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# Numerical Solution of Nonequilibrium Multicomponent Mass Transfer Operations

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**An improved model and solution procedure for nonequilibrium, multicomponent, two-phase, steady-state mass transfer problems are developed. Processes as diverse as packed column operation and the drying of porous solids are included. Ideas such as "HETP," "HTU" or "mass transfer section" are avoided. "Stiff" systems appear to be handled well.**

## SCOPE

**This paper proposes a model and solution procedure for steady state continuous contact mass transfer problems as diverse as nonequilibrium operation of packed columns and the drying of porous media. Included are all the features listed as items (a) through (g). Such a combination represents an advance over previous work.**

**(a) Energy, mass and momentum are each required to be conserved in each phase.**

**(b) Equations of state are nontrivial in each phase.**

**(c) A multicomponent system is considered.**

**(d) Phase temperatures, velocities and concentrations are not assumed constant.**

**(e) Transfer coefficients for mass, energy or momentum are assumed neither constant nor equal for all components.**

**(f) One phase at some place in the unit is not assumed to be in equilibrium with the other phase at some other place in the unit.**

**(g) The problem of obtaining a numerical solution is addressed.**

**The model is sufficiently detailed and realistic to be representative of the best currently available.**

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**The solution procedure in effect eliminates all unknown compositions at the outset. Piecewise polynomial approximations together with Newton-Raphson iteration are used to integrate the nonlinear differential equations in the model. All elements of the required Jacobian matrix are computed analytically. The linear differential equations produced in each iteration are solved by collocation using B-spline basis functions. Tests show this procedure effective in obtaining solutions for this model even when certain of the equations are "stiff."**

**The question of initial estimates is not addressed. Although the model may be extended to two or three space dimensions this aspect is not addressed either.**

## CONCLUSIONS AND SIGNIFICANCE

**The most important conclusion was that the solution to the convective diffusion equations—that is, the mass conservation equations for each component—needs to have a particular property. At collocation points, it must approximate nicely not only the component's vapor and liquid mole fractions but the first derivatives thereof as well. When this is done, convergence can be achieved in less than 10 iterations starting from machine generated initial values. Conversely, when even first derivatives of the mole fractions are badly approximated at collocation points, the numerical problem is more nonlinear than required by the physics involved. As the effective diffusivities become small this condition is aggravated, and convergence is more difficult to achieve.**

**The significance of this work is twofold. First all relevant conservation equations for each phase are included in one model together with a nonideal equation of state for each phase. Second a major source of numerical difficulty in "stiff" mass transfer problems is identified and a solution procedure developed to minimize the difficulty.**

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## INTRODUCTION

Steady state operation of continuous contact units has been most frequently analyzed under assumptions that the phase flows, temperatures and concentrations as well as eddy diffusivities and overall mass transfer coefficients are constant throughout the unit. Such assumptions linearize the problem so that analytical solutions are available for example, Hartland and Mecklenburgh, 1966; Hartland, 1970; Mickley, et al. 1957; Miyauchi and Vermeulen, 1963; Sleicher, 1959, 1960; Wilburn, 1964. When such assumptions are invalid, the approaches have been to resort to notions such as "HETP" or "HTU" (Emmert and Pigford, 1963; Sherwood and Pigford, 1952; Holland et al., 1970; Bassyoni et al., 1970; McDaniel et al., 1970) together with some simple numerical integration technique combined with a direct iteration procedure. It is clear that these ideas possess the inherent weaknesses that:

(a) The "HETP" is not the same for all components.

(b) Liquid at one point in the column is assumed to be in equilibrium with vapor at that or some other point in the column.

Numerical instability and failure to converge often further limit the usefulness of these models.

The model developed here is presented in terms of packed columns but is valid for a wider class of processes (Lyczkowski, 1979). Ideas such as "HETP," "HTU" or "mass transfer section" are not invoked. Rather a component mass transfer rate proportional to the departure from equilibrium is assumed. The eddy diffusivities, mass and heat transfer coefficients, friction factors (momentum transfer coefficients), enthalpies, thermal conductivities and equilibrium ratios for each component are assumed independent of composition but may be functions of pressure and of phase velocity, concentration and temperature. Thus each of the component variables may possess a derivative with respect to position in the column. A formulation somewhat similar to that used here has been employed by Liles and Reed (1978); however, they use finite difference approximations and require neither the energy nor the momentum to be conserved in each phase. Furthermore those authors assume both phases to have the same temperature.

Certain of the unknown functions will be classed as primary variables or iteration variables. They may also be referred to as the unknown profiles when no confusion arises. In general there will be eight or nine primary variables. These will be the concentration, temperature and velocity of each phase, the pressure, the cross section area occupied by the vapor and when desirable the interfacial area.

The next section covers the mass, energy and momentum conservation equations used in this model. Boundary value relations are also presented in this section. There follows a section devoted to the vapor and liquid equations of state employed in the model. Next is a section summarizing the correlations for interfacial area, enthalpies and equilibrium ratios. The section after this is devoted to the elimination of unknown compositions using the proposed collocation procedure. Following this a section describes how Newton-Raphson iterations are incorporated. The last section briefly covers numerical results using four test problems, two of which were "stiff."

## CONSERVATION EQUATIONS

Equations stating conservation of mass, energy and linear momentum are developed by Gray (1975), by Whitaker (1966, 1967) and in standard texts such as Bird, Stewart and Lightfoot (1960). One considers two-phase, steady-state, countercurrent flow and assumes adiabatic operation. Vapor-liquid heat and momentum transfer coefficients for a phase are taken to be linear combinations of component transfer coefficients. These are in turn assumed proportional to vapor phase concentration and that factor, $C_V$, is shown explicitly.

(a) Continuity (convective diffusion) equations for each component, $i$:

$$(A_V C_V(u_V y_i - E_{iV} y'_i))' \equiv \phi'_{iV} = -A\ r_i \equiv -A(r_i^I)' \qquad (1)$$

$$((A - A_V)C_L(u_L x_i - E_{iL} x'_i))' \equiv \phi'_{iL} = A\ r_i \equiv A(r_i^I)' \qquad (2)$$

$$(r_i^I)' \equiv r_i = (y_i - K_i x_i)k_i a \qquad (3)$$

$$\Sigma_i y_i = 1 = \Sigma_i x_i \qquad (4)$$

(b) Conservation of energy:

$$\Sigma_i\{A_V(C_V(u_V y_i - E_{iV} y'_i)H_i - y_i \kappa_{iV} T'_V)\}'$$
$$= -(T_V - T_L)C_V A a \Sigma_i g^*_i y_i - \Sigma_i \begin{cases} A h_i r_i\ , & r_i < 0 \\ A H_i r_i\ , & r_i \geq 0 \end{cases} \qquad (5)$$

$$\Sigma_i\{(A - A_V)(C_L(u_L x_i - E_{iL} x'_i)h_i - x_i \kappa_{iL} T'_L)\}'$$

$$= (T_V - T_L)C_V Aa\Sigma_i g^*_i y_i + \Sigma_i \begin{cases} Ah_i r_i \ , & r_i < 0 \\ AH_i r_i \ , & r_i \geq 0 \end{cases} \quad (6)$$

$$(A_S \kappa_S T'_S)' = (T_S - T_V)Aa_{SV}g^*_{SV} + (T_S - T_L)Aa_{SL}g^*_{SL} \quad (7)$$

Terms $A_V u_V P'$ and $(A - A_v)u_L P'$ are not significant in the case of packed columns. These terms would appear on the right sides of Eqs. 5 and 6 respectively when for instance drying of porous media were modeled (Lyczkowski, 1979). The same is true for terms $(T_S - T_V)Aa_{SV}g^*_{SV}$ and $(T_S - T_L)Aa_{SL}g^*_{SL}$ which account for heat transmission through the packing. Thus the $\kappa_{iL}$ implicitly account for heat conduction in both liquid and packing.

Terms representing internal energy dissipation due to viscous effects have been dropped. Packing temperature, $T_S$, is not of interest here; hence, Eq. 7 is dropped.

(c) Conservation of linear momentum:

$$\begin{aligned} \Sigma_i m_i(A_V C_V y_i u^2_{iV})' = {} & -(A_V P_V)' + (C_V \Sigma_i m_i y_i)(gA \\ & - u^2_V a_{SV} A f^*_{SV} \\ & - (u_V - u_L)^2 Aaf^*) - \Sigma_i \begin{cases} m_i A u_{iL} r_i \ , & r_i < 0 \\ m_i A u_{iV} r_i \ , & r_i \geq 0 \end{cases} \end{aligned} \quad (8)$$

$$\begin{aligned} \Sigma_i m_i((A - A_V)C_L x_i u^2_{iV})' = {} & (u_V - u_L)^2 C_V aAf^* \Sigma_i m_i y_i \\ & - ((A - A_V)P)' + (\Sigma_i m_i x_i)((A - A_V)C_L g \\ & + u^2_L A a_{SL} f^*_{SL}) + \Sigma_i \begin{cases} m_i A u_{iL} r_i \ , & r_i < 0 \\ m_i A u_{iV} r_i \ , & r_i \geq 0 \end{cases} \end{aligned} \quad (9)$$

with

$$\left. \begin{aligned} u_{iV} &= C_V(u_V y_i - E_{iV} y'_i)/(C_V y_i) \\ u_{iL} &= C_L(u_L x_i - E_{iL} x'_i)/(C_L x_i) \end{aligned} \right\} \quad (10)$$

Bearman and Kirkwood (1958) have shown via statistical mechanics that the component velocities $u_{iV}$ and $u_{iL}$ are actually meaningful. The diffusional contribution to momentum will be neglected. Hence we assume

$$u_{iV} = u_V \ , \ u_{iL} = u_L \quad (11)$$

Terms involving viscous stresses have been absorbed in the terms containing momentum transfer coefficients in Eqs. 8 and 9.

Equations 1 through 9 are subject to boundary conditions determined by the particular system to which they are applied. A multicomponent system fed at each end and without side draws or side feeds is assumed. The reflux ratio, $R \geq 0$, is specified from a total condenser. The total flow rate of the bottom or distillate product stream is specified as is the complete state of each feed stream. This configuration together with an analysis similar to that of Danckwerts (1953) or of Wehner and Wilhelm (1956) gives rise to the following boundary conditions. See also Hlavacek et al. (1979). Of these Eq. 12, 13, 16 and 17 express continuity of fluxes of mass and energy in the vapor phase at the bottom of the unit and in the liquid phase at the top of the unit.

$$\phi_{iV}(0) = f_{i0} = -A\ r^l_i(0) \quad (12)$$

$$\phi_{iL}(\text{top}) = -f_{iL} - R\phi_{iV}(\text{top}) \quad (13)$$

$$y'_i(\text{top}) = 0 = x'_i(0) \quad (14)$$

$$T'_V(\text{top}) = 0 = T'_L(0) \quad (15)$$

$$\Sigma_i(\phi_{iV} H_i - A_V y_i \kappa_{iV} T'_V)|_0 = F_0 H_{F0} \quad (16)$$

$$\Sigma_i(\phi_{iL} h_i - (A - A_V)x_i \kappa_{iL} T'_L)|_{\text{top}} = -F_L H_{FL} - R\Sigma_i(\phi_{iV} h_{iF})|_{\text{top}} \quad (17)$$

$$P(\text{top}) = \text{specified value} \quad (18)$$

$$A_V(\text{top}) = \text{specified value} \quad (19)$$

The boundary condition on $A_V$ will in practical problems be determined by specifying the flow rate of overhead product, or distillate, $D$. This is equivalent to a specification of $A_V$ when the problem is otherwise completely determined since one has

$$\frac{D}{(1 - R)} = \Sigma_i \phi_{iV}(\text{top}) = \Sigma_i (A_V C_V u_V y_i)|_{\text{top}} = (A_V C_V u_V)|_{\text{top}} \quad (20)$$

Boundary conditions on momentum flux and on phase concentrations have been omitted as redundant. Among Eqs. 4 through 9 there are four differential equations excluding Eq. 7. Hence boundary conditions may be assigned to exactly four quantities other than mole fractions. It is more desirable to specify boundary conditions for $A_V$ and for pressure than for momentum fluxes.

Since $\Sigma_i E_{iV} y_i = 0 = \Sigma_i E_{iL} x_i$ (Bird, Stewart and Lightfoot, 1960, p. 501) one may sum Eqs. 13 and 14 over components and find with the aid of Eqs. 4

$$\left. \begin{aligned} (A_V C_V u_V)|_0 &= F_0 \\ (A - A_V)C_L u_L|_{\text{top}} &= -F_L - (RA_V C_V u_V)|_{\text{top}} \end{aligned} \right\} \quad (21)$$

Thus, the vapor phase flow at the bottom of the unit and the liquid phase flow at the top are each required to be continuous by the boundary conditions on mole fractions. Equations 21 are implicit boundary conditions on $C_V$ and $C_L$.

## EQUATIONS OF STATE

References cited by Prausnitz (1969) and Winnick (1975) attest to the wide selection available. The form employed here for the vapor equation of state will accommodate those proposed by Beret and Prausnitz (1975), Boublik (1975, 1974, 1970), Carnahan and Starling (1972, 1969), Mansoori et al. (1971), Reed and Gubbins (1973) and Redlich and Kwong (1949). Horvath (1974) provides more recent references on the Redlich-Kwong equation.

$$\frac{P}{R_G T_V C_V} = \frac{1 + \theta_1 C_V + \theta_2 C^2_V - \theta_3 C^3_V}{(1 - \theta_0 C_V)^3} - \frac{\theta_5 C_V}{(1 + \theta_4 C_V)T^{1.5}_V} \quad (22)$$

where the mixing rules result in $\theta_m = \theta_m(T_V, C_V, y_i, x_i)$. For a perfect gas all the $\theta_m$ are zero. For demonstration the following formulae are used.

$$\left. \begin{aligned} \theta_0 &= \theta_4 = 4\theta_1 \\ \theta_1 &= \Sigma_i \frac{0.0867\ R_G T_{ci}}{4P_{ci}} y_i \\ \theta_2 &= \theta^2_1 \\ \theta_3 &= \theta^3_1 \\ \theta_5 &= \Sigma_i \frac{0.4278\ R^2_G T^{2.5}_{ci}}{P_{ci}} y_i \end{aligned} \right\} \quad (23)$$

These choices for the $\theta_m$ follow those of Carnahan and Starling (1972) and of Horvath (1974) except for $\theta_5$. This quantity should actually be the square of the sum over components with the square roots of the indicated coefficients of the $y_i$ replacing the coefficients shown.

Beret and Prausnitz (1975) report their proposed equation of state provides good liquid densities. Consequently it could be used as the liquid of state here. Since Eq. 22 embraces their equation it would only be necessary to replace $C_V$ by $C_L$ in Eq. 22 and probably replace some of Eqs. 23.

The model used here simply employs another of the available correlations, namely that of Yen and Woods (1966) for saturated liquid densities. Thus the effect on liquid density of the difference between system pressure and saturation pressure is neglected. One has from Yen and Woods (1966)

$$
\begin{aligned}
C_L &= (1 + (1 - T_r)^{1/3}A^* + (1 - T_r)^{2/3}E^* \\
&\qquad + (1 - T_r)^{4/3}G^*)/V_c \\
V_c\Sigma_i x_i &= \Sigma_i x_i V_{ci} \\
T_c\Sigma_i x_i &= \Sigma_i x_i T_{ci} \\
T_r &= T_L/T_c = T_L(\Sigma_i x_i) \div \Sigma_i x_i T_{ci} \\
A^* &= 17.4425 - 214.578\, z_c \\
&\qquad + 989.625\, z_c^2 - 1522.06\, z_c^3 \\
E^* &= -3.28257 + 13.6377\, z_c \\
&\qquad + 107.4844\, z_c^2 - 384.211\, z_c^3 \\
&\qquad z_c \le 0.26 \\
E^* &= 60.2091 - 402.063\, z_c + 501.0\, z_c^2 + 641.0\, z_c^3 \\
&\qquad z_c > 0.26 \\
G^* &= 0.93 - E^* \\
z_c\Sigma_i x_i &= \Sigma_i x_i z_{ci} \equiv \Sigma_i x_i P_{ci} V_{ci}/(R_G T_{ci})
\end{aligned}
\tag{24}
$$

The normalizing quantities $\Sigma_i x_i$ are inserted since the $x_i$ will not sum to unity until the iterations have converged.

## CORRELATIONS

A correlation for interfacial area in terms of superficial liquid velocity and of liquid composition has been taken from Treybal (1968, pp. 166-168). This correlation is specific to a packed column. When the model is used for an application such as drying of porous media (Lyczkowski, 1979) an interfacial area correlation appropriate to that system must be employed. The relations given in Treybal are placed in the form of Eq. 25. In addition the values of $\epsilon = 0.73$ and $A_S = 58/\epsilon$ have been used for packing porosity and area respectively (Treybal, 1968, p. 162).

$$
a = \frac{(0.274/0.73)L^{1.122}\theta\mu_L^{\nu}(\sigma_L/0.73)^{(0.925-0.262\, 1n\ L)}}{(0.1183\, L^{0.43} - 1)C_L\Sigma_i m_i x_i} \tag{25}
$$

where $L$ denotes superficial liquid velocity, $\mu_L$ is the liquid viscosity expressed in centipoises, $\sigma_L$ is the surface tension expressed in dynes per cm. $L$, $\theta$, $\nu$, $\sigma_L$ and $\mu_L$ are given by

$$
\left.
\begin{array}{lll}
L = |u_L|(A - A_V)/A & & \\
 & \theta & \nu \\
\mu_L < 12 & 0.897 & 0.13 \\
\mu_L \ge 12 & 0.575 & 0.31 \\
\multicolumn{3}{l}{\sigma_L = 30\left(\dfrac{(C_L\Sigma_i m_i x_i) - (C_V\Sigma_i m_i y_i)}{(C_L\Sigma_i m_i x_i)^* - (C_V\Sigma_i m_i y_i)^*}\right)^4} \\
\multicolumn{3}{l}{\mu_L = (6.36835 \div 10^5)C_L \exp(3.8\, \Sigma_i x_i T_{ib} / T_L)}
\end{array}
\right\}
\tag{26}
$$

The $T_{ib}$ and $T_L$ are the absolute normal boiling points and the absolute liquid temperature. Thus Kay's rule has been used to obtain an approximation to the normal boiling point of the liquid phase. The asterisks in the surface tension correlation denote normalizing quantities. In the present work the associated values were regarded as constants and were computed using numbers generated for the middle of the unit to start the first iteration. The viscosity correlation has been taken from Bird, Stewart and Lightfoot (1960, p. 29) while the surface tension correlation has been taken from Glasstone (1946, p. 494).

Since Eq. 25 is explicit in the interfacial area, $a$, that variable may be used as a primary variable or not as convenient. We use it as a primary variable.

According to Treybal (1968, p. 161) pressure-drop data for countercurrent flow of liquid and gas as obtained by various investigators show wide discrepancies. Consequently correlations have not been used for the three momentum transfer coefficients (friction factors), $f^*$. Instead they have been assigned constant values which are here treated as parameters. It would be interesting to use a correlation such as the Ergun equation as modified by Mehta and Hawley (1969) to compute one of the momentum transfer coefficients. One notes that the void fraction, $\epsilon$, in the Ergun equation would be $A_V/(A + A_S)$ if the gas were regarded as a single phase passing through a bed of packing and liquid. The Ergun equation would be written in differential form (Choudhary et al., 1976; Stanek, 1974) for one dimensional flow. This additional relation would permit the vapor-liquid momentum transfer coefficient for instance to be treated as another unknown profile. Alternately a correlation for the fraction of the void volume filled with liquid, $(A - A_V)/A$, such as that of Turpin and Huntington (1967) could be employed.

Equilibrium ratios are required in Eq. 3. Power series curve fit correlations are used for the product of equilibrium ratio with absolute pressure. The form of these

$$
(K_i P)^{1/4} = \sum_{n=0}^{4} \gamma_{in} T_L^n \tag{27}
$$

One notes that such correlations do not guarantee consistency between the vapor and liquid equations of state and the $K$-values.

Correlations for enthalpies used in the energy equations are also of polynomial form, namely

$$
\left.
\begin{aligned}
(H_i)^{1/2} &= \alpha_{i0} + \alpha_{i1}T_V + \alpha_{i2}T_V^2 \\
(h_i)^{1/2} &= \beta_{i0} + \beta_{i1}T_L + \beta_{i2}T_L^2
\end{aligned}
\right\}
\tag{28}
$$

Component vapor enthalpy, $H_i$, will usually be a function of pressure as well as temperature. Anticipating subsequent requirements we note that the derivative of component vapor enthalpy would then be expressed as

$$
H_i' = \frac{\partial H_i}{\partial T_V} T_V' + \frac{\partial H_i}{\partial P} P' \tag{29}
$$

Finally the mass transfer coefficients, $k_i$, the thermal conductivities, $\kappa_{iV}$ and $\kappa_{iL}$, and the effective diffusivities, $E_{iV}$ and $E_{iL}$, are for convenience taken to be constants. It is emphasized that this is not a requirement of the proposed procedure. All quantities which are here assumed constant will normally be expressed by correlations in terms of the primary variables.

## ELIMINATION OF UNKNOWN COMPOSITIONS

The sum of Eqs. 1 and 2 may always be analytically integrated once. Consequently one may obtain their exact solution in the case of variable coefficients (Billingsley, 1979). Unfortunately such a solution is in terms of the matrizant which limits its usefulness.

The numerical solution should satisfy the integrals of Eqs. 1 and 2, which are

$$
\int_0^z \phi_{iV}' dz = -A \int_0^z r_i\, dz = -A\ r_i^l\Big|_0^z \tag{30}
$$

$$
\int_z^{\text{top}} \phi_{iL}' dz = A \int_z^{\text{top}} r_i\, dz = A\ r_i^l\Big|_z^{\text{top}} \tag{31}
$$

By assigning the boundary conditions given by Eqs. 12, Eq. 30 is brought to the more compact form

$$
A_V C_V(u_V y_i - E_{iV} y_i') = \phi_{iV} = -A\ r_i^l \tag{32}
$$

Equation 32 is evaluated at the top of the unit and together with the boundary condition given by Eq. 13 substituted into Eq. 31 to yield

$$
\begin{aligned}
(A - A_V)C_L(u_L x_i - E_{iL} x_i') = \phi_{iL} &= A\ r_i^l \\
&+ (1 - R)(A_V C_V u_V y_i)_{\text{top}} - f_{iL}
\end{aligned}
\tag{33}
$$

where from Eqs. 1 and 14

$$\phi_{iV}(\text{top}) = (A_V C_V u_V y_i)_{\text{top}} \tag{34}$$

Our approximation is also required to satisfy the derivative of Eq. 3, namely

$$(r_i^l)'' = r_i' = (k_i a)y_i' - (K_i k_i a)x_i' + (k_i a)'y_i - (K_i k_i a)'x_i \tag{35}$$

All equations are solved by various forms of the finite element collocation method described by deBoor and Swartz (1973) as extended to systems of equations by Cerutti (1974). The particular variation used to obtain approximate solutions for Eqs. 1-3, 32, 33 and 35 subject to the boundary conditions given by Eqs. 12-14 is a scheme developed for that purpose (Billingsley and Chirachavala, 1979a). Each of the variables $y_i(z)$, $x_i(z)$ and $r_i^l(z)$ will be expanded according to Eqs. 36 over a set of piecewise sixth degree $B$-spline basis functions having two continuous derivatives. These are described by deBoor (1972, 1977). One has for instance

$$y_i = \Sigma_n \lambda_{in}^1 s_n \quad \text{and} \quad x_i = \Sigma_n \lambda_{in}^0 s_n \tag{36}$$

The $s_n = s_n(z)$ are basis functions while the $\lambda_{in}^1$ and $\lambda_{in}^0$ are the expansion coefficients.

The column height is divided into subintervals of not necessarily equal length. The differential equations are collocated at the Gauss-Legendre points in each subinterval (Finlayson, 1972; Villadsen and Michelsen 1968; Strang and Fix, 1973). The total number of these collocation points is $J$; the collocation point index is $j$, $j = 1, 2, \ldots, J$. Gauss-Legendre points do not occur at subinterval end points, and so are interior collocation points in the sense that none of them fall at either end of the bed. The indices $j = 0$ and $j = J + 1$ denote the bottom and top of the bed respectively. Collocation points are denoted by $z_j$ or simply by the index $j$. The degree and continuity of the $B$-splines used here accommodate two Gauss-Legendre points per subinterval since six equations will be collocated at each such point. Specifically

(a) Equations 1, 2 and 35 are to be collocated at all interior collocation points, $0 < j \le J$

(b) Equations 32, 33 and 3 are to be collocated at all collocation points, $0 \le j \le J + 1$

(c) The first of Eqs. 14 is to be collocated at the top of the unit, $j = J + 1$

(d) The second of each of Eqs. 12 and 14 is to be collocated at the bottom of the unit, $j = 0$

This collocation scheme results in all relevant boundary conditions being satisfied (Billingsley and Chirachavala, 1979a, p. 53) and provides a total number of collocation equations equal to the total number of expansion coefficients required for the three unknowns $y_i$, $x_i$ and $r_i^l$. $2J + 3$ coefficients will be required for the expansion of each of these unknowns.

Now define $s_{nj} = s_n(z_j)$ where $0 \le n \le 2J + 2$. Then define

$$S = \begin{pmatrix} s_{2J+2,J+1} & s_{2J+1,J+1} & s_{2J,J+1} & \cdots & s_{1,J+1} & s_{0,J+1} \\ s_{2J+2,J} & s_{2J+1,J} & s_{2J+1,J} & \cdots & s_{1,J} & s_{0,J} \\ & & \cdots & & & \\ s_{2J+2,1} & s_{2J+1,1} & s_{2J-1,1} & \cdots & s_{1,1} & s_{0,1} \\ s_{2J+2,0} & s_{2J+1,0} & s_{2J-1,0} & \cdots & s_{1,0} & s_{0,0} \end{pmatrix}$$

$S^- = S$ with its first and last rows removed.

$S_4^- = S^-$ using quartic $B$-splines with two continuous derivatives.

(37)

Recalling Eqs. 36 one sets

$$\lambda_1^1 = (\lambda_{2J+2}^1, \lambda_{2J+1}^1, \ldots, \lambda_1^1, \lambda_0^1)^T \tag{38}$$

and has corresponding vectors of expansion coefficients $\lambda_i^0$ and $\lambda_i$ and $x_i$ and $r_i^l$ respectively. Let $y_{ij} \equiv y_i(z_j)$. Then write

$$\left.\begin{aligned} y_i^+ &\equiv (y_{i,J+1}, y_{i,J}, \ldots, y_{i,1}, y_{i,0})^T = S\lambda_i^1 \\ y_i^- &\equiv (y_{i,J}, Y_{i,J-1}, \ldots, y_{i,2}, y_{i,1})^T = S^-\lambda_i^1 \end{aligned}\right\} \tag{39}$$

and analogous expressions for $x_i^+$, $x_i^-$, $r_i^{l+}$ and $r_i^{l-}$.

The collocation representations for Eqs. 32, 33, 3, 1, 2 and 35 may now be expressed as a single matrix-vector equation, namely

$$Z_i \begin{pmatrix} \lambda_i^1 \\ \lambda_i^0 \\ \lambda_i \end{pmatrix} = f_i^0 \tag{40}$$

By assumption the quantities in the matrix $Z_i$ depend explicitly only upon the primary variables. The vector $f_i^0$ contains only specified quantities. The manipulations leading to Eq. 40 are available (Billingsley, 1979).

One has

$$\left.\begin{aligned} y_i^- &= (S^-, 0, 0)Z_i^{-1}f_i^0 \\ x_i^- &= (0, S^-, 0)Z_i^{-1}f_i^0 \\ r_i^{l-} &= (0, 0, S^-)Z_i^{-1}f_i^0 \end{aligned}\right\} \tag{41}$$

where 0 denotes an array of zeros which has the same dimensions as $S^-$. The spatial derivatives of $y_i^-$, $x_i^-$ and $r_i^{l-}$ are obtained simply by differentiating $S^-$. That is by replacing $S^-$ in Eqs. 41 by $S^{-\prime}$. It is unnecessary to compute $Z_i^{-1}$ since it is always postmultiplied by a vector say $a_0$. If this product is denoted as the vector $w$ it may be computed as the solution to the linear system $Z_i w = a_0$.

## NEWTON-RAPHSON ITERATION

Equations 41 may in effect be used to eliminate all unknown compositions from the conservation equations for energy (Eqs. 5 and 6) and momentum (Eqs. 8 and 9) as well as from the equations of state (Eqs. 22 and 24), the correlations (Eq. 25) and the requirements that mole fractions sum to unity (Eq. 4). These manipulations are given by Billingsley (1979). By a procedure similar to that employed to assemble Eq. 40 one obtains the nonlinear vector equation

$$w(\chi) = w(\chi, y_i^-(\chi), x_i^-(\chi), r_i^{l-}(\chi)) = c_{\text{known}} \tag{42}$$

where $c_{\text{known}}$ is a vector of zeros and specified elements, and the vector $\chi$ is defined by

$$\begin{aligned} \chi \equiv (&C'_{V,J}, C_{V,J}, C_{V,J-1}, \ldots, C_{V,1}, C_{L,J}, C_{L,J-1}, \ldots, \\ &C_{L,1}, C'_{L,1}, T'_{V,J}, T'_{V,J-1}, T_{V,J}, T_{V,J-1}, \ldots, T_{V,1}, \\ &T'_{V,2}, T'_{V,1}, T'_{L,J}, T'_{L,J-1}, T_{L,J}, T_{L,J-1}, \ldots, T_{L,1}, \\ &T'_{L,2}, T'_{L,1}, u'_{V,J}, u_{V,J}, u_{V,J-1}, \ldots, u_{V,1}, u_{L,J}, \\ &u_{L,J-1}, \ldots, u_{L,1}, u'_{L,1}, a_J, a_{J-1}, \ldots, a_1, a'_1, A'_{V,J}, \\ &A_{V,J}, A_{V,J-1}, \ldots, A_{V,1}, A'_{V,1}, P'_J, P_J, P_{J-1}, \ldots, P_1)^T \end{aligned} \tag{43}$$

Newton-Raphson iterations are performed on Eq. 42 using $\chi$ as the unknown vector. Since $w(\chi)$ contains first and second derivatives of various elements of $\chi$ it is necessary to relate these derivatives to $\chi$ itself. Accordingly, one expands the primary variables over different sets of $B$-spline basis functions as indicated by Table 1.

Let $S_{CV}^-$, $S_{CL}^-$, $S_{TV}^-$, $S_{TL}^-$, $S_{uV}^-$, $S_{uL}^-$, $S_a^-$, $S_{AV}^-$ and $S_P^-$ denote matrices defined as is $S^-$ in Eqs. 37 but formed using the basis functions employed, according to Table 1, for the variable indicated by the subscript. These matrices will have the same number of rows as $S^-$ but will have only about half as many columns. Thus the first subscripts in the first columns will be on the order of $J$. Let $Q$ stand for any of $CV$, $CL$, $\ldots$, $P$ and define

$$S_Q^+ = \begin{pmatrix} \text{first row of } (S_Q^-)' \\ S_Q^- \end{pmatrix}$$

$$S_{Q+} = \begin{pmatrix} S_Q^- \\ \text{last row of } (S_Q^-)' \end{pmatrix}$$

TABLE 1. BASIS FUNCTION SPECIFICATIONS FOR ITERATION VARIABLES

| Variable | $C_V$ | $C_L$ | $T_V$ | $T_L$ | $u_V$ | $u_L$ | $a$ | $A_V$ | $P$ |
|---|---|---|---|---|---|---|---|---|---|
| Spline degree | 2 | 2 | 3 | 3 | 2 | 2 | 2 | 3 | 2 |
| No. cont. derivs. | 0 | 0 | 1 | 1 | 0 | 0 | 0 | 1 | 0 |
| Extra splines[1] | no | no | yes | yes | no | no | no | no | no |
| No. of *b.c.*[2] | 0 | 0 | 2 | 2 | 0 | 0 | 0 | 1 | 1 |
| Additional iter. variables[3] | $C'_{VJ}$ | $C'_{L0}$ | $T'_{VJ}$<br>$T'_{VJ-1}$<br>$T'_{V2}$<br>$T'_{V1}$ | $T'_{LJ}$<br>$T'_{LJ-1}$<br>$T'_{L2}$<br>$T'_{L1}$ | $u'_{VJ}$ | $u'_{L0}$ | $a'_0$ | $A'_{VJ}$<br>$A'_{V0}$ | $P'_J$ |

---

Notes (BC indicates Billingsley and Chirachavala, 1979a, b):

[1] "Extra splines" denotes two additional quartic spline basis functions having two continuous derivatives. One of these is nonzero at $j = 0, 1$ and zero for $j > 1$. The other is zero for $j < J$ and nonzero at $j = J, J + 1$ (BC).

[2] "*b.c.*" denotes boundary conditions.

[3] "Additional iter. variables" denotes items which are to be iterated upon in addition to the profile values at all interior collocation points. The number of interior collocation points plus the number of additional iteration variables equals the number of spline basis functions for the profile in question (BC).

TABLE 2. NUMBER OF ITERATIONS FOR CONVERGENCE

| Problem | I | II | III | IV |
|---|---|---|---|---|
| Iterations | 9 | 9 | 6 | 4 |

$$S^+_{Q4} = ((\text{first column of } S^-_4),\ S^-_Q,\ (\text{last column of } S^-_4))$$

$$S^+_{Q+} = \begin{pmatrix} \text{first two rows of } (S^+_{Q4})' \\ S^+_{Q4} \\ \text{last two rows of } (S^+_{Q4})' \end{pmatrix} \tag{44}$$

Let $\sigma$ denote the vector of expansion coefficients for $C_V$. With $S^+_{CV}$ defined according to the first of Eqs. 44 one verifies that

$$\left.\begin{aligned} (C'_{V,J}, C_{V,J}, C_{V,J-1}, \ldots, C_{V,1})^T &= S^+_{CV}\,\sigma \\ (C''_{V,J}, C'_{V,J}, C'_{V,J-1}, \ldots, C'_{V,1})^T &= S^{+\prime}_{CV}\sigma \end{aligned}\right\} \tag{45}$$

and thus since $S^+_{CV}$ is a square matrix

$$\begin{aligned} &(C''_{V,J}, C'_{V,J}, C'_{V,J-1}, \ldots, C'_{V,1})^T \\ &\quad = S^{+\prime}_{CV}(S^+_{CV})^{-1}(C'_{V,J}, C_{V,J}, C_{V,J-1}, \ldots, C_{V,1})^T \end{aligned} \tag{46}$$

Define $S_0$ as the block diagonal matrix having $S^+_{CV}$, $S_{CL+}$, $S^+_{TV+}$, $S^+_{TV+}$, $S^+_{uV}$, $S_{uL+}$, $S_{a+}$, $S_{AV+}$ and $S^+_P$ as its diagonal blocks. $S_0$ is not used in computation but only to describe the procedure. Denote the $m$'th derivative with respect to $z$ by the superscript $(m)$. Then in the same way that Eq. 46 was derived one may show that

$$\chi^{(m)} = S_0^{(m)} S_0^{-1}\,\chi,\ \ m = 0, 1, 2 \tag{47}$$

Using Eq. 47 the vector Eq. 42 may be expanded about the current estimate of $\chi$ and its derivatives to provide

$$\begin{aligned} c_{\text{known}} - w(\chi) &= \frac{\partial w}{\partial \chi}\,\Delta\chi + \frac{\partial w}{\partial \chi'}\,\Delta\chi' + \frac{\partial w}{\partial \chi''}\,\Delta\chi'' \\ &= \left(\frac{\partial w}{\partial \chi} + \left\{\frac{\partial w}{\partial \chi'}\,S'_0 + \frac{\partial w}{\partial \chi''}\,S''_0\right\} S_0^{-1}\right)\Delta\chi \end{aligned} \tag{48}$$

where for instance $\partial w/\partial\chi'$ denotes the Jacobian matrix of a vector $w$ with respect to $\chi'$. The element in row $m$ and column $p$ in this matrix is the partial derivative of the $m$'th element of $w$ with respect to the $p$'th element of $\chi'$. Repeated application of Eq. 48 constitutes the Newton-Raphson iteration procedure. Equations for the requisite partial derivatives are obtained by straightforward partial differentiation of various equations previously obtained (Billingsley, 1979).

## NUMERICAL DEMONSTRATION

Four test problems, in which the packing is assumed to be completely wetted, have been used in this work. The data for these problems together with graphs of their primary variables are available in Billingsley and Chirachavala, 1979b. Test problems I and II were constructed to be "stiff" problems representative of what would be computationally very difficult packed column models. Test problems III and IV were taken from McDaniel (1968, 1970) in so far as his data went. McDaniel's data came from operating packed columns in a commercial plant. Each problem was approximated using four subintervals of equal length and two collocation points per subinterval. Convergence of the foregoing procedure is shown in Table 2.

## NOTATION

$A$ = cross section area of unit exclusive of packing, m$^2$

$A_q$ = cross-sectional area occupied by phase $q$, m$^2$

$a_{pq}$ = surface area of phase $p$ exposed to phase $q$. Vapor-liquid if subscripts are absent, m$^2$/m$^3$ of vapor plus liquid

$C_q$ = concentration within the phase $q$, kg mol of phase $q$/m$^3$ of phase $q$

$c_{\text{known}}$ = vector of specified or known values. Defined by Eq. 42

$E$ = effective diffusivity, m$^2$/min

$F$ = total rate of feed in one external stream, kg mol/min

$f^*_{pq}$ = friction coefficient between phases $p$ and $q$. A factor of vapor concentration is removed if one phase is vapor. Vapor-liquid if no phase subscript. See Eq. 8

$f$ = component feed rate, kg mol/min

$f^0$ = vector right side of Eq. 40

$g$ = acceleration due to gravity (negative), m/min$^2$

$g^*_{pq}$ = heat transfer coefficient between phases $p$ and $q$. Same conventions as for $f^*_{pq}$

$H$ = vapor molar enthalpy or feed (vapor or liquid) molar enthalpy, kJ/kg mol

$h$ = liquid molar enthalpy, kJ/kg mol

$J$ = total number of interior collocation points

$K$ = equilibrium ratio, $K = y/x$

$k$ = mass transfer coefficient, mol/(min × m$^2$ of interfacial area)

$m$ = molecular weight

$P$ = pressure, atm

$R$ = reflux ratio as moles reflux per mole vapor leaving the top of the bed

$R_G$ = gas constant

$r$ = rate of mass transfer from vapor to liquid, mol/m$^3$ of vapor and liquid. Defined by Eq. 3

$r^I_i$ = integral of $r_i$ from bottom of bed to height $z$, mol/m$^2$. Defined by Eq. 3

$r^{I+}_i$, $r^{I-}_i$ = vectors defined after Eqs. 39

$S$ = matrix of spline basis functions. Definitions in Eqs. 37, 43 and 44 and after 46

$s$ = spline basis function

$T$ = temperature, °C except where specified otherwise

$t$ = time, usually minutes

$u$ = velocity, m/min, negative for downward flow

$V$ = volume, m$^3$/kg mol, Eqs. 24

$x$ = mol fraction in the liquid phase

$x^+_i$, $x^-_i$ = vectors defined after Eqs. 39

$y$ = mol fraction in the vapor phase

$y^+_i$, $y^-_i$ = vectors defined in Eqs. 39

$Z$ = coefficient matrix of Eq. 40; does not depend explicitly upon component mol fractions

$z$ = distance above the bottom of the bed, m

$z_c$ = critical compressibility of a mixture, Eqs. 24

### Greek Letters

$\Delta$ = an increment in the quantity to which it is applied

$\kappa$ = thermal conductivity, Eqs. 5 and 6

$\lambda$, $\lambda^1$, $\lambda^0$ = expansion coefficients for $r^I_i$, $y_i$ and $x_i$ respectively, Eqs. 36

$\lambda_i$, $\lambda^1_i$, $\lambda^0_i$ = vectors of expansion coefficients for $r^I_i$ $y_i$ and $x_i$

respectively, Eqs. 38
$\phi$ = flux of a component, Eqs. 1 and 2
$\equiv$ = "is defined as" or "is identical to"
$\chi$ = vector of unknown ("iteration") profiles defined by Eq. 43

**Superscripts and Subscripts**

$c$ = denotes a critical property
$F$ = external feed stream
$i$ = component index. Range is 1 through $I$
$j$ = collocation point index. Range is 0 or 1 through $J$ or $J + 1$
$L$ = liquid phase or when following $F$ liquid feed at top of bed
$(m)$ = superscript specifying the $m$'th derivative
$n$ = index for a basis function or its corresponding expansion coefficient as in Eq. 36
$r$ = denotes a reduced property as in $T_r = T/T_c$
$S$ = solid phase; usually the packing in the case of a packed column
$T$ = superscript denoting the transpose of a matrix
$V$ = vapor phase
$0$ = bottom of bed
$'$ $''$ = denote first and second derivatives respectively with respect to $z$

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