Exact Calculation Methods for Systems of Interlinked Columns

HSIEN HSU
and
J. W. TIERNEY
Chemical and Petroleum Engineering Department
University of Pittsburgh
Pittsburgh, PA 15261

Part I: Separation of Binary Heterogeneous Azeotropes

A mathematical model and iterative correction algorithm are described for the exact solution of separation systems which contain interlinked columns in which some stages have two liquid phases and others have a vapor and liquid phase. The correction algorithm is based on Newton's method and provides for simultaneous correction of all iteration variables. The derivatives are calculated analytically from the model equations. The separation of a binary mixture which forms a heterogeneous azeotrope is analyzed. Modifications to the correction algorithm which provide for fixed condenser temperature and fixed product flows are described. The separation of butanol and water is used to illustrate the method.

SCOPE

Separation systems which combine liquid extraction with distillation are commonly used in the chemical industry. An exact solution to the equations describing such a system may be difficult to obtain because the columns are usually interlinked by extensive recycle flows; the mixtures are necessarily highly nonideal; and both liquid-liquid and vapor-liquid equilibria are encountered. A mathematical model developed in our laboratories (Tierney and Bruno, 1967; Bruno et al., 1972) is modified for the solution of these extraction-distillation systems.

The model uses matrix notation and can accommodate any number of components, any interstage flow pattern, and any combination of feeds and products. Both liquid-liquid and vapor-liquid equilibria can be included. An iterative calculation sequence is used to solve the model equations. The V-phase compositions, stage temperatures, and V-phase flows are basic iteration variables. The remaining unknowns are found by solving sets of simultaneous linear equations. The iteration variables are corrected simultaneously using Newton's method with the needed partial derivatives being obtained by analytic differentiation of the model equations.

The model is applied to the distillation of a binary heterogeneous azeotrope—the simplest example of a system with interlinked columns which requires both vapor-liquid and liquid-liquid equilibria. A more complicated application—the separation of a three component mixture using interlinked extraction and distillation columns—has been studied, and another paper is being prepared describing the results. A binary heterogeneous azeotrope can be separated using two distillation columns and a common condenser-decanter as shown in Figure 1.

Vapors near the azeotrope composition will separate into two liquid phases when condensed. The compositions must span the azeotrope composition so each can be distilled in a separate column, yielding near azeotrope at the top and relatively pure product at the bottom. Van Winkle (1967) described a graphical method of solution, but in addition to the usual limitations of graphical methods, it is not in a form suitable for extension to multicomponent mixtures. Hess and Holland (1976) and Jelinek et al. (1973) have dealt with the problems of solving simultaneously two interlinked columns, but have not considered the difficulties which arise when the distillate separates into two liquid phases. Block and Hegner (1976) treated a single column with more than two phases in equilibrium.

In this work, we assume that there are two phases in each stage. The symbols V and L are used in the model to represent the two phases. Where possible, vapor phases are labeled as V-phases and liquid phases as L-phases. In the condenser-decanter, however, one of the liquids must be designated as V-phase. Equilibrium relations and enthalpy calculations must also be specially defined for the condenser. Since the mixture is binary and there are two liquid phases in the condenser, the compositions of both phases are known at a given temperature. This fact is used to define an equilibrium ratio for the condenser which is only a function of temperature, and it is not necessary to calculate activity coefficients for the liquid-liquid equilibrium in the condenser.

The basic calculation algorithm described above must usually be modified to allow fixing the temperature of the condenser and one of the product flow rates. It is highly desirable that these modifications be incorporated into the calculation sequence in such a way that the computational efficiency is maintained. This is done by changing the iteration variables and, as a result, the Jacobian correction matrix. Equations are developed which permit these changes to be treated as modifications of the basic correction algorithm.

Mr. Hsu is presently with the Chemical Engineering Department, Tianjin University, Tianjin, The People's Republic of China.

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CONCLUSIONS AND SIGNIFICANCE

The algorithms proposed were applied to the separation of butanol and water. Quadratic convergence was obtained for the basic problem with condenser temperature fixed and also with the product flows fixed. The results provide a published exact solution for the distillation of a binary heterogeneous azeotrope. The fact that convergence was quadratic indicates that the equations for the Jacobian matrix are correct. The model equations, together with the correction algorithm and the modifications of the algorithm, provide a versatile framework for obtaining rigorous solutions for distillation of binary heterogeneous azeotropes. They are written in a form which can conveniently be extended to more complicated multicomponent systems.

MATHEMATICAL MODEL

A general mathematical model for equilibrium staged separations was presented previously (Tierney and Bruno, 1967; Bruno et al., 1972). It is based on the assumption that each stage is well mixed and contains two phases which are in equilibrium; that there is no reaction; and that the system is at steady state. Any interstage flow pattern is permitted, and there can be any number of feeds and products. The model consists of six matrix equations for the material balances, energy balances, and equilibrium relations plus equations to define the physical properties of the materials. The overall material balance is

$$\underset{\sim}{A}V + \underset{\sim}{B}L + \sum_{j=1}^{m} F^j = 0 \tag{1}$$

where $\underset{\sim}{A}$ is the flow distribution matrix for the V-phase and $\underset{\sim}{B}$ is the flow distribution matrix for the L-phase. V and L are vectors giving the flow rates of the V-phase and L-phase flows leaving each stage. F^j is a vector of feeds of component j. Definitions of these and other variables which form the model are given in the notation.

A component material balance can be written for each component as follows:

$$\underset{\sim}{A}\underset{\sim}{V}Y^j + \underset{\sim}{B}\underset{\sim}{L}X^j + F^j = 0 \quad 1 \le j \le m \tag{2}$$

where Y^j and X^j are column vectors giving the mole fractions of component j in the V-phase and L-phase for each stage. Since the mole fractions must sum to 1.0 in each stage,

$$\sum_{j=1}^{m} Y^j = U \tag{3}$$

$$\sum_{j=1}^{m} X^j = U \tag{4}$$

where U is a vector with 1.0 in each element.

The energy balance equation for the system is given by:

$$\underset{\sim}{A}\underset{\sim}{V}G + \underset{\sim}{B}\underset{\sim}{L}H + Q + Q_f = 0 \tag{5}$$

where Q is a vector of heat interchanges between each stage and the surroundings; Q_f is a vector of feed enthalpies; and G and H are vectors containing the enthalpies of the V-phase and L-phase for each stage.

The equilibrium relations are given by:

$$\underset{\sim}{\Gamma}^j Y^j = \underset{\sim}{\Lambda}^j \underset{\sim}{K}^j X^j \quad 1 \le j \le m \tag{6}$$

where $\underset{\sim}{\Gamma}^j$ and $\underset{\sim}{\Lambda}^j$ are diagonal matrices with the activity coefficients for component j in the V-phase and L-phase for each stage. $\underset{\sim}{K}^j$ is a diagonal matrix of fugacity ratios for component j.

In addition, it is necessary to have equations which give the physical properties of the mixture. These are assumed to be of the form:

$$\underset{\sim}{K} = \underset{\sim}{K}(T, P) \tag{7}$$

$$H = H(\underset{\sim}{X}, T, P) \tag{8}$$

$$G = G(\underset{\sim}{Y}, T, P) \tag{9}$$

$$\underset{\sim}{\Gamma} = \underset{\sim}{\Gamma}(\underset{\sim}{Y}, T, P) \tag{10}$$

$$\underset{\sim}{\Lambda} = \underset{\sim}{\Lambda}(\underset{\sim}{X}, T, P) \tag{11}$$

We assume that these equations are explicit so that if the arguments on the right side are known, the physical property can be calculated without iteration. Compositions are normalized before using Eqs. 8 through 11.

ALGORITHM FOR SOLUTION OF MODEL

Equations 1 through 11 define the mathematical model and must be solved simultaneously. There are more variables than equations, so the problem statement must specify which variables will be fixed and which are to be found. We define the former as *independent* variables and the latter as *dependent* variables. There are many different combinations of independent variables, and the calculation method for each will be different. We first of all define a *basic* set of independent variables and present a computational algorithm for solving the problem in this form. Then solutions for other sets of independent variables are treated as modifications to the solution for the basic set. This will be discussed in a later section.

The basic set of independent variables are $\underset{\sim}{A}$, $\underset{\sim}{B}$, $\underset{\sim}{F}$, P, Q, and Q_f. Dependent variables are $\underset{\sim}{X}$, $\underset{\sim}{Y}$, T, V, L, G, H, $\underset{\sim}{K}$, $\underset{\sim}{\Gamma}$, and $\underset{\sim}{\Lambda}$. It is not possible to solve the model equations directly, and an iterative calculation method must be used. To do this, the dependent variables are divided into two groups—iteration variables and noniteration variables. The calculation sequence will be to assume values for all the iteration variables, evaluate all of the noniteration variables using a subset of the model equations; check to see if the assumed values of the iteration variables are close enough using the remaining model equations; and, if not, to correct the iteration variables and repeat the calculation. The criterion for selection of a set of iteration variables is that the number of variables be as small as possible and still permit the evaulation of all noniteration variables by solving nothing more complicated than a set of simultaneous linear equations. A set which satisfies this requirement is the vapor compositions for components 2 through m, the temperatures, and the V-phase flow rates. With these as iteration variables the calculation sequence is as follows.

1. Assume values for Y^2, Y^3, . . . Y^m, T and V.
2. Calculate L from Eq. 1.
3. Calculate Y^1 from Eq. 3.
4. Calculate X^1, X^2 . . . X^m from Eq. 2.

5. Calculate G, H, $\underset{\sim}{K}$, $\underset{\sim}{\Gamma}$, and $\underset{\sim}{\Lambda}$ from Eqs. 7 through 11.
6. Check to see if the remaining independent equations in the model are satisfied. To do this error vectors and norms are defined as follows.

$$E^j = \underset{\sim}{\Gamma}^j Y^j - \underset{\sim}{\Lambda}^j \underset{\sim}{K}^j X^j \quad 1 \le j \le m \tag{12}$$

$$E^{m+1} = \underset{\sim}{A}\underset{\sim}{V} G + \underset{\sim}{B}\underset{\sim}{L} H + Q + Q_f \tag{13}$$

$$\sigma_1 = \left[\sum_{i=1}^{n} \sum_{j=1}^{m} \{(e_i^j)^2\} \right]^{1/2} \tag{14}$$

$$\sigma_2 = \left[\sum_{i=1}^{n} (e_i^{m+1})^2 \right]^{1/2} \tag{15}$$

If each norm is less than some preselected value, a solution has been obtained. If not, the iteration variables are corrected as described in the next section and calculation resumed at step 2 above. Two error norms are used because the errors in Eq. 12 are usually orders of magnitude smaller than those from the energy balance, Eq. 13.

The iteration variables chosen here include V-phase compositions instead of L-phase compositions as used by Bruno et al. (1972). This is necessary because $\underset{\sim}{A}$ is singular for a system such as shown in Figure 1, and the Jacobian submatrixes would be undefined. The singular $\underset{\sim}{A}$ results from a characteristic of a heterogeneous azeotrope separation—there are no vapor products because all vapor streams are recycled internally.

JACOBIAN CORRECTION MATRIX

If the assumed values for the iteration variables in the calculation sequence do not satisfy the model equations, a new set of iteration variables must be calculated. A general algorithm is:

$$(\underset{\sim}{J}) \begin{bmatrix} C^1 \\ \vdots \\ C^{m+1} \end{bmatrix} = - \begin{bmatrix} E^1 \\ \vdots \\ E^{m+1} \end{bmatrix} \tag{16}$$

where C^1 to C^{m+1} are the corrections in the iteration variables.

$$C^j = (Y^{j+1})_{\nu+1} - (Y^{j+1})_\nu; \quad 1 \le j \le m-1 \tag{17}$$

$$C^m = (T)_{\nu+1} - (T)_\nu \tag{18}$$

$$C^{m+1} = (V)_{\nu+1} - (V)_\nu \tag{19}$$

If $\underset{\sim}{J}$ is the Jacobian matrix, then the correction defined by Eq. 16 will converge quadratically near the solution. The advantages of using a quadratically convergent method are well known. The major disadvantage is the necessity to calculate a large number of partial derivatives. The use of matrix notation greatly simplifies these calculations and is a major advantage of the notation.

Each element of $\underset{\sim}{J}$ is a partial derivative of one of the errors with respect to one of the iteration variables. Since there are $(m + 1)$ kinds of error terms and $(m + 1)$ kinds of iteration variables, the derivatives subdivide naturally into $(m + 1)^2$ groups. If $\underset{\sim}{J}$ is partitioned into $(m + 1)^2$ submatrixes of equal size, then submatrix $\underset{\sim}{J}_{pq}$ contains partial derivatives of the pth error with respect to the qth iteration variable and can be represented by (dE^p/dC^q) with all other iteration variables held constant. When the operator $\underset{\sim}{d}$ is used in the equations which follow, it is understood that iteration variables are held constant. The symbol $\underset{\sim}{\partial}$ will be used when expressing the partial derivatives of physical properties in terms of the arguments as indicated in Eqs. 8 through 11. From Eq. 11, for example, the activity coefficient of component 1 in the liquid phase would be expressed in terms of liquid composition, temperature, and pressure as follows:

$$d\Lambda^1 = \sum_{j=1}^{m} \left(\frac{\partial \Lambda^1}{\partial X^j}\right) dX^j + \left(\frac{\partial \Lambda^1}{\partial T}\right) dT + \left(\frac{\partial \Lambda^1}{\partial P}\right) dP \tag{20}$$

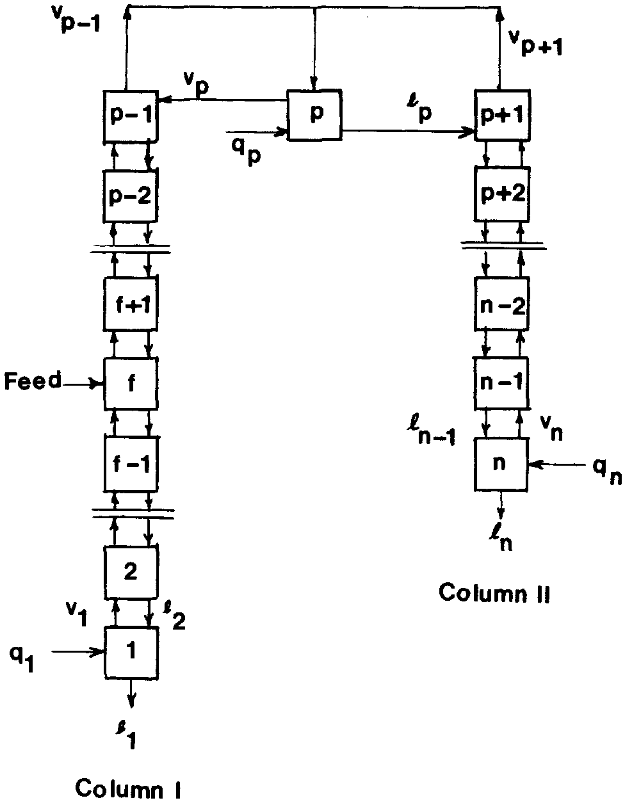

Figure 1. Flow sheet of two column system for distillation of a binary heterogeneous azeotrope.

Each partial derivative is obtained from the equation defining the liquid phase activity coefficient and the variables which are held constant are the other arguments in Eq. 11.

The submatrixes of $\underset{\sim}{J}$ are obtained by differentiating each of the error equations (Eqs. 12 and 13) with respect to each of the iteration variable vectors. Pressure is an independent variable and is constant. The results are summarized in the following equations.

$$\begin{aligned} \underset{\sim}{J}_{j,k-1} = \left(\frac{dE^j}{dY^k}\right) &= \underset{\sim}{\Gamma}^j \left(\frac{dY^j}{dY^k}\right) + \underset{\sim}{Y}^j \left[-\left(\frac{\partial \Gamma^j}{\partial Y^1}\right) + \left(\frac{\partial \Gamma^j}{\partial Y^k}\right) \right] \\ &\quad - \underset{\sim}{K}^j \underset{\sim}{X}^j \left[-\left(\frac{\partial \Lambda^j}{\partial X^1}\right) + \left(\frac{\partial \Lambda^j}{\partial X^k}\right) \right] \left(\frac{dX^k}{dY^k}\right) \\ &\quad - \underset{\sim}{K}^j \underset{\sim}{\Lambda}^j \left(\frac{dX^j}{dY^k}\right); \quad 1 \le j \le m, \quad 2 \le k \le m \end{aligned} \tag{21}$$

$$\begin{aligned} \underset{\sim}{J}_{j,m} = \left(\frac{dE^j}{dT}\right) &= \underset{\sim}{Y}^j \left(\frac{\partial \Gamma^j}{\partial T}\right) - \underset{\sim}{K}^j \underset{\sim}{X}^j \left(\frac{\partial \Lambda^j}{\partial T}\right) \\ &\quad - \underset{\sim}{K}^j \underset{\sim}{\Lambda}^j \left(\frac{\partial K^j}{\partial T}\right); \quad 1 \le j \le m \end{aligned} \tag{22}$$

$$\begin{aligned} \underset{\sim}{J}_{j,m+1} = \left(\frac{dE^j}{dV}\right) &= - \underset{\sim}{K}^j \underset{\sim}{\Lambda}^j \left(\frac{dX^j}{dV}\right) \\ &\quad - \underset{\sim}{K}^j \underset{\sim}{X}^j \sum_{k=1}^{m} \left[\left(\frac{\partial \Lambda^j}{\partial X^k}\right) \left(\frac{dX^k}{dV}\right) \right]; \quad 1 \le j \le m \end{aligned} \tag{23}$$

$$\begin{aligned} \underset{\sim}{J}_{m+1,k-1} = \left(\frac{dE^{m+1}}{dY^k}\right) &= \underset{\sim}{A}\underset{\sim}{V} \left[-\left(\frac{\partial G}{\partial Y^1}\right) + \left(\frac{\partial G}{\partial Y^k}\right) \right] \\ &\quad + \underset{\sim}{B}\underset{\sim}{L} \left[-\left(\frac{\partial H}{\partial X^1}\right) + \left(\frac{\partial H}{\partial X^k}\right) \right] \left(\frac{dX^k}{dY^k}\right); \quad 2 \le k \le m \end{aligned} \tag{24}$$

$$\underset{\sim}{J}_{m+1,m} = \left(\frac{dE^{m+1}}{dT}\right) = \underset{\sim}{A}\underset{\sim}{V} \left(\frac{\partial G}{\partial T}\right) + \underset{\sim}{B}\underset{\sim}{L} \left(\frac{\partial H}{\partial T}\right) \tag{25}$$

$$\underset{\sim}{J}_{m+1,m+1} = \left(\frac{dE^{m+1}}{dV}\right) = \underset{\sim}{A}\underset{\sim}{G} + \underset{\sim}{B}\underset{\sim}{L} \sum_{j=1}^{m} \left[\left(\frac{\partial H}{\partial X^j}\right)\left(\frac{dX^j}{dV}\right)\right] - \underset{\sim}{B}\underset{\sim}{H}\underset{\sim}{B}^{-1} \quad (26)$$

Derivatives indicated with the operator ∂ are found from Eqs. 8 through 11. The derivatives with the operator d are obtained from Eqs. 1 through 6 and are as follows.

$$\frac{dX^j}{dY^k} = -(\underset{\sim}{B}\underset{\sim}{L})^{-1}\underset{\sim}{A}\underset{\sim}{V}\delta_{jk}; \quad 2 \le j,\ k \le m \quad (27)$$

$$\frac{dY^j}{dY^k} = \delta_{jk}\underset{\sim}{I}; \quad 2 \le j,\ k \le m \quad (28)$$

$$\frac{dX^1}{dY^k} = -\left(\frac{dX^k}{dY^k}\right); \quad 2 \le k \le m \quad (29)$$

$$\frac{dY^1}{dY^k} = -\underset{\sim}{I}; \quad 2 \le k \le m \quad (30)$$

$$\frac{dX^j}{dV} = (\underset{\sim}{B}\underset{\sim}{L})^{-1}(\underset{\sim}{B}\underset{\sim}{X}^j\underset{\sim}{B}^{-1}\underset{\sim}{A} - \underset{\sim}{A}\underset{\sim}{Y}^j); \quad 1 \le j \le m \quad (31)$$

SEPARATION OF A BINARY HETEROGENEOUS AZEOTROPE

The model equations and correction method described above will now be applied to the distillation of a binary heterogeneous azeotrope. This system is simple because it has only two components and only one stage in which liquid-liquid equilibrium is found. It does, however, pose difficult computational problems. It should be noted that for a binary system it is possible to devise a correction algorithm which requires fewer iteration variables than outlined above. The method is based on the fact that the equilibrium data can be put in the form of, say, $X^1 = X^1(Y^1)$ and $T = T(Y^1)$. By using Y^1 as the iteration variable, X^1 and T can be obtained as well as Y^2 and X^2. The flows can then be found from the material balance equations. This form for the equilibrium equations is the equivalent of a *T-x-y* diagram used in graphical calculations. We have not developed this algorithm further because it cannot conveniently be extended to multicomponent systems.

Figure 1 is a diagram of a typical system for the distillation of a binary system which forms a heterogeneous azeotrope. The stages are numbered upward starting with the reboiler in column I to the condenser at stage p and then downward through column II to the reboiler which is stage n. This numbering system keeps the $\underset{\sim}{A}$ and $\underset{\sim}{B}$ matrixes tridiagonal and can shorten computation time. It is not necessary, however. The feed is shown as added to one of the stages in column I. It could be added to any stage or to the condenser, and there could be more than one feed. The model is based on the assumption that there are two phases in equilibrium in each stage. We call these two phases the V-phase and the L-phase. For all stages except the condenser the V-phase is vapor, and the L-phase is liquid. Since both phases in the condenser are liquid, one must be called a V-phase. The choice is arbitrary, and in Figure 1 the liquid flowing to stage $p - 1$ is designated as V-phase.

MODIFICATIONS TO SET OF INDEPENDENT VARIABLES

The basic set of independent variables defined previously needs to be modified for a system such as shown in Figure 1. First, instead of fixing the heat exchange to the condenser, stage p, it is much more likely that the temperature in the condenser would be fixed with the heat exchange being adjusted to achieve this temperature. Second, instead of fixing the heat exchanges with the reboilers, the product flows or compositions would be fixed by adjusting the heat flows. In each case an interchange is required between an independent variable, a heat exchange, and one of the dependent variables. We will treat two cases. The first is the interchange of a heat exchange variable and a stage temperature, and the second is the interchange of a heat exchange variable and a L-phase flow rate. The algorithm defined above must be modified to account for these interchanges.

The temperature for stage j, t_j, is to be fixed, and the heat exchange with stage k, q_k, is to be found. Stages j and k may be the same or they may be different. We note first of all that q_k appears only in the error equation for e_k^{m+1}. Furthermore e_k^{m+1} can always be made zero by a suitable selection of q_k. Therefore e_k^{m+1} can be removed from the model equations and used to calculate q_k when a solution is found. We eliminate e_k^{m+1} by defining a modified error vector,

$$E^{(m+1)*} = \underset{\sim}{I}_k E^{(m+1)} \quad (32)$$

in which $\underset{\sim}{I}_k$ is an identity matrix with row k removed. Since t_j is now known, it can also be removed from the iteration variables and the correction variables.

$$T^* = \underset{\sim}{I}_j T \quad (33)$$

$$C^{m*} = \underset{\sim}{I}_j C^m \quad (34)$$

One equation and one iteration variable have been removed, and now the Jacobian matrix must be modified by eliminating the $(mn + k)$ row and the $(n + j)$ column. This is represented in matrix form as:

$$\underset{\sim}{J}^*_{m+1,l} = \underset{\sim}{I}_k \underset{\sim}{J}_{m+1,l}; \quad 1 \le l \le m - 1 \quad (35)$$

$$\underset{\sim}{J}^*_{m+1,m} = \underset{\sim}{I}_k \underset{\sim}{J}_{m+1,m} \underset{\sim}{I}_j^T \quad (36)$$

$$\underset{\sim}{J}^*_{m+1,m+1} = \underset{\sim}{I}_k \underset{\sim}{J}_{m+1,m+1} \quad (37)$$

$$\underset{\sim}{J}^*_{l,m} = \underset{\sim}{J}_{l,m} \underset{\sim}{I}_j^T; \quad 1 \le l \le m \quad (38)$$

where an asterisk is used to indicate a modified Jacobian submatrix. The unmodified submatrix on the right side is found from Eqs. 21 through 26. The modified algorithm is exactly the same as the basic algorithm except that the error vector, the correction vector, and the Jacobian in Eq. 16 are all modified.

Interchanging an L-phase flow rate and a heat exchange is more complicated because the flow rate is a noniteration variable. The flow rate of L-phase from stage j, l_j, is to be fixed, and q_k is to be found. Equation 32 can be used to modify the error vector as before. The number of iteration variables must also be reduced by one, but l_j is not an iteration variable, so it is necessary to select an iteration variable in such a way that l_j remains constant. Letting v_r, the flow of V-phase from stage r, be the iteration variable which becomes a noniteration variable, we define the modified iteration variable as

$$V^* = \underset{\sim}{I}_r V \quad (39)$$

In the calculation sequence, values for V^* will be assumed and then v_r calculated using the condition that l_j must remain constant. Then V can be calculated:

$$V = \underset{\sim}{I}_r^T V^* + V_r^+ \quad (40)$$

where V_r^+ is a vector with all zeros except for the rth element which is v_r. An expression is now needed for V_r^+ in terms of V^* and the condition that l_j remain constant. Solving Eq. 1 for L and then premultiplying by a matrix which is all zeros except for the jj element gives a vector which has l_j in the jth element and zeros elsewhere.

$$L_j^+ = \underset{\sim}{I}_j^+ L = -\underset{\sim}{I}_j^+\left[\underset{\sim}{B}^{-1}\underset{\sim}{A}V + \underset{\sim}{B}^{-1}\sum_{j=1}^{m} F^j\right] \quad (41)$$

Substituting for V from Eq. 40 and rearranging gives:

$$\underset{\sim}{I}_j^+(\underset{\sim}{B}^{-1}\underset{\sim}{A})V_r^+ = -L_j^+ - \underset{\sim}{I}_j^+\underset{\sim}{B}^{-1}\underset{\sim}{A}\underset{\sim}{I}_r^T V^* - \underset{\sim}{I}_j^+\underset{\sim}{B}^{-1}\sum_{j=1}^{m} F^j \quad (42)$$

Defining β as the jr element of $(\underset{\sim}{B}^{-1}\underset{\sim}{A})$ this simplifies to:

$$V_r^+ = -\left(\frac{1}{\beta}\right)[\underset{\sim}{I}_r^+\underset{\sim}{U}\underset{\sim}{I}_j^+]\left[\underset{\sim}{B}^{-1}\underset{\sim}{A}\underset{\sim}{I}_r^T V^* + \underset{\sim}{B}^{-1}\sum_{j=1}^{m} F^j + L_j^+\right] \quad (43)$$

TABLE 1. INITIAL VALUES FOR ITERATION VARIABLES IN SAMPLE PROBLEM

Stage	V-Phase Flow kg · mol/h	Stage Temp. °C	V-Phase Composition Mol Fraction
1	0.950	118.50	0.0050
2	0.950	114.25	0.0100
3	0.950	110.00	0.0500
4	0.950	105.75	0.1000
5	0.950	101.50	0.3000
6	0.950	97.25	0.5000
7	0.950	93.00	0.6700
8	0.650	93.00	0.5086
9	0.039	93.00	0.8000
10	0.039	94.75	0.8500
11	0.039	96.50	0.9000
12	0.039	98.25	0.9500
13	0.039	100.00	0.9800

The Jacobian must also be modified to be consistent with the modified iteration variables and errors. The submatrixes which change are as follows:

$$\underset{\sim}{J}^*_{l,m+1} = \underset{\sim}{J}_{l,m+1}\left(\frac{dV}{dV^*}\right); \quad 1 \le l \le m \tag{44}$$

$$\underset{\sim}{J}^*_{m+1,l} = \underset{\sim}{I}_k \underset{\sim}{J}_{m+1,l}; \quad 1 \le l \le m \tag{45}$$

$$\underset{\sim}{J}^*_{m+1,m+1} = \underset{\sim}{I}_k \underset{\sim}{J}_{m+1,m+1}\left(\frac{dV}{dV^*}\right) \tag{46}$$

Using Eq. 38,

$$\frac{dV}{dV^*} = \underset{\sim}{I}_r^T + \frac{dV_r^+}{dV^*} \tag{47}$$

and from Eq. 41

$$\frac{dV_r^+}{dV^*} = -\left(\frac{1}{\beta}\right)(\underset{\sim}{I}_r^+ \underset{\sim}{U} \underset{\sim}{I}_j^+)\underset{\sim}{B}^{-1}\underset{\sim}{A}\underset{\sim}{I}_r^T \tag{48}$$

Either or both of the interchanges described above can be made. If more than one is used, then the modifications are made sequentially. A different heat exchange variable, q_k, must be used for each interchange.

SELECTION OF INITIAL VALUES AND STEP LIMITING

It is desirable that the initial values assumed for the iteration variables be reasonably close to the correct values. A good estimate of the temperature distribution can be made by assuming that stages $p - 1$ and $p + 1$ are at the known azeotrope temperature and that stages 1 and n are at the boiling points for the pure components. The remaining temperatures are estimated by linear interpolation. The vapor flow leaving stage $p - 1$ can be estimated by using an overall energy and material balance on column I. The composition $y_{p-1,j}$ can then be calculated because the composition of $y_{p,j}$ is known. The value so calculated must be consistent with the known azeotrope composition for the mixture. A similar procedure can be used for v_{p+1}. The V-phase flows can be estimated assuming constant molal overflow, and the V-phase compositions can be estimated by assuming the reboilers are almost pure components and interpolating between these compositions and the compositions in $p - 1$ and $p + 1$.

The first step in the calculation procedure is to use the initial values of the iteration variables to calculate the noniteration variables, L and $\underset{\sim}{X}$. A check should be made to see if any of these values are negative. If so, the initial estimates must be revised.

It is sometimes necessary to limit the size of the correction calculated by Eq. 16. We cut the correction in half if a temperature change is too large or if a negative vapor composition or negative V-phase flow is calculated. Another check is made after the noniteration variables are calculated in the subsequent step, and if any of them is negative the correction calculated in the previous iteration is cut in half and new values for the iteration variables are calculated.

APPLICATION TO A SAMPLE PROBLEM

The distillation of a butanol-water mixture in the two column system of Figure 1 is used to illustrate the algorithms presented above. Column I has seven equilibrium stages, and the condenser-decanter is stage 8. Column II contains stages 9 through 13. The feed enters stage 7 and is liquid at 97°C with 70% butanol (component 1) and 30% water (component 2). The columns are at one atmosphere pressure, and all vapor phases have an activity coefficient of one. Vapor-liquid equilibrium data for the system (Kato et al., 1970) were correlated using the modified Wilson equation. The interaction coefficients were obtained by a least squares method.

$$\xi_{12} = 3593.94 \text{ J/mol}$$

$$\xi_{21} = 498.86 \text{ J/mol}$$

The derivatives of the activity coefficients needed for Eqs. 21 through 23 are given in the Appendix. The condenser is maintained at 93°C, and the phase compositions are known to be 0.5086 and 0.9801 mole fraction water in the V-phase and L-phase (Weast, 1978). The enthalpy of mixing is assumed small compared to the latent heat. Physical properties of butanol were taken from Counsell et al. (1965).

The phase compositions in the condenser are known, but it would require a modification of the correction algorithm to

TABLE 2. SOLUTION FOR SAMPLE PROBLEM

Flow is in kg · mol/h, and heat duties are given in kJ/h.
Feed is 1.0 kg · mol/h to stage 7.

Stage Number	V-Phase		L-Phase		Stage Temp.	Heat Duty
	Flow	Composition	Flow	Composition		
1	0.9792	0.0037	0.7003	0.0006	117.87	42307.4
2	0.9749	0.0135	1.6795	0.0024	117.63	0
3	0.9629	0.0446	1.6752	0.0081	116.88	0
4	0.9390	0.1321	1.6632	0.0261	114.66	0
5	0.9174	0.3154	1.6393	0.0760	109.51	0
6	0.9186	0.5346	1.6177	0.1792	102.12	0
7	0.9316	0.6665	1.6190	0.3036	96.83	0
8	0.6319	0.5086	0.3352	0.9801	93.00	−41000.3
9	0.0355	0.8159	0.3364	0.9852	94.73	0
10	0.0367	0.8683	0.3375	0.9914	96.31	0
11	0.0378	0.9267	0.3387	0.9960	97.99	0
12	0.0390	0.9685	0.3394	0.9984	99.15	0
13	0.0398	0.9902	0.2997	0.9995	99.74	1632.2

TABLE 3. ERROR NORMS FOR SAMPLE PROBLEM WITH TEMPERATURE OF THE CONDENSER FIXED

Iteration	Composition, σ_1	Energy Balance, σ_2, kJ/h
1	0.4853	0.2120E+4
2	0.6052E−1	0.4150E+2
3	0.1074E−2	0.3687
4	0.1858E−5	0.1352E−2

TABLE 4. ERROR NORMS FOR SAMPLE PROBLEM WITH CONDENSER TEMPERATURE FIXED AND PRODUCT FLOW FROM STAGE 1 FIXED

	Error Norms	
Iteration	Equilibrium, σ_1	Energy Balance, σ_2, kJ/h
1	0.4898	0.2130E+4
2	0.6895E−1	0.4812E+2
3	0.3016E−1	0.1580E+2
4	0.1157E−1	0.2828
5	0.3616E−4	0.1016E−1

include this information. It is just as convenient to use the known phase compositions to calculate an equilibrium ratio for each component in stage 8. These are 24.69 for butanol and 0.5189 for water. The equilibrium error Eq. 12 for stage 8 is written as $e_8^j = y_{8j} - (\lambda_{8j}/\gamma_{8j})x_{8j}$ where the quantity in parentheses is the equilibrium ratio. In calculating the Jacobian, the activity coefficients and fugacity ratios for stage 8 are assumed to be constant.

In the first case to be considered, the temperature in stage 8 is fixed at 93°C and the heat exchange variable, q_8, becomes a dependent variable. All other heat exchanges are fixed with values given in Table 2. The initial conditions listed in Table 1 were used. Temperatures were obtained by linear interpolation, and V-phase flows were estimated assuming constant molal overflow. V-phase compositions were estimated using smaller changes near the ends of each column than in the center. Heat duties for stages 1 and n are consistent with the flows and feed condition. The correction algorithm was modified to fix t_8 and calculate q_8.

The solution to the sample problem is shown in Table 2. Four iterations were required, and the error norms for each iteration are shown in Table 3. It is evident that convergence is quadratic with the norms roughly squaring near the solution. A norm of 2 E-6 in equilibrium error corresponds to an average error of approximately 5.5E-7 in the equilibrium relations, and a value of 1.4E-3 in the energy balance error norm to an average error of approximately 0.41 J/h.

It was observed from results using other sets of initial conditions that the number of iterations required for solution was not very sensitive to the initial temperature distribution but was sensitive to the assumed V-phase flows and compositions, especially to the assumed values for v_8 and $y_{8,2}$. The computer time required for the sample problem was 5.99 s using the University of Pittsburgh DECsystem-1099.

It is evident from Table 2 that the phase compositions in stage 8 are the correct equilibrium compositions. This is a useful check on the accuracy of the calculations because these compositions were not used directly in the model. Instead, equilibrium ratios calculated from the compositions were used. The vapor flow from stage 7 is high because the temperature of the feed is higher than the temperature on stage 7.

The values obtained for the product flow rates, l_1 and l_{13}, are determined by the values selected for the independent variables. As mentioned earlier it is usually preferable to fix the product flows. As a second example, we repeat the sample problem with all conditions the same except that l_1 is an independent variable and q_1 is a dependent variable. In order to keep the solution the same as shown in Table 2, l_1 was fixed at 0.7003. Since l_1 is not an iteration variable, it is necessary to make one of the V-phase flows a noniteration variable as described above. The choice is not a free one because from Eq. 43 it can be seen that β, the jr element of $(\underline{B}^{-1}\underline{A})$, must be nonzero. In this case j is 1, and examination of the first row of $(\underline{B}^{-1}\underline{A})$ shows that only the seventh column is nonzero, so v_7 must become the noniteration variable. Using the same starting conditions as before and the modifications to the correction algorithm given by Eqs. 32, 39, and 44-46 the solution shown in Table 2 was obtained, as expected. Intermediate values were of course different, and the error norms are given in Table 4. The rate of convergence in Table 4 is somewhat slower than for Table 3, but it is evident that it is quadratic as it should be if the modification technique is correct. The computer time for this case was 9.58 s. In obtaining the results shown in Tables 3 and 4, we calculated the Jacobian matrix for each iteration.

NOTATION

General: A lower case symbol is a scalar. An upper case symbol is a column vector. An upper case symbol with a superscript is a column vector formed by removing the column indicated by the superscript from the matrix with the same name. Underlined upper case symbols are matrixes. If a symbol is defined as a vector then when underlined, it represents a diagonal matrix with the same elements as the vector. A matrix with a superscript is always a diagonal matrix.

$\underline{A}$ = V-phase distribution matrix: $a_{ii} = -1$, a_{ij} = fraction of total V-phase leaving stage j which goes to stage i
$\underline{B}$ = L-phase distribution matrix: $b_{ii} = -1$, b_{ij} = fraction of total L-phase leaving stage j which goes to stage i
$\underline{C}$ = correction matrix. Columns defined by Eqs. 18 to 20
$\underline{E}$ = error matrix. Columns defined by Eqs. 12 to 14
$\underline{F}$ = feed matrix: f_{ij} is the total feed of component j to stage i
G = V-phase enthalpy vector: g_i is enthalpy of V-phase in stage i
H = L-phase enthalpy vector: h_i is enthalpy of L-phase in stage i
$\underline{I}$ = identity matrix
$\underline{I}_j$ = identity matrix with row j removed; $(n - 1)$ rows, n columns
$\underline{I}_j^+$ = matrix in which each element is zero except for element jj which is +1
$\underline{J}$ = Jacobian matrix. Defined by Eqs. 21 through 31
$\underline{K}$ = fugacity ratio matrix: k_{ij} is the fugacity ratio of component j in stage i
L = L-phase flow vector: l_i is flow rate of L-phase leaving stage i
L_j^+ = vector with each element zero except element j which is l_j
m = number of components
n = number of stages
P = pressure vector: p_i is pressure in stage i
Q = heat duty vector: q_i is heat interchange between stage i and the surroundings
Q_f = feed enthalpy vector: q_{fi} is the enthalpy of feed entering stage i
r = gas constant, J/mol · °K
T = temperature vector: t_i is the temperature in stage i, °K
U = vector in which each element is 1.0
$\underline{U}$ = matrix in which each element is 1.0
V = V-phase flow vector: v_i is flow rate of V-phase leaving stage i
V_j^+ = vector with each element zero except element j which is v_j
$\underline{X}$ = L-phase composition matrix: x_{ij} is mole fraction of component j in L-phase in stage i

$\underset{\sim}{Y}$ = V-phase composition matrix: y_{ij} is the mole fraction of component j in the V-phase in stage i
β = rj element of $(\underset{\sim}{B}^{-1})\underset{\sim}{A}$: j is the number of the L-phase variable being fixed, and r is the number of the V-phase variable which becomes a noniteration variable
$\underset{\sim}{\Gamma}$ = activity coefficient matrix for V-phase: γ_{ij} = activity coefficient for component j in V-phase in stage i
δ_{kl} = Dirac delta function; $\delta_{kl} = 1$ if $k = l$, otherwise it is zero
ν = iteration number
ξ_{jk} = interaction energy between the j-k pair of components
ρ_{ijk} = molar volume of component j divided by molar volume of component k in stage i
σ_1, σ_2 = Euclidean error norms, defined by Eqs. 15 and 16
$\underset{\sim}{\Lambda}$ = activity coefficient matrix for L-phase: λ_{ij} = activity coefficient for component j in L-phase in stage i
ω_{ijk} = modified Wilson parameter between the j-k pair of components in stage i

Superscripts

$*$ = a modified vector or matrix obtained by eliminating one or more rows and/or columns
T = matrix transpose

APPENDIX

The modified Wilson Equation (Tsuboka and Katayama, 1975) was used for calculation of activity coefficients for the liquid phase. The derivatives of the activity coefficient with respect to composition and temperature are needed in the calculation of the Jacobian matrix. The partial derivatives for stage i are as follows.

$$\begin{aligned}\frac{d\lambda_{ij}}{dt_i} = -\Bigl(\frac{\lambda_{ij}}{rt_i^2}\Bigr)\Bigl(\sum_k^m (x_{ik}\omega_{ikj}\xi_{kj}) \Big/ \sum_k^m (x_{ik}\omega_{ikj}) \\ + \sum_k^m \Bigl(x_{ik}\omega_{ijk} \sum_l^m x_{il}\omega_{ilk}(\xi_{jk} - \xi_{lk}) \Big/ \\ \Bigl(\sum_l^m (x_{il}\omega_{ilk})\Bigr)^2\Bigr) - \sum_k^m \Bigl(x_{ik}(d\rho_{ikj}/dt_{i-}\Bigr)\Big/\sum_k^m (x_{ik}\rho_{ikj}) \\ - \sum_k^m \Bigl((x_{ik}(d\rho_{ijk}/dt_i)\Bigl(\sum_l^m (x_{il}\rho_{ilk})\Bigr) - x_{ik}\rho_{ijk}\sum_l^m \\ (x_{il}(d\rho_{ilk}/dt_i))\Bigr)\Big/\Bigl(\Bigl(\sum_l^m (x_{il}\rho_{ilk})\Bigr)^2\Bigr)\Bigr) \qquad \text{(A-1)}\end{aligned}$$

$$\begin{aligned}d\lambda_{ij}/dx_{ik} = -\lambda_{ij}\Bigl(\omega_{ikj}\Big/\sum_l^m (x_{il}\omega_{ilj}) \\ + \sum_l^m \Bigl(\Bigl(\omega_{ijk}\delta_{lk}\Bigl(\sum_p^m (x_{ip}\omega_{ipl})\Bigr) \\ - x_{il}\omega_{ijl}\omega_{ikl}\Bigr)\Big/\sum_p^m (x_{ip}\omega_{ipl})\Bigr)^2\Bigr) - \rho_{ikj}\Big/\sum_p^m (x_{ip}\rho_{ipj}) \\ - \sum_l^m \Bigl(\Bigl(\omega_{ijk}\delta_{lk}\Bigl(\sum_p^m (x_{ip}\rho_{ipl})\Bigr) - x_{il}\omega_{ipl}\omega_{ikl}\Bigr)\Big/ \\ \Bigl(\sum_p^m (x_{ip}\rho_{ipl})\Bigr)^2\Bigr)\Bigr) \qquad \text{(A-2)}\end{aligned}$$

where

ω_{ijk} = the modified Wilson parameter between the j-k pair of component in stage i and defined by:

$$\omega_{ijk} = \rho_{ijk} \exp(-\xi_{jk}/rt_i)$$

ρ_{ijk} = molar volume of component j divided by molar volume of component k in stage i

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Asymptotic Expansions for the Description of Gas Bubble Dissolution and Growth

R. S. SUBRAMANIAN

and

M. C. WEINBERG

Jet Propulsion Laboratory
Materials Research and Technology Group
California Institute of Technology
Pasadena, CA 91103

A new asymptotic expansion is presented to describe the dissolution or growth of an isolated, stationary gas bubble in a liquid. With the exception of long times, bubble radii calculated via this expansion are in excellent agreement with values obtained by numerical methods over a wide range of gas under(super)-saturations.

SCOPE

Even the simplest problem of mass transport between a gas bubble and the surrounding liquid, namely that of the dissolution (growth) of an isolated, stationary gas bubble in an isothermal, isobaric, liquid of infinite extent is complex. Although the governing equations are well known, exact solutions cannot be obtained in general because of the motion of the

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Correspondence concerning this paper may be addressed to R. S. Subramanian, Department of Chemical Engineering, Clarkson College of Technology, Potsdam, New York 13676.

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