j$ is tridiagonal, the special case for countercurrent flow, then an especially efficient algorithm is available (see, for example, reference *7*).

The use of the **L**, **V**, and $\mathbf{K}^j$ matrices to form $\mathbf{Z}^j$ has advantages over previous methods. The most important is that any interstage flow arrangement is easily accommodated. Thus multiple-column operation and stage bypassing present no special problems. Bypassing seems to have been generally neglected in computational methods, yet Strand (*8*) has reported that the use of a liquid bypass model greatly improved the correlation of stage efficiencies. A second advantage is that phase flows are used rather than total flows, and entrainment can be readily included. Finally, in matrix form the equations are simple. If, for example, **L** and **V** are used as input data, even a beginning student can program the solution to Equation (6), using a standard matrix handling subroutines, and can find all the phase compositions in the column.

CONCLUSIONS

It has been shown that a Newton-Raphson correction process can be developed for the equilibrium stage problem and that this method does exhibit quadratic convergence rates for the constant molal overflow problem and the constant temperature extraction problem. Furthermore, these same correction techniques can form part of an overall correction method in which temperatures and flow rates are corrected simultaneously. Many aspects of the correction process remain to be investigated. Among these are:

1. The efficiency (measured perhaps by total computing time) of these methods as compared to other methods.
2. The most efficient ways to calculate $\mathbf{E}_t$ and $\mathbf{E}_v$.
3. The region of convergence as compared to other methods.
4. The efficiency in using combination methods or iterating several times with the same correction matrix.
5. Modifications of $\mathbf{E}_t$ and $\mathbf{E}_v$ to include the effect of composition on equilibrium ratios.
6. The possibility that simplified forms of $\mathbf{E}_t$ and $\mathbf{E}_v$ will give almost quadratic convergence and be simpler to calculate.
7. Extension to unsteady state and reacting systems.

Finally, it remains to be demonstrated that the energy balance equations can be analyzed in a similar way and that $\mathbf{J}_t$ and $\mathbf{J}_v$ can be calculated.

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NOTATION

$\mathbf{A}, \mathbf{B}$ = vapor and liquid flow restriction matrices for variable flows
a_{ii} = -1, $b_{ii} = -1$
a_{ij}, b_{ij} = fraction of total variable vapor or liquid flow leaving stage j which goes to stage i
C_t = temperature variation vector
$c_{t,k}$ = variation in temperature in stage k
C_v = flow rate variation vector
$c_{v,i}$ = variation in vapor flow rate variable in stage i
D_e = deviation or error in energy balance equations
D_m = deviation or error in material balance equations
$\mathbf{E}_t, \mathbf{E}_v$ = temperature and flow rate correction matrices for material balance errors
$\mathbf{F}$ = feed matrix
f_{ij} = total amount of component j entering stage i from outside the system
$F^{(j)}$ = feed vector for component j; column j of **F**
$\mathbf{I}$ = identity matrix
$\mathbf{I}^k$ = matrix in which all elements are zero except the diagonal element in k^{th} row, which is 1
$\mathbf{J}_t, \mathbf{J}_v$ = temperature and flow rate correction matrices for energy balance errors
$\mathbf{K}^j$ = equilibrium ratio matrix for component j (diagonal)
k_i^j = y_{ij}/x_{ij}
$\mathbf{L}, \mathbf{V}$ = liquid and vapor flow connection matrices
$-l_{ii}, -v_{ii}$ = total flow rate of liquid or vapor phase leaving stage i
l_{ij}, v_{ij} = flow rate of liquid or vapor phase from stage j to stage i in fixed streams
$\mathbf{L}^*, \mathbf{V}^*$ = variable liquid and vapor flow matrices (diagonal)
l_i^*, v_i^* = total flow of liquid or vapor phase from stage i in streams which are allowed to vary
$\mathbf{L}', \mathbf{V}'$ = liquid and vapor flow connection matrices for fixed flows
$\mathbf{M}^j$ = weighted equilibrium ratio temperature dependence matrix for component j (diagonal)
m_i^j = $\dfrac{\partial k_i^j}{\partial t_i}(x_{ij})$
$\mathbf{N}$ = normalization matrix
n_i = $\dfrac{1}{\sum_j (x_{ij})}$
$\mathbf{R}$ = $\mathbf{B}^{-1}\mathbf{A}$
$\mathbf{R}^k$ = diagonal matrix formed from column k of **R**
r_i^k = r_{ik}
$R^{(k)}$ = column k of **R**
T = temperature vector
t_k = temperature in stage k
U = unity vector
u_i = 1
$\mathbf{X}, \mathbf{Y}$ = liquid and vapor composition matrices
x_{ij}, y_{ij} = liquid or vapor composition of component j in stage i
$X^{(j)}, Y^{(j)}$ = liquid and vapor composition vector for component j. Column j of **X** and **Y**
$\mathbf{X}_t^{(j)}, \mathbf{Y}_t^{(j)}$ = temperature dependence matrices for liquid and vapor compositions

$x_{t,ik}^{(j)} = \frac{\partial x_{ij}}{\partial t_k}$; $y_{t,ik}^{(j)} = \frac{\partial y_{ij}}{\partial t_k}$

$\mathbf{X}_v^{(j)}, \mathbf{Y}_v^{(j)}$ = flow rate dependence matrices for liquid and vapor composition. The volumes of $\mathbf{X}_v^{(j)}$ and $\mathbf{Y}_v^{(j)}$ are calculated from Equation (38)

$x_{v,ik}^{(j)} = \frac{\partial x_{ij}}{\partial v_k^*}$

$y_{v,ik}^{(j)} = \frac{\partial y_{ij}}{\partial v_k^*}$

$\mathbf{Z}^j = \mathbf{L} + \mathbf{V}\ \mathbf{K}^j$

Greek Letters

Φ = correction matrix used to calculate temperature and flow rate corrections

Ψ = Jacobian form of the correction matrix

$\psi_{ij} = \frac{\partial \lambda_i}{\partial \delta_j}$

$\Delta = \begin{bmatrix} C_t \\ C_v \end{bmatrix} = (\delta_i)$

$\Lambda = \begin{bmatrix} D_m \\ D_e \end{bmatrix} = (\lambda_i)$

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Local and Macroscopic Transport from a 1.5-In. Cylinder in a Turbulent Air Stream

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The local and macroscopic thermal transfer coefficients were experimentally investigated for a 1.5-in. copper cylinder located in a transverse flowing turbulent air stream. Measurements of local transport and pressure coefficient were made throughout the entire perimeter of the cylinder. The Reynolds number was varied from 2,600 to 86,000 and the free-stream turbulence from 0.013 to 0.25. The estimated integral turbulence scale was found to vary from 0.3 to 0.5 in. over the range of conditions of flow investigated. The local transfer coefficient near stagnation increased 35% as a result of an increase in turbulence over the range indicated. Displacements of the locus of separation with varying Reynolds numbers and turbulence level were found.

The effects of free-stream turbulence on the local thermal transfer from a blunt body are particularly interesting in revealing the mechanism of transport. These experimental studies are directed, in part, to an understanding of the behavior of the wake. It is the purpose of this discussion to present experimental results concerning the effect of free-stream turbulence on the local transport from a cylinder.

THEORY AT STAGNATION

One of the most significant and extensive contributions to local transport, both theoretically as well as experimentally, was the work of Frössling (*1*). He suspended liquid drops over an air jet and measured the change in radius by photomicrography. The drop radii varied from 0.1 to 0.9 mm. and the air velocity from 0.2 to 7 m./sec., corresponding to a Reynolds number as defined in the Notation from 2 to 800 for the evaporation of nitrobenzene, aniline, and water. Local convective rates were determined by measuring the pointwise variation in the radius of a solid naphthalene sphere in an air jet stream. Frössling (*1*) showed theoretically that

$$N_{Nu} = 2(1 + k\, N_{Re}^{1/2}) \qquad (1)$$

where his k was dependent only on the Prandtl number,