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A Nonequilibrium Stage Model of Multicomponent Separation Processes

Part I: Model Description and Method of Solution

A nonequilibrium stage model is developed for the simulation of countercurrent multicomponent separation processes. A feature of the model is that the component material and energy balance relations for each phase together with mass and energy transfer rate equations and equilibrium equations for the phase interface are solved to find the actual separation directly. Computations of stage efficiencies are entirely avoided. A procedure for solving the model equations simultaneously using Newton's method is outlined.

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SCOPE

Rigorous simulation of multistage processes such as distillation or absorption is, more often than not, based upon the equilibrium stage model. This model is well enough known not to need a detailed description here (see, for example, the textbooks by King, 1980, p. 446; Henley and Seader, 1981, pp. 24, 557; Holland, 1975, p. 47; 1981, p. 6). Briefly, of course, the model includes the assumption that the streams leaving any particular stage are in equilibrium with each other. Component *M*aterial balances, the equations of phase *E*quilibrium, *S*ummation equations, and *H*eat balance for each stage (the so-called MESH equations) are solved using one of the very many ingenious algorithms presently available to give product distributions, flow rates, temperatures, and so on.

In actual operation, stages rarely, if ever, operate at equilibrium despite attempts to approach this condition by proper design and choice of operating conditions. The usual way of dealing with departures from equilibrium is by incorporating a stage efficiency into the equilibrium relations. It is with the introduction of this quantity that the problems begin.

The first problem is that there are several different definitions of stage efficiency: Murphree (1925), Hausen (1953), generalized Hausen (Standart, 1965), vaporization (Holland, 1975, p. 268), and others. There is by no means a consensus on which definition is best. Arguments for and against various possibilities are presented by, among others, Standart (1965, 1971), Holland (1975, pp. 268, 327), Holland and McMahon (1970), King (1980, p. 637), and Medina et al. (1978, 1979). Possibly the most soundly based (in a thermodynamic sense), the generalized Hausen efficiencies are ridiculously complicated to calculate; the least soundly based, the Murphree efficiency, is the one most widely used because it is easily combined with the equilibrium equations. Thermal efficiencies may also be defined but almost always are taken to have a value of unity (except, perhaps, when inert species are involved). Whichever definition of stage efficiency is adopted, it must either be specified in advance or calculated from an equation derived by dividing by some reference separation the actual separation obtained from a solution of the component material balance equations for each phase. Many different models of stage efficiency (i.e., different solutions of the component phase balances) have been proposed for binary systems (King, 1980, p. 612). The extension of these models to multicomponent systems provides further complications.

In a c component system there are $c - 1$ independent com-

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ponent efficiencies, which, for lack of anything bettter to do, have usually been taken to be the same for all components (King, 1980, p. 636). In fact, the individual component efficiencies are rarely equal, simply because different species exhibit varying facilities for mass transfer.

Mass transfer in multicomponent mixtures is more complicated than in binary systems because of the possible coupling between the individual concentration gradients. Phenomena such as reverse diffusion (diffusion of a species against its own concentration gradient) or osmotic diffusion (diffusion of a species even though no concentration gradient for that species exists) are possible in multicomponent systems but not in binaries (Toor, 1957). One of the interesting consequences of these interaction effects is that the individual *point efficiencies* of different species are not constrained to lie between zero and one. Instead, they may be found anywhere in the range from $-\infty$ to $+\infty$ (Toor, 1964). Binary as well as multicomponent *tray efficiencies* may, for other reasons (e.g., weeping or entrainment), be greater than one. Experimental confirmation of Toor's (1964) prediction has recently been published by Krishna et al. (1977). Vogelpohl (1979) provides further evidence that the component point efficiencies are unequal and unbounded. The substantial body of other data affirming that individual efficiencies are unequal is reviewed by Krishna et al. (1977).

Models of mass transfer that are able to account for interaction effects now are available (see Krishna and Standart, 1979, for a recent review). In general, they lead to rate equations of the form of Eq. 13 below. These models have been used as a basis for developing methods for calculating efficiencies in multicomponent systems (Toor and Burchard, 1960; Toor, 1964; Diener and Gerster, 1968; Krishna et al., 1977; Medina et al., 1979; Vogelpohl, 1979). However, these models have been tested against a rather limited quantity of data, and, with the exception of the early work of Toor and Burchard (1960), there has not yet been an attempt to combine these efficiency models with a method for simulating multistage separation processes. In fact, some care in doing this would have to be exercised in order to avoid violating the material balances (King, 1980, p. 637).

All things considered we believe that the sometimes arbitrary and ambiguous multicomponent stage efficiency adds unnecessary complexity to separation process modeling. It is our contention that multistage separation processes are more effectively modeled by a sequence of nonequilibrium stages for which the solution of the conservation equations for each phase is used directly (rather than indirectly in the form of an efficiency factor). It is the objective of this paper to present a fairly general nonequilibrium stage model of countercurrent multicomponent separation processes and to describe a method of solving the resulting set of equations. Other nonequilibrium models of staged equipment in the same class as ours are due to Waggoner and Loud (1977) (distillation), to Waggoner and Burkhart (1978) (extraction), and to Ricker et al. (1981) (extraction with backmixing). The simplifications made by them (but not by us) will be mentioned at appropriate points in the text. Probably the most sophisticated two-phase model is that of Billingsley and Chirachavalla (1981) for continuous contact equipment. Some of the properties of component efficiencies in staged equipment (unequal and unbounded) are shared by component NTUs in continuous contact equipment, properties that Billingsley and Chirachavalla included in their model. The model proposed here may be (and is in Part II) applied to both stagewise and continuous contact equipment.

CONCLUSIONS AND SIGNIFICANCE

A nonequilibrium stage model of multicomponent separation processes has been developed. The features of the model are:

1. The mass and energy conservation equations are split into two parts, one for each phase. The equations for each phase are connected by mass and energy balances around the interface and by the assumption that the interface be at thermodynamic equilibrium.
2. The process of simultaneous mass and energy transfer through the interface is modeled by means of rate equations and transfer coefficients. Abstract and somewhat arbitrary concepts like efficiency or number of transfer units are avoided entirely.
3. Resistances to mass and energy transfer offered by both fluid phases can be accounted for by using separate rate equations for each phase. Interfacial effects are ignored in the present development.
4. The model is formulated in such a way as to make the describing equations and the method of solving them largely independent of the methods used to predict the transfer rates as well as physical and thermodynamic properties of the system.
5. The equations are best solved simultaneously using Newton's method or one of its relatives.

A NONEQUILIBRIUM STAGE MODEL

A schematic representation of a nonequilibrium stage or section of a packed or wetted-wall column is shown in Figure 1. Packed towers and multistage columns consist of a sequence of such stages. Vapor and liquid streams from adjacent stages are brought into contact on the stage and allowed to exchange mass and energy across their common interface represented in the diagram by the vertical wavy line. The stage is assumed to be at mechanical equilibrium; $P_j^V = P_j^L = P_j$. Provision is made for vapor and liquid feed streams, side stream drawoffs of vapor and liquid, and for the addition or removal of heat. Steady state operation is assumed. The equations used to model the behavior of this stage are now presented.

Conservation Relations

As with all models of chemical processes, the analysis of the nonequilibrium stage starts with the construction of material and energy balances. The mass balance for component i on stage j is

$$M_{ij} \equiv (1 + r_j^V)v_{ij} + (1 + r_j^L)l_{ij} - v_{i,j+1} - l_{i,j-1} - f_{ij} = 0 \quad (1)$$

where

$$r_j^V = S_{Vj}/V_j; r_j^L = S_{Lj}/L_j \quad (2)$$

The energy balance for the stage is

$$E_j \equiv (1 + r_j^V)V_jH_j^V - V_{j+1}H_{j+1}^V + (1 + r_j^L)L_jH_j^L - L_{j-1}H_{j-1}^L + Q_j - F_jH_j^F = 0 \quad (3)$$

In equilibrium stage calculations, Eqs. 1–3 are solved subject to the requirement that the vapor and liquid streams leaving stage j are in complete thermal, mechanical, and chemical equilibrium. In our development of the nonequilibrium stage model, Eqs. 1–3 are not useful as they stand. Instead, the stage balances are split into two parts, one for each phase. For the vapor phase, the component mass balance is

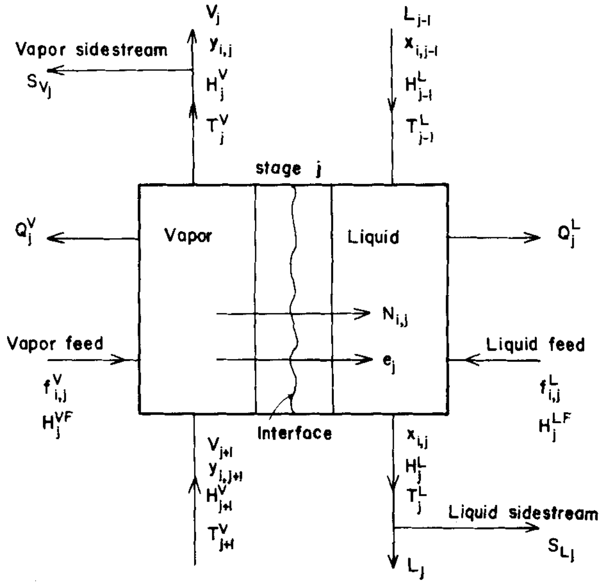

Figure 1. Schematic representation of a nonequilibrium stage.

$$M_{ij}^V \equiv (1 + r_j^V)v_{ij} - v_{i,j+1} - f_{ij}^V + \mathcal{N}_{ij}^V = 0 \qquad (4)$$

and for the liquid phase

$$M_{ij}^L \equiv (1 + r_j^L)l_{ij} - l_{i,j-1} - f_{ij}^L - \mathcal{N}_{ij}^L = 0 \qquad (5)$$

The last terms in Eqs. 4 and 5 represent the net loss or gain of species i due to interphase transport. Formally, we may write

$$\mathcal{N}_{ij}^V = \int N_{ij}^V da_j; \; \mathcal{N}_{ij}^L = \int N_{ij}^L da_j \qquad (6)$$

where N_{ij} is the molar *flux* of species i at a particular point in the two-phase dispersion, and da_j represents the small amount of interfacial area through which that flux passes. We adopt the convention that transfers from the vapor phase to the liquid phase are positive.

It follows directly from Eqs. 1, 4, and 5 that

$$M_{ij}^I \equiv \mathcal{N}_{ij}^V - \mathcal{N}_{ij}^L = 0 \qquad (7)$$

a result that may also be derived straightforwardly by constructing a material balance around the entire interface (hence the notation in Eq. 7). Equation 7 is a statement of the assumption that there is no accumulation of mass at the interface.

The energy balance for the vapor phase is

$$E_j^V \equiv (1 + r_j^V)V_jH_j^V - V_{j+1}H_{j+1}^V + Q_j^V - F_j^VH_j^{VF} + \mathcal{E}_j^V = 0 \qquad (8) \;)$$

and for the liquid phase the energy balance reads

$$E_j^L \equiv (1 + r_j^L)L_jH_j^L - L_{j-1}H_{j-1}^L + Q_j^L - F_j^LH_j^{LF} - \mathcal{E}_j^L = 0 \qquad (9)$$

Here, $\mathcal{E}_j$ represents the net loss or gain of energy due to interphase transport. This term may be defined by

$$\mathcal{E}_j^V = \int e_j^V da_j; \; \mathcal{E}_j^L = \int e_j^L da_j \qquad (10)$$

where e_j is the energy flux at some particular point in the dispersion. An energy balance around the interface yields

$$E_j^I \equiv \mathcal{E}_j^V - \mathcal{E}_j^L = 0 \qquad (11)$$

Transport Relations

It is worth emphasizing that Eqs. 1–11 hold regardless of the models used to calculate the interphase transport rates $\mathcal{N}_{ij}^V, \mathcal{N}_{ij}^L, \mathcal{E}_j^V, \mathcal{E}_j^L$. With a mechanistic model of sufficient complexity, it is possible, at least in principle, to account for mass transfer from bubbles in the froth as well as to entrained droplets and to liquid weeping through the tray floor (in these last two cases the material balance relations would have to be modified). However, a comprehensive model for estimating mass transfer rates in each of the possible flow regimes does not exist at present, and simpler approaches are needed. It is our purpose in this section to discuss the determination of the interphase transport rates in a fairly general way. We consider it more appropriate to describe the precise form the rate relations may take in Part II, where the model is applied to some specific separations.

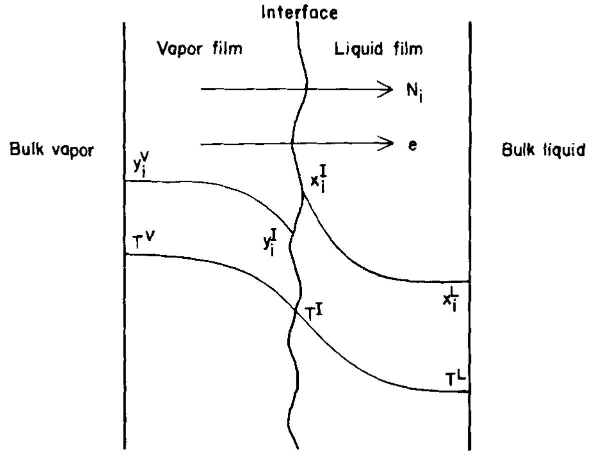

Figure 2. Typical composition and temperature profiles in the region of the interface.

Mass transfer is a rate process driven by gradients in concentration (more precisely, by gradients in chemical potential). Thus the rates of mass transfer in the vapor phase will depend on the difference between the bulk vapor compositions, y_{ij}^V, and the vapor compositions at the interface, y_{ij}^I (Figure 2). Similarly, the rates of mass transfer in the liquid phase will depend on the liquid composition at the interface, x_{ij}^I, and on the bulk liquid composition, x_{ij}^L (Figure 2). Many other factors (such as temperature, concentration, the physical properties of the fluids, system geometry and hydrodynamics, and the mass transfer rates themselves) influence the actual rates that are achieved (Sherwood et al., 1975, p. 148). Current practice is to lump the effects of most of these variables into mass transfer coefficients and write

$$N_i^V = k_i^V(y_i^V - y_i^I); \; N_i^L = k_i^L(x_i^I - x_i^L) \quad i = 1,2\,..\,c \qquad (12)$$

Rate equations of this form are used in the two-phase models of Waggoner and coworkers, of Ricker et al., and of Billingsley and Chirachavalla. Rate equations of this form are consistent with the material balance equations for the interface region only when all the k_i^V have the same value and all the k_i^L are equal (but not necessarily equal to k_i^V). Under these circumstances the component efficiencies would all be equal on any stage j (they may, of course, vary from one stage to another) and there would be no point in writing this paper.

A more rigorous treatment of mass transfer in multicomponent systems will lead us to the rate equations (Krishna and Standart, 1979):

$$N_i^V = \sum_{k=1}^{c-1} k_{ik}^V(y_k^V - y_k^I) + y_i^VN_t^V \quad i = 1,2\,..\,c-1 \qquad (13)$$

$$N_i^L = \sum_{k=1}^{c-1} k_{ik}^L(x_k^I - x_k^L) + x_i^LN_t^L \quad i = 1,2\,..\,c-1 \qquad (14)$$

where k_{ik}^V, k_{ik}^L are multicomponent mass transfer coefficients. We shall assume that methods for obtaining these coefficients are available (see Part II).

If, as is the case with the more rigorous mass transfer models, the coefficients k_{ik}^L and k_{ik}^V depend on the mass transfer rates themselves, then we might represent the flux equations (12 and 13) by implicit and nonlinear relations of the general functional form

$$N_i^V = N_i^V(k_{ik}^V, y_k^I, y_k^V, N_k^V, k = 1,2\,..\,c) \quad i = 1,2\,..\,c-1 \qquad (15)$$

$$N_i^L = N_i^L(k_{ik}^L, x_k^I, x_k^L, N_k^L, k = 1,2\,..\,c) \quad i = 1,2\,..\,c-1 \qquad (16)$$

It should be recognized that only $c - 1$ of Eq. 15 and $c - 1$ of Eq. 16 can be written down. The flux of component c is determined from the first $c - 1$ fluxes and from the energy transfer rate equation as shown below.

The local energy flux, e, is made up of a conductive heat flux and a convective contribution due to the transport of enthalpy by interphase transport (Bird et al., 1960, p. 566):

$$e^V = q^V + \sum_{i=1}^{c} N_i^V \overline{H}_i^V; e^L = q^L + \sum_{i=1}^{c} N_i^L \overline{H}_i^L \tag{17}$$

where $\overline{H}_i$ are the partial molar enthalpies of species i. The conductive heat fluxes, q, are driven by temperature gradients in the fluid

$$q^V = h^V(T^V - T^I); q^L = h^L(T^I - T^L) \tag{18}$$

where h^V and h^L are heat transfer coefficients, which depend, among other things, on the mass transfer rates themselves. If we assume that these coefficients are available (from a suitable correlation or theoretical expression perhaps), then the local energy fluxes may be represented by

$$e^V = e^V(h^V, T^V, T^I, N_k^V) \tag{19}$$

$$e^L = e^L(h^L, T^L, T^I, N_k^L) \tag{20}$$

The calculation of the total mass and energy transfer rates, $\mathcal{N}_{ij}$ and $\mathcal{E}_j$ requires the integration of the point flux relations (14–17) over some model flow path. (This, of course, is what's done in the efficiency models, but with a different result in mind.) Many different models could be discussed here, but we shall confine ourselves to some of the simplest. In order to simplify the integrations required by Eqs. 6 and 10, we assume that the interface state is the same throughout the dispersion on any stage j. (All other two-phase models make the same assumption, usually without explicitly stating it.) We further assume that the mass transfer coefficients can be considered constant on any stage (again, this is the usual assumption). Then, by imposing a particular shape on the bulk phase composition profiles we find that the integrated total transport rates are equal to the average fluxes multiplied by the total interfacial area, a_j:

$$\mathcal{N}_{ij}^V = N_{ij}^V a_j \equiv \mathcal{N}_{ij}^V(k_{ik}^V a_j, y_{kj}^I, \overline{y}_{kj}^V, \overline{T}_j^V, T_j^I, \mathcal{N}_{kj}^V, \quad k = 1,2\,..\,c) \tag{21}$$

$$\mathcal{N}_{ij}^L = N_{ij}^L a_j \equiv \mathcal{N}_{ij}^L(k_{ik}^L a_j, x_{kj}^I, \overline{x}_{kj}^L, \overline{T}_j^L, T_j^I, \mathcal{N}_{kj}^L, \quad k = 1,2\,..\,c) \tag{22}$$

$$\mathcal{E}_j^V = e_j^V a_j \equiv \mathcal{E}_j^V(h_j^V a_j, \overline{T}_j^V, T_j^I, \overline{y}_k^V, \mathcal{N}_{kj}^V) \tag{23}$$

$$\mathcal{E}_j^L = e_j^L a_j \equiv \mathcal{E}_j^L(h_j^L a_j, \overline{T}_j^L, T_j^I, \overline{x}_k^L, \mathcal{N}_{kj}^L) \tag{24}$$

where the mole fractions $\overline{y}_{ij}^V$ and $\overline{x}_{ij}^L$ and temperatures, $\overline{T}_j^V$ and $\overline{T}_j^L$ represent the integrated average bulk phase conditions. If the bulk composition is assumed to be constant throughout the dispersion, then the average mole fractions simply are equal to the mole fractions of the streams leaving the stage: $\overline{y}_{ij}^V = v_{ij}/V_j, \overline{x}_{ij}^L = l_{ij}/L_j$. On the other hand, if the bulk composition varies linearly between the entering and leaving values, then the average mole fractions are the arithmetic averages: $\overline{y}_{ij}^V = \frac{1}{2}(v_{ij}/V_j + v_{i,j+1}/V_{j+1}), \overline{x}_{ij}^L = \frac{1}{2}(l_{ij}/L_j + l_{i,j-1}/L_{j-1})$. Finally, if we impose an exponential profile on the bulk mole fractions, the average composition is the logarithmic average of the entering and leaving values. Average temperatures can be calculated in an analogous fashion.

In our simulations of laboratory and pilot-plant-scale tray columns we use the arithmetic average composition for the vapor phase (the logarithmic average gives virtually identical results) and the outlet composition for the liquid phase. This corresponds almost exactly with the conventional model of plug flow of vapor through a well-mixed liquid (see, for example, King, 1980, p. 615). In our simulations of small-scale wetted-wall columns we use the arithmetic average for both phases. These simple models give good agreement with the experimental data (Part II), better even than some more complicated models.

In writing Eqs. 21–24 we have combined the interfacial area term directly with the heat and mass transfer coefficients. This is because many correlations (e.g., the AIChE method for bubble-cap trays) give the coefficient-area product. It is, of course, possible to use separate sources for these quantities, as would be done in a simulation of an operation in a wetted-wall column for which the interfacial area would be known from the geometry of the system and the transfer coefficients only obtained from a correlation. Zuiderweg (1982) presents separate correlations for k and a for distillation on sieve trays. Notice also that Eqs. 21–24 are implicit in the mass transfer rates but not in the energy transfer rates; there are $c - 1$ of Eq. 21, $c - 1$ of Eq. 22, and one each of Eqs. 23 and 24.

All this is done so that the rate equations (21–24) need be solved only once for each stage j. The assumptions that were made above may be relaxed if desired by further dividing *each phase* into a number of regions and writing separate balance and rate equations for each region. The penalty is a large increase in the number of equations to be solved with a corresponding increase in the cost of obtaining a solution.

Interface Model

We adopt the conventional model of a phase interface: a singular surface offering no resistance to transport and where equilibrium prevails. The usual equations of phase equilibrium relate the mole fractions on each side of the interface:

$$Q_{ij}^I \equiv K_{ij} x_{ij}^I - y_{ij}^I = 0 \tag{25}$$

$$S_j^V \equiv \sum_{i=1}^{c} y_{ij}^I - 1 = 0; S_j^L \equiv \sum_{i=1}^{c} x_{ij}^I - 1 = 0 \tag{26}$$

where $K_{ij} \equiv K_{ij}(x_{ij}^I, y_{ij}^I, T_j^I, P_j)$ are the equilibrium ratios defined in the usual way. We have already mentioned the reasoning leading to our considering the interfacial state to be uniform throughout the dispersion.

Variables and Functions for a Single Nonequilibrium Stage

Given the state of all feed streams, the flow rate of all side streams, heat loads, and pressures on the stage there is a total of $6c + 5$ unknown quantities for each stage j. These are the component vapor flow rates (v_{ij}: c in number), the component liquid flow rates (l_{ij}: c), the vapor temperature (T_j^V), the liquid temperature (T_j^L), the interface temperature (T_j^I), the vapor composition at the interface (y_{ij}^I: c), the liquid composition at the interface (x_{ij}^I: c), the mass transfer rates ($\mathcal{N}_{ij}^V$: c; $\mathcal{N}_{ij}^L$: c), and the energy transfer rates ($\mathcal{E}_j^V, \mathcal{E}_j^L$). The $6c + 5$ independent equations that permit the calculation of these unknowns are as follows: component material balances for the vapor (M_{ij}^V: c), component material balances for the liquid (M_{ij}^L: c), component material balances around the interface (M_{ij}^I: c), the vapor phase energy balance (E_j^V), the liquid phase energy balance (E_j^L), the interface energy balance (E_j^I), the interface equilibrium relations (Q_{ij}^I: c), the summation equations (S_j^V; S_j^L), the vapor phase mass transfer rate equations (Eq. 21) ($c - 1$), the liquid phase mass transfer rate equations (Eq. 22) ($c - 1$), and the energy transfer rate equations (23 and 24).

The nonlinearity in these equations stems from the presence of the K values and enthalpies, as well as the mass and energy transfer rate terms.

A reduction in this rather large number of equations and unknowns can be obtained by eliminating certain equations that are simple linear combinations of variables. Recognizing that there is really only one set of c strictly independent transfer rates, the $\mathcal{N}_{ij}(=\mathcal{N}_{ij}^V = \mathcal{N}_{ij}^L)$ say, we can eliminate the $\mathcal{N}_{ij}^V$ from Eq. 21 and the $\mathcal{N}_{ij}^L$ from Eq. 22 using the balance equations (Eq. 7):

$$R_{ij}^V \equiv \mathcal{N}_{ij} - \mathcal{N}_{ij}^V(k_{ikj}^V a_j, y_{kj}^I, \overline{y}_{kj}^V, \overline{T}_j^V, T_j^I, \mathcal{N}_{kj}, k = 1,2\,..\,c) = 0 \qquad i = 1,2\,..\,c-1 \tag{27}$$

$$R_{ij}^L \equiv \mathcal{N}_{ij} - \mathcal{N}_{ij}^L(k_{ikj}^L a_j, x_{kj}^I, \overline{x}_{kj}^L, \overline{T}_j^L, T_j^I, \mathcal{N}_{kj}, k = 1,2\,..\,c) = 0 \qquad i = 1,2\,..\,c-1 \tag{28}$$

The energy transfer rate equations (Eqs. 23 and 24) are substituted into the interface energy balance to give

$$E_j^I \equiv \mathscr{E}_j^V(h_j^V a_j,\overline{T}_j^V,T_j^I,\overline{y}_{kj}^V,\mathscr{N}_{kj}) - \mathscr{E}_j^L(h_j^L a_j,\overline{T}_j^L,T_j^I,\overline{x}_{kj}^L,\mathscr{N}_{kj}) = 0 \quad (29)$$

Note that only c mass transfer rates N_{ij} appear in Eqs. 27–29; the transfer rates N_{ij}^L (*or* N_{ij}^V), E_j^V and E_j^L are eliminated from the list of independent variables. The balance equations (M_{ij}^I: c) and the energy transfer rate equations (Eqs. 23 and 24) are removed from the set of independent functions.

Two more variables, x_{cj}^I and y_{cj}^I can easily be eliminated from the set of variables. They can be computed directly from the summation equations (S_j^V,S_j^I), which, therefore, are dropped from the list of independent equations.

The final set of $5c + 1$ independent variables per stage is ordered into a vector (X_j) as follows

$$(X_j)^T \equiv (v_{1j},v_{2j} \ldots v_{cj},T_j^V,T_j^L,l_{1j},l_{2j} \ldots l_{cj},\mathscr{N}_{1j},\mathscr{N}_{2j}, \ldots \mathscr{N}_{cj},y_{1j}^I,y_{2j}^I, \ldots y_{c-1,j}^I,T_j^I,x_{1j}^I,x_{2j}^I \ldots x_{c-1,j}^I)$$

The $5c + 1$ independent equations corresponding to this set of variables are ordered into a vector $(\mathscr{F}_j)$ as

$$(\mathscr{F}_j)^T \equiv (M_{1j}^V,M_{2j}^V \ldots M_{cj}^V,E_j^V,E_j^L,M_{1j}^L,M_{2j}^L \ldots M_{cj}^L,R_{1j}^V,R_{2j}^V \ldots R_{c-1,j}^V,E_j^I,Q_{1j}^I,Q_{2j}^I \ldots Q_{cj}^I,R_{1j}^L,R_{2j}^L \ldots R_{c-1,j}^L)$$

This concludes the formal development of the model. It remains to show how what we refer to as the MERQ equations (Material balances, Energy balances, Rate equations and Equilibrium relations) are solved and, in Part II, to present some of our results.

SOLVING THE MERQ EQUATIONS

Methods of solving the equilibrium stage MESH equations fall into two groups; tearing methods (where subsets of the complete set of equations are solved in sequence) and simultaneous correction (SC) methods (where all of the equations are solved simultaneously). The same classification applies to the methods used to solve the various nonequilibrium models that have been devised. Waggoner and coworkers, for example, adopt a tearing strategy. Actually, they, as do Ricker et al. (1981), consider their stages to be in thermal and mechanical equilibrium, and so they need only be concerned with solving what we might call the MRQ equations. Waggoner's algorithm cannot be used whenever the mass transfer rates are coupled, since the phase balances for component i depend on the composition of all components. Ricker et al. use Newton's method to linearize all of the equations describing their stages. Billingsley and Chirachavalla (1981) use a collocation method to solve the differential equations that model their system.

We have tried several different approaches to solving the MERQ equations and found solving all of the equations simultaneously using Newton's method (or one of its relatives) to be most effective.

Newton's Method and Related Fixed-Point Algorithms

Let $(\mathscr{F}) \equiv (\mathscr{F}(X))$ denote any collection of equations, nonlinear in (X), the collection of variables, with solution $(\mathscr{F}) = (0)$. The direct prediction Newton correction is given by a solution of the equations linearized about the current estimate (X_k) of (X)

$$[J_k](X_{k+1} - X_k) = -(\mathscr{F}(X_k)) \quad (30)$$

where $[J_k]$ is the Jacobian matrix with elements

$$J_{ij} = \partial \mathscr{F}_i / \partial X_j \quad (31)$$

Newton's method is very versatile and quite robust; if it has a weakness, it is the computation of $[J]$. For most engineering applications of reasonable complexity, complete derivative information is rarely available in analytical form. In the present case, "unavailable" derivatives include derivatives of thermodynamic and transport properties with respect to quantities like temperature, composition, and mass transfer rates (e.g., $\partial K_{ij}/\partial x_{kj}^I$, $\partial H_j^L/\partial x_{kj}^L$, $\partial k_{ikj}^V/\partial \mathscr{N}_{kj}$, etc.). Finite-difference approximations of these derivatives can greatly increase the cost of solution because many more physical property evaluations are required. Further, neglect of these derivatives is not generally justified; it can increase the number of iterations or even cause failure.

One way to avoid the repeated calculation of $[J]$ is to use a "quasi-Newton" method (see Dennis and Moré, 1977). Broyden's (1965) method, for example, computes an approximate Jacobian $[J_k']$ from the formula

$$[J_{k+1}'] = [J_k'] + [((Y) - [J_k'](S))(S)^T]/(S)^T(S) \quad (32)$$

where $(Y) = (\mathscr{F}(X_{k+1}) - \mathscr{F}(X_k))$ and $(S) = (X_{k+1} - X_k)$. Schubert's (1970) method is an extension of the Broyden method that preserves any known sparseness in $[J]$. The quasi-Newton correction is given by a solution of the linear system (Eq. 30) with $[J_k']$ replacing $[J_k]$.

Unfortunately, quasi-Newton methods are not without problems. The first is that they are not scale invariant (Newton's method is) and may, as a result, perform poorly on problems that are ill-conditioned. This is an important consideration in the present case since material and energy balance equations as well as transfer rate equations are part of the model. This particular set of equations is quite badly scaled: If SI units are used then the MERQ equations include terms typically ranging over 10 orders of magnitude [$0(10^5) - 0(10^{-5})$]. A second problem sometimes arises because of the need to supply an initial approximation to $[J]$. A poor first approximation can increase the number of iterations or even cause failure.

A Hybrid Method

A judicious combination of Newton's method and a quasi-Newton update can, as shown recently by Lucia and coworkers (Lucia and Macchietto, 1983; Lucia and Westman, 1983), be a very efficient means of solving the kinds of equations found in chemical process models. In what they call the hybrid method, the Jacobian matrix is divided into two parts, a computed part $[C_k]$ and an approximated part $[A_k]$:

$$[J_k] = [C_k] + [A_k] \quad (33)$$

$[C_k]$ contains any partial derivatives for which analytical expressions can *easily* be derived. $[A_k]$ is made up of any terms that contain partial derivatives that are difficult to derive analytically and expensive to compute by numerical differentiation (e.g., $\partial K_{ij}/\partial x_{kj}$). In their algorithm, $[C_k]$ is computed in each iteration while $[A_k]$ only is updated from an initial approximation (the null matrix in our applications) using the Broyden or Schubert updates. The correction to (X_k) again is provided by Eq. 30 with $[J_k]$ given by Eq. 33. A stepwise procedure for implementing the hybrid method can be found in the papers by Lucia and coworkers cited above.

In an early stage of this work, we compared the performance of three methods (Newton's method, with finite-difference computations of the "unavailable" derivatives; Schubert's method; and the hybrid method) of solving the MERQ equations. Almost always, Newton's method took fewest iterations (~5) with the hybrid method requiring around ten iterations. However, the hybrid method typically takes 50% less time (sometimes much less than 50%, never much more). Schubert's method generally worked well in these examples because we can usually provide very good initial guesses of the independent variables. Occasionally, this is not possible, and then Schubert's method has failed. Newton's method and the hybrid algorithm were used with complete success to solve the problems described in Part II.

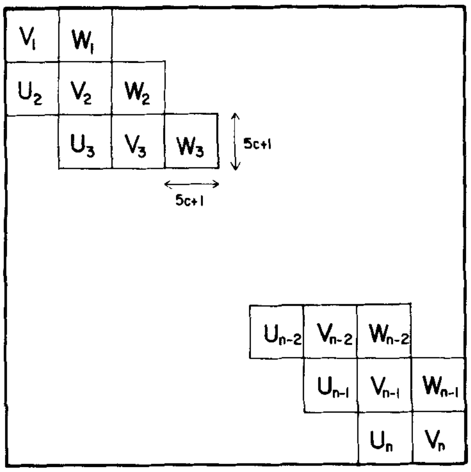

Figure 3. Block tridiagonal structure of the Jacobian for an absorber.

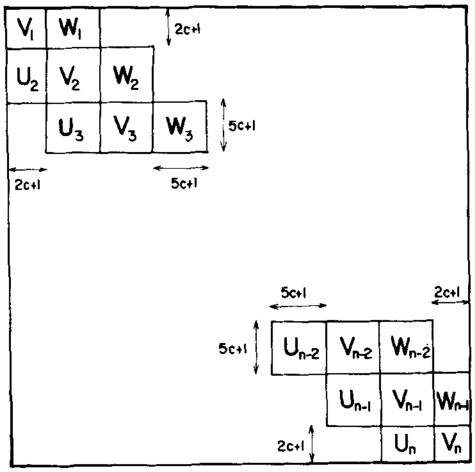

Figure 4. Block tridiagonal structure of the Jacobian for a distillation column with an equilibrium reboiler and condenser.

APPLICATIONS OF THE MODEL

A Multistage Process: An Absorber Perhaps

Absorbers frequently are modeled as simple sequences of equilibrium stages (King, 1980, chapter 10; Henley and Seader, 1981, chapter 15; Holland, 1975, chapter 4, 1981, chapter 4). If, instead, we choose to model the column by a sequence of n nonequilibrium stages, the vectors of variables and functions corresponding to the entire column are

$$(X)^T \equiv ((X_1)^T,(X_2)^T \ldots . (X_n)^T)$$

$$(\mathcal{F})^T \equiv ((\mathcal{F}_1)^T,(\mathcal{F}_2)^T \ldots . (\mathcal{F}_n)^T)$$

where the variables and functions have been grouped by stage, as done by Naphtali and Sandholm (1971) in their formulation of the MESH equations. When grouped in this way, the vector of stage functions, $(\mathcal{F}_j)$, depends only on the variables for the three adjacent stages, $j-1$, j, and $j+1$. Thus the Jacobian matrix has the familiar block tridiagonal structure shown in Figure 3. The linear system (Eq. 30) is easily and efficiently solved when $[J]$ is block tridiagonal using the matrix generalization of the well-known Thomas algorithm (Henley and Seader, 1981, p. 600, for example, give the steps necessary to implement what is just Gaussian elimination of submatrices). The submatrices $[U_j]$,$[V_j]$,$[W_j]$ are extremely sparse; $[U_j]$ and $[W_j]$ are almost empty. The structure of these submatrices can be derived by straightforward differentiation of the MERQ equations. The results of this exercise and diagrams of the sparsity patterns of the submatrices are given in the appendix. The terms that are assigned to the computed and approximated parts of the submatrices are indicated there as well.

It is interesting to compare our total of $5c+1$ variables per stage with the $2c+1$ variables per stage in the formulation of the MESH equations due to Naphtali and Sandholm (1971) (see also Henley and Seader, 1981, p. 595; Holland, 1981, p. 581). For example, for a ten-stage column separating a ternary mixture, the equilibrium stage model comprises a mere 70 equations compared to 160 equations for the nonequilibrium stage model. For a 50-stage, five-component separation process, the equilibrium stage model boasts 550 equations. This compares to our nonequilibrium stage model with no less than 1,300 equations. Clearly, there is a considerable difference in the size of the problem being solved. However, we consider large size only a minor drawback of this nonequilibrium stage model. With suitable sparse matrix-handling computer codes, the large size of the system can easily be accommodated.

Multicomponent Distillation in a Multi-Nonequilibrium Stage Column

Distillation is the single most important process presently employed by the chemical process industries. In this section we discuss the application to this process of the general stage model developed above. The formulations presented here are used in our simulations of some actual multicomponent distillations described in Part II.

Consider, first, a distillation column equipped with a partial condenser and a partial reboiler. Nonequilibrium models of multicomponent condensers/reboilers have been devised (for a review of recent developments in these areas see, for example, chapter 6 of volume 2 of the recently published *Heat Exchanger Design Handbook*, Schlunder, 1983). However, these models involve the numerical solution of differential rather than algebraic equations. Although it certainly is possible to use the results of these models to compute the MERQ functions, we have not attempted to do this yet. Instead, we prefer, for simplicity, to solve algebraic equations only (at this stage anyway) and, therefore, we model the partial condenser/reboiler as equilibrium stages, as do Waggoner and Loud (1977) in their much simpler nonequilibrium stage model. The $2c+1$ variables corresponding to this set of equations are the component flow rates, l_{ij} and v_{ij}, and the temperature, T_j (see, e.g., Henley and Seader, 1981, p. 594). The $2c+1$ equations that model these stages include the c component material balances and c equilibrium relationships. The energy balance is replaced by one specification equation (e.g., distillate rate specified).

A total condenser/reboiler may also be described by a set of $2c+1$ equations: c component material balances, a specification function (to replace the energy balance as for a partial condenser/reboiler), $c-1$ equations equating the mole fractions in the product and reflux streams, and an equation specifying the temperature of the product streams (e.g., $T = T_{\text{bub}}$, the bubble point temperature of the product).

For a column modeled in either way, the Jacobian matrix retains its block band structure, but the submatrices $[W_1]$, $[U_2]$, $[W_{n-1}]$, and $[U_n]$ are no longer square. Rather, they are rectangular with dimensions $2c+1 \times 5c+1$ or $5c+1 \times 2c+1$, as indicated in Figure 4. It should be recognized that the steps of the matrix generalization of the Thomas algorithm apply unchanged to the triangularization of the matrix in Figure 4. Provision need only be made for multiplication of rectangular matrices.

Distillation at Total Reflux

The maximum separation possible in a given number of stages is attained at total reflux when the overhead vapor is completely condensed and returned to the column. This situation is also attractive for experimental purposes, as no material is lost from the column. Using a mass balance around any top section of the column it is easy to show that

$$v_{i,j+1} = l_{ij} \tag{31}$$

This suggests that either the set of component vapor flows, v_{ij}, or the component liquid flows, l_{ij}, can be removed from the set of variables representing the jth nonequilibrium stage. The component material balance equations (M_{ij}^V or M_{ij}^L) would then be removed from the set of equations for that stage. We will then be left with $4c + 1$ variables and functions per stage.

Single Phase Control

In many separation processes the resistance to mass transfer lies predominantly in one phase. Distillation is a process that sometimes is controlled by the vapor phase resistance (Vogelpohl, 1979; Kayihan et al., 1977; Krishna et al., 1977; Dribika and Sandall, 1979). If we *assume* that the liquid phase resistance can be neglected, then the interface liquid composition is that of the bulk liquid and it is no longer necessary to consider the $c - 1$ x_{ij}^I as independent variables. We are then left with $4c + 2$ variables per stage, which, of course, means that the number of equations must also be reduced by $c - 1$. As there is no resistance to mass transfer in the liquid phase, it is no longer possible to calculate the mass transfer rates in the liquid from the $c - 1$ rate equations R_{ij}^L, which, therefore, are dropped from the set of equations for the jth stage.

For liquid phase control the y_{ij}^I and R_{ij}^V would be eliminated from the sets of variables and equations.

Vapor-Phase-Controlled Distillation at Total Reflux

For a vapor-phase-controlled distillation at total reflux, we have to deal with only $3c + 2$ equations and variables per nonequilibrium stage:

$$(X_j)^T \equiv (v_{1j} \ldots v_{cj}, T_j^V, T_j^L, \mathcal{N}_{1j} \ldots \mathcal{N}_{cj}, y_{1j}^I \ldots y_{c-1,j}^I, T_{jI})$$

$$(\mathcal{F}_j)^T \equiv (M_{1j}^V \ldots M_{cj}^V, E_j^V, E_j^L, R_{1j}^V \ldots R_{c-1,j}^V, E_j^I, Q_{1j} \ldots Q_{cj})$$

We note that this situation is encountered in many of the experimental simulations more fully described in Part II.

Other Applications

The model developed in this paper can be applied to many other situations: distillation with chemical reaction, dynamic simulations, and distillation of systems in which the presence of two liquid phases are of particular interest. These particular cases require some modification and/or extension of the model equation set presented here (rather than simple elimination of equations and variables as in the examples considered above). We will consider these variations on a theme in future parts of this series.

ACKNOWLEDGMENT

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NOTATION

a = interfacial area (m^2)
$[A]$ = approximated part of Jacobian
c = number of components
$[C]$ = computed part of Jacobian
e = point energy flux (J/m^{2}s)
E = energy balance function (J/s)
$\mathcal{E}$ = total interphase energy transfer rate (J/s)
f = component feed rate (kmol/s)
F = total feed rate (kmol/s)
$\mathcal{F}$ = discrepancy function vector
h = heat transfer coefficient (J/m^2·s·K)
H = enthalpy (J/kmol)
$[J]$ = Jacobian matrix of partial derivatives
k = mass transfer coefficient (kmol/m^2·s)
K = equilibrium ratio
l = component liquid flow (kmol/s)
L = total liquid flow (kmol/s)
M = mass balance function
n = number of stages
N = point molar flux (kmol/m^2·s)
N_t = total molar flux (kmol/m^2·s)
$\mathcal{N}$ = total interphase mass transfer rate (kmol/s)
P = pressure (Pa)
q = conductive heat flux (J/m^2·s)
Q^L = heat removal from liquid phase (J/s)
Q^V = heat removal from vapor phase (J/s)
Q_{ij}^I = interface equilibrium function (dimensionless)
r = ratio of side stream to interstage flow
R = rate relation functions
S = summation functions
S_V = side stream vapor flow (kmol/s)
S_L = side stream liquid flow (kmol/s)
T = temperature (K)
$[U]$ = subdiagonal block submatrix
$[V]$ = diagonal block submatrix
v = component vapor flow (kmol/s)
V = total vapor flow (kmol/s)
$[W]$ = superdiagonal block submatrix
x = liquid phase compositions
X = vector of variables
y = vapor phase compositions

Subscripts

i,k = component number
j = stage number

Superscripts

I = interface
L = liquid bulk
LF = liquid feed
V = vapor bulk
VF = vapor feed
$-$ = partial molar property
$'$ = approximation

Matrices

( ) = column matrix
$( )^T$ = row matrix
[ ] = square or rectangular matrices

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A Nonequilibrium Stage Model of Multicomponent Separation Processes

Part II: Comparison with Experiment

A nonequilibrium stage model of countercurrent separation processes is used to predict composition and temperature profiles during binary and multicomponent distillation in wetted-wall and bubble-cap-tray columns. The profiles predicted by the model are compared with experimental data for the binary systems benzene-toluene, ethanol-water, and acetone-chloroform and for the ternary systems benzene-toluene-ethylbenzene, acetone-methanol-water, methanol-isopropanol-water, acetone-methanol-ethanol, and benzene-toluene-*m*-xylene. The model does a *very* commendable job of predicting the composition profiles measured for these systems; average absolute differences between predicted and measured mole fractions are seldom greater than 4 mole percent and are often very much less.

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SCOPE

In Part I of this series, a nonequilibrium stage model of countercurrent multicomponent separation processes was described. The motivation for developing the model was the observation that the equilibrium stage model modified by the inclusion of a stage efficiency that has the same value for all components (the model presently used to simulate separation processes) is unable to predict accurately the composition profiles in processes separating multicomponent mixtures in which

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