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Condensation of Vapor Mixtures. 1. Nonequilibrium Models and Design Procedures

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Nonequilibrium models of multicomponent condensation are reviewed with particular attention to the various ways in which the rates of condensation can be calculated. Ways of solving the mixed set of differential and algebraic equations that constitute the model are discussed, and it is suggested that differential conservation equations be approximated by finite differences and the resulting set of only algebraic equations solved *simultaneously* (using Newton's method) with the nonlinear equations representing the processes of interphase transport and interfacial equilibrium. With regard to the various models of vapor-phase transport, it is shown that simple effective diffusivity models may lead to *significant* over- or underdesign when compared to more soundly based models which take vapor-phase diffusional interaction effects into account. It is also demonstrated that there is little to distinguish models based on the use of the Chilton–Colburn analogy to obtain the heat- and mass-transfer coefficients from turbulent eddy diffusivity models when both are used to predict the performance of multicomponent condensers.

Introduction

Condensation of vapor mixtures is an operation of great significance in the chemical process industries. The two words "vapor mixture" cover a wide range of situations. One limit of this range is one in which all components have boiling points above the maximum coolant temperature; in this case, the mixture can be totally condensed. The other limit is a mixture in which at least one component in the initial vapor stream has a boiling point lower than the minimum coolant temperature and, also, is negligibly soluble in the liquid condensate formed from the other components and hence cannot be condensed at all. Examples of such components include nitrogen and helium. An intermediate case of some importance is typified by a mixture of light hydrocarbons in which the lightest members often cannot be condensed as pure components

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at the temperatures encountered in the condenser but, instead, will dissolve in the heavier components. In each of these cases, the vapor mixture may form a partially or totally immiscible condensate.

Existing methods for *designing* heat exchangers to condense multicomponent mixtures are of two basic kinds: equilibrium methods, such as those of Kern (1950), Silver (1947), and Bell and Ghaly (1972), and the differential or nonequilibrium methods that have developed following the original work of Colburn and Drew (1937). In the latter class of methods, a set of one-dimensional differential material and energy balances is integrated numerically along the length of the condenser. Each step of the integration requires the local mass- and energy-transfer rates to be calculated by using, for example, equations based on a film model (Colburn and Drew, 1937; Schrodt, 1973; Price and Bell, 1974; Krishna et al., 1976; Krishna and Panchal, 1977; Krishna, 1979a; Röhm, 1980; Bandrowski and Kubaczka, 1981; Webb and McNaught, 1980; Webb and Sardesai, 1981; Webb, 1982; Taylor and Noah, 1982; Shah and Webb, 1983). Still more sophisticated nonequilibrium models based on boundary layer theory are limited primarily to describing the condensation of binary vapors or of one vapor in the presence of a noncondensing gas. Extensions of the boundary layer models to multicomponent systems are few in number (Taitel and Tamir, 1974; Tamir and Merchuk, 1979; Sage and Estrin, 1976) and have not been developed to the point where they could be used in the design of heat exchangers of complex geometry. While the equilibrium methods are widely used (the reasons being because they are simple, rapidity in computation and because there is no need to compute intermediate vapor compositions or to obtain diffusivity data), the one-dimensional nonequilibrium methods are more soundly based and appear to be attracting increasing interest (see, for example: McNaught, 1983a,b; Owen and Lee, 1983; Butterworth, 1983). It is interesting to observe that Butterworth (1983) has included a summary of both the equilibrium and the one-dimensional nonequilibrium approaches in his chapter on condensation in Vol 2, which covers the fundamentals of fluid mechanics and heat transfer, of the recently published "Heat Exchanger Design Handbook" (Schlünder, 1983), whereas Vol 3, which presents design procedures for heat exchangers of all kinds, includes only a procedure based on the equilibrium methods in the chapter on condensers. It is our belief that it will be only a short time before the more fundamental nonequilibrium models are accorded a section of their own in future editions of Vol 3.

It is the objective of this paper to describe a new variation on this latter class of models, to discuss an efficient method of solving the nonlinear *algebraic* equations that constitute our model, and, finally, to present some numerical examples that demonstrate the features of the models. In particular, we compare the predictions of the various multicomponent film models to the recently developed turbulent eddy diffusivity model of Krishna (1982). In part 2 of this series, we show that the most rigorous models do a better job of predicting the performance of some test condensers.

Model of Multicomponent Condensation

A schematic representation of a short section of a single condenser tube is shown in Figure 1. The heat lost by the vapor, thereby causing some of it to condense, is transferred through the condensate, through the tube wall, and into the coolant. The coolant may flow cocurrently with or countercurrently to the vapor and liquid streams which are flowing cocurrently along the tube.

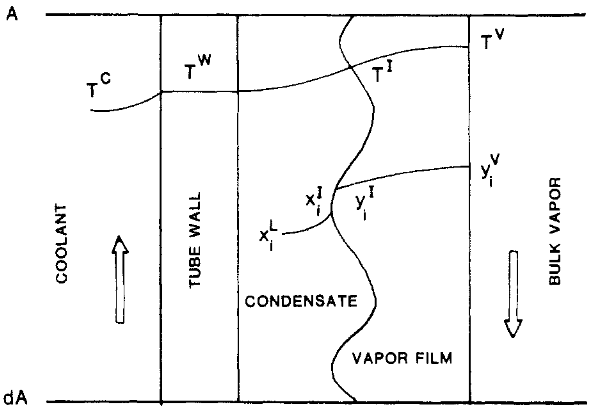

Figure 1. Schematic representation of a section of a condenser.

Material and Energy Balance Relations. As always with chemical process calculations, we start from the appropriate material and energy balances which, here, are written around a section of condenser tube of differential area (Figure 1). For the vapor phase, the component material balance reads

$$\frac{\mathrm{d}v_i}{\mathrm{d}A} = -N_i^{\mathrm{V}} \qquad i = 1, 2, ..., n \tag{1}$$

and for the liquid phase

$$\frac{\mathrm{d}l_i}{\mathrm{d}A} = N_i^{\mathrm{L}} \qquad i = 1, 2, ..., n \tag{2}$$

The terms on the right-hand sides of eq 1 and 2 are the molar fluxes of species i in the vapor and liquid phases, respectively; we assume that transfers from the vapor phase to the liquid phase are positive. From a component material balance around the entire differential section, we conclude that

$$N_i^{\mathrm{V}} = N_i^{\mathrm{L}} = N_i \qquad i = 1, 2, ..., n \tag{3}$$

Equation 3, which expresses the requirement that the fluxes be continuous across the vapor/liquid interface, will prove useful when the nonlinear equations from which the mass-transfer rates are calculated are solved numerically; more on this below.

The differential energy balance for the vapor phase is

$$VC_p^{\mathrm{V}}\frac{\mathrm{d}T^{\mathrm{V}}}{\mathrm{d}A} = -q^{\mathrm{V}} \tag{4}$$

where q^{V} is the conductive heat flux out of the bulk vapor. The energy balance for the liquid phase is

$$LC_p^{\mathrm{L}}\frac{\mathrm{d}T^{\mathrm{L}}}{\mathrm{d}A} = q^{\mathrm{L}} - q^{\mathrm{W}} \tag{5}$$

where q^{L} is the heat flux into the liquid and q^{W} is the heat flux across the tube wall into the coolant. The energy balance for the coolant in this section of the condenser is

$$L_{\mathrm{C}}C_p^{\mathrm{C}}\frac{\mathrm{d}T^{\mathrm{C}}}{\mathrm{d}A} = \pm q^{\mathrm{W}} \quad (+,\text{ cocurrent; } -,\text{ countercurrent}) \tag{6}$$

From an energy balance around the entire differential section, we find that

$$E^{\mathrm{V}} = E^{\mathrm{I}} = E^{\mathrm{L}} = E^{\mathrm{W}} = E \tag{7}$$

where E is the *energy* flux, related to the conductive heat fluxes by (Krishna and Standart, 1979)

$$E = q + \sum_{i=1}^{n} N_i\bar{H}_i \tag{8}$$

$\bar{H}_i$ is the partial molar enthalpy of component i. Equation

8 can be written for each phase, vapor, condensate, and coolant (for which the second term drops out). Equation 7 expresses the requirement that the energy fluxes be continuous across a phase boundary. Differences between the area of the vapor/liquid, liquid/wall, and wall/coolant interfaces are ignored in the present analysis; it would, however, be easy to allow for such variations.

The balance equations presented above are quite independent of the methods used to calculate the mass- and energy-transfer rates. The equations that permit this calculation are the subject of the next sections.

Mass Transfer in Multicomponent Gas/Vapor Mixtures. There are a large number of methods that could be used to calculate the mass-transfer rates in the vapor phase. The calculation of mass-transfer rates in multicomponent systems is complicated by the coupling between the individual composition gradients. This coupling gives rise to various interaction effects such as reverse or osmotic diffusion that are not possible in binary systems. Most prior work in this area has been carried out by using rate equations based on a film model of steady-state one-dimensional transfer (see the list of citations in the Introduction). Even for this, the simplest of all models of mass transfer, there is, rather, more than one way of performing the calculations. The methods fall into three categories:

(i) The first is methods of the effective diffusivity type (which neglect interaction effects) with the molar fluxes given by

$$N_i^{\rm V} = c_{\rm t}^{\rm V} k_{i\rm eff}^{\rm V} \Xi_{i\rm eff}(y_i^{\rm V} - y_i^{\rm I}) + y_i^{\rm V} N_{\rm t}^{\rm V} \qquad (9)$$

$$i = 1, 2, ..., n$$

with

$$\Xi_{i\rm eff} = \Phi_{i\rm eff}/(e^{\Phi_{i\rm eff}} - 1);\ \Phi_{i\rm eff} = N_{\rm t}^{\rm V}/(c_{\rm t}^{\rm V} k_{i\rm eff}^{\rm V})$$

where $k_{i\rm eff}^{\rm V}$ is an effective mass-transfer coefficient, a function of an effective diffusivity, $D_{i\rm eff}$ (Bird et al., 1960). The effective diffusivity itself may be defined in a number of different ways (see Smith and Taylor (1983) for a comparison of methods); a common choice, because it represents an exact definition of the effective diffusivity for dilute gases—a situation sometimes approached at the condenser outlet—is to take $D_{i\rm eff}$ as $\mathcal{D}_{in}$. Webb et al. (1981) discuss the conditions which must prevail in order that eq 9 be an adequate representation of the more rigorous methods discussed below. One of them is that $\Phi_{i\rm eff}$ be less than 0.4. This value is frequently exceeded in our condenser simulations.

(ii) The second is methods which take interaction effects into account and which are implicit in the molar fluxes $N_i^{\rm V}$. The method of Krishna and Standart (1976), based on an exact solution of the Maxwell–Stefan equations, and the solution of the linearized equations due to Toor (1964) and to Stewart and Prober (1964) are in this category. In these methods, the mass-transfer rates are obtained from a matrix equation of the form (Krishna and Standart, 1979)

$$(N^{\rm V}) = c_{\rm t}^{\rm V}[k_{\rm V}^{\bullet}](y^{\rm V} - y^{\rm I}) + N_{\rm t}^{\rm V}(y^{\rm V}) \qquad (10)$$

where $[k_{\rm V}^{\bullet}]$ is a square matrix of the order $n - 1$ of multicomponent mass-transfer coefficients. $[k_{\rm V}^{\bullet}]$ can be written as the product of a matrix of low-flux mass-transfer coefficients and a matrix of correction factors $[\Xi]$

$$[k_{\rm V}^{\bullet}] = [k^{\rm V}][\Xi] \qquad (11)$$

with $[\Xi]$ given by

$$[\Xi] = [\Phi]\{\exp[\Phi] - [I]\}^{-1} \qquad (12)$$

and where $[\Phi]$ is a matrix of mass-transfer rate factors. The structure of the matrices $[k^{\rm V}]$ and $[\Phi]$ is most easily defined by introducing a square matrix $[M]$ which has elements

$$M_{ii} = \frac{m_i}{\mathcal{K}_{in}} + \sum_{\substack{k=1\\k\neq i}}^{n} \frac{m_k}{\mathcal{K}_{ik}} \qquad (13)$$

$$M_{ij} = -m_i\left(\frac{1}{\mathcal{K}_{ij}} - \frac{1}{\mathcal{K}_{in}}\right) \qquad (14)$$

The $\mathcal{K}_{ij}$'s in eq 13 and 14 are *binary* mass-transfer coefficients; that is, they are the mass-transfer coefficients that would be used in the calculations if the vapor phase contained just two species.

In the method of Krishna and Standart, $[k^{\rm V}]$ is equal to $[M]^{-1}$ with m_i equal to $y_i^{\rm V}$ and $[\Phi]$ is equal to $[M]$ with $m_i = N_i^{\rm V}/c_{\rm t}^{\rm V}$. In the linearized theory, $[k^{\rm V}]$ is equal to $[M]^{-1}$ with $m_i = y_{i\rm av}$ and $[\Phi]$ is equal to $[M]$ with $m_i = y_{i\rm av}^{\rm V} N_{\rm t}^{\rm V}/c_{\rm t}^{\rm V}$.

(iii) The third is methods which account for interaction effects but which do not require an a priori knowledge of the mass-transfer rates themselves. There are two methods in this category, due to Krishna (1979b) and to Taylor and Smith (1982) (as a generalization and modification of a method due to Burghardt and Krupiczka (1975)). The fluxes are obtained from an expression of the form

$$(N^{\rm V}) = c_{\rm t}^{\rm V}[K^{\rm V}]\Xi(y^{\rm V} - y^{\rm I}) \qquad (15)$$

Here, $[K^{\rm V}]$ is a matrix of multicomponent total mass-transfer coefficients (see Smith and Taylor (1983) for possible structures of $[K^{\rm V}]$) and Ξ is a scalar correction factor (unity in the method of Krishna (1979)) that depends only on the boundary conditions and flux ratios.

The *binary* mass-transfer coefficients $\mathcal{K}_{ij}$ appearing in equations 13–15 usually are estimated from an appropriate correlation of, for example, the Chilton–Colburn *j*-factor type

$$\mathrm{St}_{ij} = \mathcal{K}_{ij}/(V/A_{\rm c}) = (f/2)\mathrm{Sc}_{ij}^{-2/3} = (f/2)(\rho_{\rm t}\mathcal{D}_{ij}/\mu)^{2/3} \qquad (16)$$

where f is the friction factor, a function of the Reynolds number, and where $A_{\rm c}$ is the cross-sectional area for downstream flow.

Another way of estimating $[k^{\rm V})$ for use with the linearized equations is to generalize the Chilton–Colburn analogy as (Stewart and Prober, 1964)

$$[\mathrm{St}] = [k^{\rm V}]/(V/A_{\rm c}) = (f/2)[\mathrm{Sc}]^{-2/3} = (f/2)\{[D]\rho_{\rm t}/\mu\}^{2/3} \qquad (17)$$

where $[D]$ is the matrix of multicomponent diffusion coefficients relative to the molar average velocity $(N_{\rm t}^{\rm V}/c_{\rm t})$. For gas mixtures, $[D]$ is equal to $[M]^{-1}$ defined by eq 13 and 14 if the $\mathcal{K}_{ij}$'s are replaced by the binary diffusion coefficients $\mathcal{D}_{ij}$. $[D]$ should be evaluated at a composition that is the average of the bulk and interface compositions. If eq 17 is used to obtain $[k^{\rm V}]$, the rate factor matrix should be calculated from $[\Phi] = N_{\rm t}^{\rm V}[K^{\rm V}]^{-1}/c_{\rm t}$.

A fundamental objection to the use of the Chilton–Colburn analogy in order to obtain the matrix of mass-transfer coefficients may be raised on the grounds that it does not correctly allow for the decreasing influence of coupled diffusion effects as the level of turbulence increases (through increasing the Reynolds number). It is easy to check, using equations 12–14 and 16, that the ratio of mass-transfer coefficients $k_{ij}^{\rm V}/k_{ii}^{\rm V}$ is independent of the numerical value of the Reynolds number. In fact, turbulent transport of mass is not species-specific, and this ratio should decrease as the Reynolds number increases. Krishna (1982) has developed a model of multicomponent mass transfer in which the contributions of molecular and turbulent diffusion are separately allowed for. The final expression from which the *mass* fluxes, n_i, are calculated is

$$(n^{\mathrm{V}}) = \rho_{\mathrm{t}}[k^{\bullet}_{\mathrm{m}}](\omega^{\mathrm{V}} - \omega^{\mathrm{I}}) + n_{\mathrm{t}}(\omega^{\mathrm{V}}) = \rho_{\mathrm{t}}[k^{\mathrm{V}}_{\mathrm{m}}][\Xi](\omega^{\mathrm{V}} - \omega^{\mathrm{I}}) + n_{\mathrm{t}}(\omega^{\mathrm{V}}) \quad (18)$$

where the ω_i are *mass* fractions and where $[k^{\mathrm{V}}_{\mathrm{m}}]$ the matrix of low-flux mass-transfer coefficients in the mass frame of reference is obtained from

$$[St]^{-1} = (2/f)[I] + 5(2/f)^{1/2}\{[Sc^0] - [I] + \ln\{[I] + \tfrac{5}{6}[Sc^0 - I]\}\} = u[k^{\mathrm{V}}_{\mathrm{m}}]^{-1} \quad (19)$$

Here, $[\mathrm{Sc}^0]^{-1} = [D^0]\rho_{\mathrm{t}}/\mu$ where $[D^0]$ is a matrix of multicomponent diffusion coefficients relative to the mass average velocity. The matrices $[D]$ and $[D^0]$ are related by the transformation (Krishna and Taylor, 1985)

$$[D^0] = [B^0]^{-1}[x][\omega]^{-1}[D][\omega][x]^{-1}[B^0] \quad (20)$$

The elements of the matrix $[B_m]$ are given by

$$B^0_{ij} = \delta_{ij} - \omega_i\left(\frac{x_j}{\omega_j} - \frac{x_n}{\omega_n}\right) \quad (21)$$

The correction factor $[\Xi]$ is still given by eq 12 but the matrix of rate factors $[\Phi]$ is given by

$$[\Phi] = [k^{\mathrm{V}}_{\mathrm{m}}]^{-1}n_{\mathrm{t}}/\rho_{\mathrm{t}} \quad (22)$$

It is important to recognize a number of essential differences between the film models and the turbulent eddy diffusivity model of Krishna (1982). First, the film models are based on the assumption of constant molar density, whereas the turbulent eddy diffusivity model requires that the mass density be assumed constant. Second, a knowledge of the velocity profile in the thin region close to the interface is not necessary in the film models; in the turbulent eddy diffusivity model, the variation with position of the turbulent eddy diffusivity model and the velocity profile must be known in order that the integration of the continuity and diffusion equations be carried out. Thus, if we use the Von-Karman velocity profile, we obtain eq 19 above for the mass-transfer coefficient matrix $[k^{\mathrm{V}}]$. Other velocity profiles yield different expressions for the mass-transfer coefficient matrix (see Krishna and Taylor (1985) for details). Finally, as stated above, the turbulent eddy diffusivity model predicts that the degree of interaction between the individual composition gradients should decrease as the Reynolds number increases. Krishna (1982) provides an illustrative example that shows that the turbulent eddy diffusivity models could predict directions of mass transfer for some species that are different from the directions predicted by using the Chilton–Colburn analogy to calculate $[k^{\mathrm{V}}]$.

The Chilton–Colburn analogy may also be used in the mass frame of reference; the mass fluxes are still given by eq 18 but the mass-transfer coefficient matrix $[k^{\mathrm{V}}_{\mathrm{m}}]$ is obtained from

$$[St] = [k^{\mathrm{V}}_{\mathrm{m}}]/(V/A_{\mathrm{c}}) = (f/2)[Sc^0]^{-2/3} = (f/2)([D^0]\rho_{\mathrm{t}}/\mu)^{2/3} \quad (23)$$

There is some evidence to show that the various film models that take interaction effects into account give very similar results when used to predict the performance of a condenser (Krishna et al., 1976; Krishna, 1979a; Röhm, 1980; Bandrowski and Kubaczka, 1981; Webb and Sardesai, 1981; Taylor and Noah, 1982). The film models that neglect interaction effects may sometimes give results that are quite different from those obtained by the more rigorous models (Krishna and Panchal, 1977; Krishna, 1979a). This paper is the first in which the turbulent eddy diffusivity models are compared to the film models in a simulation calculation.

Mass Transfer in the Liquid Phase. A description of the mass-transfer process in the liquid phase is not often included in condensation calculations because the principle resistance to mass and energy transfer resides in the vapor phase. For completeness, we provide a brief summary of possible approaches to modeling the liquid-phase resistance. We assume that the condensate is completely miscible (see, for example, Sardesai and Webb (1982) if it is not).

All the methods described above for calculating mass-transfer rates in gas/vapor mixtures may, in principle, be extended to deal with the liquid phase. Thus, for example, the effective diffusivity approach would lead to a rate equation of the form

$$N^{\mathrm{L}}_i = c^{\mathrm{L}}_{\mathrm{t}}k^{\mathrm{L}}_{i\mathrm{eff}}\Xi^{\mathrm{L}}_i(x^{\mathrm{I}}_i - x^{\mathrm{L}}_i) + x^{\mathrm{L}}_iN^{\mathrm{L}}_{\mathrm{t}} \quad (24)$$

$$i = 1, 2, ..., n$$

$$\Phi^{\mathrm{L}}_i = N^{\mathrm{L}}_t/(c^{\mathrm{L}}_{\mathrm{t}}k^{\mathrm{L}}_{i\mathrm{eff}})$$

$$\Xi^{\mathrm{L}}_i = \Phi^{\mathrm{L}}_i\exp(\Phi^{\mathrm{L}}_i)/(\exp(\Phi^{\mathrm{L}}_i) - 1)$$

A more rigorous approach to the calculation of the mass transfer in the liquid phase would lead to the rate equation

$$(N^{\mathrm{L}}) = c^{\mathrm{L}}_{\mathrm{t}}[k^{\mathrm{L}}][\Xi^{\mathrm{L}}](x^{\mathrm{I}} - x^{\mathrm{L}}) + N^{\mathrm{L}}_{\mathrm{t}}(x^{\mathrm{L}}) \quad (25)$$

which is the analogue of eq 10. Methods of calculating the various coefficient matrices involved may be derived as extensions of the methods presented above for multicomponent gas mixtures (see, for example, Krishna (1977, 1979b)). The most uncertain part of the calculation is obtaining the liquid-phase diffusivity matrix; this is still a subject for research. We shall deal with just two situations in this paper, the first in which the condensate is a binary liquid (for which the calculation of a diffusion coefficient and a mass-transfer coefficient poses no real problem—see below and part 2) and the second, a condensate formed from members of a homologous series of hydrocarbons for which the effective diffusivity approach is quite satisfactory.

Two limiting cases of condensate behavior may be derived from eq 24 and 25:

(i) The liquid phase is completely mixed with regard to composition (but not to temperature), corresponding to infinite liquid-phase mass-transfer coefficients and the liquid composition calculated from a material balance along the flow path

$$x^{\mathrm{I}}_i = x^{\mathrm{L}}_i = l_i/L \quad (26)$$

(ii) The liquid phase is completely unmixed, corresponding to zero liquid-phase mass-transfer coefficients. In this case, the interfacial composition is given by the relative rates of condensation

$$x^{\mathrm{I}}_i = N_i/N_{\mathrm{t}} \quad (27)$$

Most prior work in this area has used one or the other of these two limiting cases (see, for example: Schrodt, 1973; Krishna and Panchal, 1977). The former is applicable to vertical condensers where the two phases remain in close proximity, the latter to horizontal condensers where the condensate is continuously separated from the vapor (see for further discussion of this point: Schrodt, 1973; Webb and McNaught, 1980; Butterworth, 1983). Since there is no condensate at the top of a vertical condenser, initial condensation rates have usually been calculated by using the no-mixing limiting case. In fact, it is easy to show that the two limiting cases (eq 27 and 28) are equivalent at the vapor inlet. There is some evidence that the final design is insensitive to whichever extreme is chosen if inert species are present in the vapor mixture (Webb and Sardesai, 1981). We shall return to this topic later in this paper.

Energy Transfer. As noted above, eq 7, the local energy flux is made up of a conductive heat flux and a convective contribution due to the transport of energy by interphase mass transport.

$$E^{V} = q^{V} + \sum_{i=1}^{n} N_i \bar{H}_i^{V}(T^{V}) = E^{I} = q^{IL} + \sum_{i=1}^{n} N_i \bar{H}_i^{L}(T^{I}) = E^{L} = q^{L} + \sum_{i=1}^{n} N_i \bar{H}_i^{L}(T^{L}) = E^{W} = q^{W} \quad (28)$$

The film model of simultaneous mass and energy transfer leads to the following expression for the heat flux out of the bulk vapor, q^V (Krishna and Standard, 1979)

$$q^{V} = h^{V} \frac{\epsilon^{V}}{(e^{\epsilon^{V}} - 1)} (T^{V} - T^{I}) \quad (29)$$

where ϵ^V is defined by

$$\epsilon^{V} = \sum_{i=1}^{n} N_i C_{pi}^{V} / h^{V} \quad (30)$$

and where h^V is the low-flux heat-transfer coefficient. The function $\epsilon^V(\exp(\epsilon^V) - 1)$ serves to correct the low-flux coefficient for the effects of simultaneous mass transfer and is known as the Ackermann correction factor. In practice, h^V is estimated from an appropriate correlation, the j_H half of the Chilton–Colburn analogy, for example,

$$h^{V} = \mathcal{K}_{av} C_{pm}^{V} (Le^{V})^{2/3} \quad (31)$$

A turbulent eddy diffusivity model of simultaneous heat and mass transfer can easily be derived by paralleling the treatment of the corresponding mass-transfer problem, eq 23, derived by Krishna (1982). The final result, see Krishna and Taylor (1985) for a derivation, is identical in form with eq 23; the only difference is that the low-flux heat-transfer coefficient is given by (cf. eq 31)

$$\mathrm{St_H}^{-1} = (\rho u C_p / h^{V}) = (2/f) + 5(2/f)^{1/2}(\mathrm{Pr} - 1 + \ln(1 + \tfrac{5}{6}(\mathrm{Pr} - 1))) \quad (32)$$

For the liquid phase, a relation similar to eq 29 can be written

$$q^{IL} = h_{o}^{L}(T^{I} - T^{W}); \quad q^{L} = h^{L}(T^{I} - T^{L}) \quad (33)$$

where h_o^L is the heat-transfer coefficient that accounts for the resistance to heat transfer in the entire condensate film. Here, we have ignored the high-flux correction to h^L; the resistance to heat transfer in the liquid phase is very much smaller than in the vapor phase, and the correction factor would be very close to unity. The heat-transfer coefficient for the condensate can be estimated from, for example, Nusselts equation; other methods are discussed by Webb and McNaught (1980) and by Butterworth (1983).

There is no mass transfer through the tube wall into the coolant; thus the energy flux E^W is given by

$$E^{W} = q^{W} = h^{C}(T^{W} - T^{C}) \quad (34)$$

where h^C is the heat-transfer coefficient in the coolant.

If we substitute eq 29, 33, and 34 into the energy flux continuity eq (7), we find, noting that the choice of reference temperature (T_{ref}) is immaterial,

$$h^{V} \frac{\epsilon^{V}}{(e^{\epsilon^{V}} - 1)} (T^{V} - T^{I}) + h^{V}\epsilon^{V}(T^{V} - T^{I}) + \sum_{i=1}^{n} N_i \lambda_i = h_{o}^{L}(T^{I} - T^{W}) = h^{C}(T^{W} - T^{C}) = h_{o}(T^{I} - T^{C}) \quad (35)$$

where h_o is an overall heat-transfer coefficient accounting for the resistances to conductive heat transfer in the condensate and in the coolant (the resistance in the tube walls will normally be neglible).

$$1/h_{o} = 1/h_{o}^{L} + 1/h^{C} \quad (36)$$

h_o can be estimated from correlations applicable to the geometry of the condenser.

Interface Model. We adopt the conventional model of a phase interface, a surface offering no resistance to mass transfer and where equilibrium prevails. The usual equations of phase equilibrium relate the *mole* fractions on each side of the interface

$$y_i^{I} = K_i x_i^{I} \qquad i = 1, 2, ..., n \quad (37)$$

where K_i are the equilibrium ratios defined in the usual way.

This completes the formal development of the model; it remains to discuss how the equations can be solved. This is the subject of the next section.

The Computational Problem

The set of differential and algebraic equations given above must be solved numerically in general. The calculations start at the inlet to the condenser where the vapor temperature, pressure, and composition are known and proceed until either a specified area has been reached (a simulation problem) or until a specified amount has been condensed (a design problem). Each time the derivatives are calculated, the nonlinear algebraic equations from which the fluxes are obtained must be solved. If the simple forward Euler method of integration is used, then the rate equations need be solved only once per step. However, the solution so obtained pertains to the conditions at the beginning of the step where driving forces and, consequently, condensation rates are highest. Thus, the use of only a "few" Euler steps—by, for example, Webb and McNaught (1980)— may result in overprediction of the condensation rates and to an underdesigned condenser. For greater accuracy, a larger number of steps will have to be taken or, alternatively, a higher order integration method will have to be used; fourth order Runge-Kutta, for example, used by Webb and Sardesai (1981) and by Schrodt (1973). In either case the nonlinear rate equations will need to be solved quite a number of times in order to obtain a safer design. One way to obtain a more conservative design using a "first-order" method would be to use an implicit Euler method (Finlayson, 1980) and calculate the fluxes at the conditions pertaining to the end of the step where driving forces and concensation rates will be lowest. Perhaps a compromise solution in which the transfer rates are evaluated at some average conditions over the length of the step would be best. Either of these two approaches would lead to a more conservative design with relatively few integration steps. What we do is replace the derivatives in eq 1–6 by finite difference approximations (as is done in the simple Euler method); thus the balance equations become algebraic equations which can then be solved simultaneously with the rate equations to give the conditions at the end of the step. The difference between our approach and a correct implementation of the Euler method of integration is that we no longer need a separate routine for advancing the differential balance equations and the fluxes can be calculated by using, as boundary conditions, any combination of the conditions at the beginning and end of the step. In effect, we are dividing the condenser into a number of sections as shown on Figure 2. The equations representing the *j*th section (written in the form $F(X) = 0$ for reasons which the next section will make clear) are summarized below.

Equations and Variables for a Section of the Condenser. The balance equations for the *j*th section are as follows (derived from eq 1–6 as described above):

(i) material balance for the vapor phase

$$\mathcal{M}^{\mathrm{V}}_{ij} \equiv v_{i,j-1} - v_{ij} - N_{ij}\Delta A_j = 0 \quad i = 1, 2, ..., n \tag{38}$$

(ii) material balance for the liquid phase

$$\mathcal{M}^{\mathrm{L}}_{ij} \equiv l_{i,j-1} - l_{ij} + N_{ij}\Delta A_j = 0 \quad i = 1, 2, ..., n \tag{39}$$

(iii) energy balance for the vapor phase

$$\mathcal{E}^{\mathrm{V}}_j \equiv \bar{V}_j C^{\mathrm{V}}_{pj}(T^{\mathrm{V}}_{j-1} - T^{\mathrm{V}}_j) + q^{\mathrm{V}}_j \Delta A_j = 0 \tag{40}$$

with $\bar{V}_j = 0.5(V_j + V_{j-1})$

(iv) energy balance for the liquid phase

$$\mathcal{E}^{\mathrm{L}}_j \equiv \bar{L}_j C^{\mathrm{L}}_{pj}(T^{\mathrm{L}}_{j-1} - T^{\mathrm{L}}_j) - (q^{\mathrm{L}} - q^{\mathrm{W}})\Delta A_j = 0 \tag{41}$$

with $\bar{L}_j = 0.5(L_j + L_{j-1})$

(v) energy balance for the coolant

$$\mathcal{E}^{\mathrm{C}}_j \equiv L_c C^{\mathrm{C}}_{pj}(T^{\mathrm{C}}_{j-1} - T^{\mathrm{C}}_j) + q^{\mathrm{W}}_j \Delta A_j = 0 \tag{42}$$

The subscript *j* denotes the conditions at the end of the *j*th section (second subscript if component properties are involved) unless it is attached to a physical property or to a quantity with an overline (the significance of these quantities is discussed below).

These equations are augmented by

(vi) rate equations for the vapor phase

$$\mathcal{R}^{\mathrm{V}}_{ij} \equiv N_{ij} - c^{\mathrm{V}}_{\mathrm{t}j}\sum_{k=1}^{n-1} k^{\bullet}_{ik}(\bar{y}^{\mathrm{V}}_k - y^{\mathrm{I}}_k) - N_{\mathrm{t}j}\bar{y}^{\mathrm{V}}_{ij} = 0 \tag{43}$$

$$i = 1, 2, ..., n - 1$$

if the Krishna-Standart or Toor-Stewart-Prober film models are used or

$$\mathcal{R}^{\mathrm{V}}_{ij} \equiv N_{ij} - \{\rho^{\mathrm{V}}_{\mathrm{t}j}\sum_{k=1}^{n-1} k^{\bullet}_{\mathrm{m}ik}(\bar{\omega}^{\mathrm{V}}_k - \omega^{\mathrm{I}}_k) - n_{\mathrm{t}j}\bar{\omega}^{\mathrm{V}}_{ij}\}/M_i = 0 \tag{44}$$

$$i = 1, 2, ..., n - 1$$

if the turbulent eddy diffusivity models are used.

(vii) rate equations for the liquid phase, for example

$$\mathcal{R}^{\mathrm{L}}_{ij} \equiv N_{ij} - k^{\mathrm{L}}_{i\mathrm{eff}}\Xi^{\mathrm{L}}_i(x^{\mathrm{I}}_{-} - \bar{x}^{\mathrm{L}}_i) - N_{\mathrm{t}j}\bar{x}^{\mathrm{L}}_i = 0 \tag{45}$$

$$i = 1, 2, ..., n - 1$$

(viii) energy balance at the vapor liquid interface

$$\mathcal{E}^{\mathrm{I}}_j \equiv h^{\mathrm{V}}_j \frac{\epsilon^{\mathrm{V}}_j e^{\epsilon^{\mathrm{V}}{}_j}}{(e^{\epsilon^{\mathrm{V}}{}_{j-1}})}(\bar{T}^{\mathrm{V}}_j - T^{\mathrm{I}}_j) + \sum_{i=1}^{n} N_i\lambda_i - h_{\mathrm{o}j}(T^{\mathrm{I}}_j - \bar{T}^{\mathrm{C}}_j) \tag{46}$$

(ix) energy balance at the wall

$$\mathcal{E}^{\mathrm{W}}_j \equiv h^{\mathrm{C}}_j(T^{\mathrm{W}}_j - \bar{T}^{\mathrm{C}}_j) - h^{\mathrm{L}}_j(T^{\mathrm{I}}_j - T^{\mathrm{W}}_j) = 0 \tag{47}$$

(x) equilibrium equations for the interface

$$\mathcal{Q}^{\mathrm{I}}_{ij} \equiv K_{ij}x^{\mathrm{I}}_{ij} - y^{\mathrm{I}}_{ij} = 0 \quad i = 1, 2, ..., n \tag{48}$$

In compiling the above list of independent equations, we have used the mass continuity equations (3) to eliminate one set of molar fluxes (N^{V}_i or N^{L}_i). The bulk-phase conditions denoted by the overlines, $\bar{y}^{\mathrm{V}}_{ij}$, $\bar{T}^{\mathrm{V}}_j$, $\bar{x}^{\mathrm{L}}_{ij}$, $\bar{T}^{\mathrm{L}}_j$, $\bar{T}^{\mathrm{C}}_j$, appearing in the rate equations may be calculated by using the inlet conditions [e.g., $\bar{y}^{\mathrm{V}}_{ij} = v_{i,j-1}/V_{j-1}$], the outlet conditions [e.g., $\bar{y}^{\mathrm{V}}_{ij} = v_{ij}/V_j$], or at some average condition [e.g., $\bar{y}^{\mathrm{V}}_{ij} = 0.5[v_{i,j-1}/V_{j-1} + v_{ij}/V_j]$. All physical properties are evaluated at the bulk conditions used in the determination of the mass- and energy-transfer rates and are considered constant in the section. The interface state and wall temperature also are considered to be uniform in the *j*th section; thus the mass- and energy-transfer rate equations as well as the equilibrium equations need to be solved only once per step.

Given the state of all streams leaving section $j - 1$, then there is a total of $5n + 3$ unknown quantities for each section *j*. These are the component vapor flow rates (v_{ij}: n in number), the component liquid flow rates (l_{ij}: n in number), the vapor temperature (T^{V}_j), the liquid temperature (T^{L}_j), the interface temperature (T^{I}_j), the wall temperature (T^{W}_j), the coolant temperature (T^{C}_j), the vapor composition at the interface (y^{I}_{ij}: $n - 1$ in number), the liquid composition at the interface (x^{I}_{ij}: $n - 1$ in number), and the mass-trasfer rates (N_{ij}: n). The $5n + 3$ equations that permit the calculation of these unknowns are as follows: component material balances for the vapor phase (M^{V}_{ij}: n), component material balances for the liquid phase (M^{L}_{ij}: n), the vapor-phase energy balance (E^{V}_j), the liquid-phase energy balance (E^{L}_j), the interface energy balance (E^{I}_j), the coolant energy balance (E^{C}_j), the interface equilibrium equations (Q^{I}_{ij}: n), the vapor-phase mass-transfer rate equations (R^{V}_{ij}: $n - 1$ in number), and the liquid-phase mass-transfer rate equations (R^{L}_{ij}: $n - 1$ in number).

The independent equations are ordered into a vector of functions as a

$$(F_j)^{\mathrm{T}} \equiv (\mathcal{M}^{\mathrm{V}}_{1j}, \mathcal{M}^{\mathrm{V}}_{2j}, ..., \mathcal{M}^{\mathrm{V}}_{nj}, \mathcal{M}^{\mathrm{L}}_{1j}, \mathcal{M}^{\mathrm{L}}_{2j}, ..., \mathcal{M}^{\mathrm{L}}_{nj}, \mathcal{E}^{\mathrm{V}}_j, \mathcal{E}^{\mathrm{L}}_j, \mathcal{E}^{\mathrm{C}}_j, \mathcal{E}^{\mathrm{W}}_j, \mathcal{R}^{\mathrm{V}}_{1j}, \mathcal{R}^{\mathrm{V}}_{2j}, ..., \mathcal{R}^{\mathrm{V}}_{n-1,j}, \mathcal{E}^{\mathrm{I}}_j, \mathcal{Q}^{\mathrm{I}}_{1j}, \mathcal{Q}^{\mathrm{I}}_{2j}, ..., \mathcal{Q}^{\mathrm{I}}_{n-1,j}, \mathcal{Q}^{\mathrm{I}}_{nj}, \mathcal{R}^{\mathrm{L}}_{1j}, \mathcal{R}^{\mathrm{L}}_{2j}, ..., \mathcal{R}^{\mathrm{L}}_{n-1,j})$$

The vector of variables corresponding to this set of equations is

$$(X_j)^{\mathrm{T}} \equiv (v_{1j}, v_{2j}, ..., v_{nj}, l_{1j}, l_{2j}, ..., l_{nj}, T^{\mathrm{V}}_j, T^{\mathrm{L}}_j, T^{\mathrm{C}}_j, T^{\mathrm{W}}_j, N_{1j}, N_{2j}, ..., N_{n-1,j}, N_{nj}, y^{\mathrm{I}}_{1j}, y^{\mathrm{I}}_{2j}, ..., y_{n-1,j}, T^{\mathrm{I}}_j, x^{\mathrm{I}}_{ij}, x^{\mathrm{I}}_{2j}, ..., x^{\mathrm{I}}_{n-1,j})$$

Solving the MERQ Equations. We now address the problem of solving what we refer to as the MERQ (an acronym for material balance, energy balance, rate, and equilibrium) equations represented by the function vectors (F_j). The equations are nonlinear (due to the presence of K values, enthalpies, and the mass- and energy-transfer rate terms) and must therefore be solved by some iterative method. Most of the methods described in the literature employ some kind of tearing strategy to solve the condensation equations. Equation tearing involves iteratively solving a subset of the complete set of governing equations for a subset (the tear variables) of the complete set of unknowns. Within the loop that determines how the tear variables are to be reestimated, all other equations are satisfied exactly. Thus, if the remaining subset of equations also requires iteration (or, possibly, further tearing), the end result is a series of nested iteration loops. For example, Krishna et al. (1976) solve the mass- and energy-transfer rate equations (by repeated substitution of the N_i) and the vapor/liquid equilibrium equations (bubble point calculations) within an outer loop that, in effect, solved the liquid mixing equations by using Newton's method. The outer-loop tear variables were the $n - 1$ interfacial compositions x_i^I. Other tearing algorithms, those of Price and Bell (1974) and of Webb and co-workers (Webb and McNaught, 1980; Webb and Taylor, 1982; Webb, 1982) involve up to three levels of iteration loop.

One problem with tearing is the number of times physical properties must be evaluated (several times per outer-loop iteration) if temperature- and composition-dependent physical properties are used. It is the physical property calculations that generally dominate the cost of chemical process design problems (Westerberg et al., 1979) (the present problems are no exception). A second problem can arise if the inner iteration loops are hard to converge. The mass-transfer rate equations, R_{ij}^V, can sometimes be hard to converge by using repeated substitution of the N_i (Taylor and Webb, 1981), and the difficulties of converging bubble and dew point calculations are well-known. All these problems have been encountered in solving by tearing the condensation equations presented above. We wonder what point there is to requiring subsets of the complete set of equations to be satisfied exactly (by iteration) if the current estimate of the tear variables does not pertain to the solution. We suggest that a better strategy is to solve *all* the equations simultaneously by guessing enough unknown quantities to permit *all* other quantities appearing in eq 38–48 to be calculated explicitly *and* by not requiring any of the equations to be satisfied until complete convergence has been achieved. In the present case, this means solving the MERQ equations simultaneously for the vector of unknowns that gives $(F_j) = (0)$.

Having decided to solve all of the MERQ equations simultaneously, we must now choose a particular method to get us the solution. There are a great many methods that one may choose from (see, for example, the book by Ortega and Rheinbolt (1970)). However, we recommend that Newton's method, or the so-called hybrid method of Lucia and co-workers (Lucia and Machietto, 1983; Westman, Lucia and Miller, 1984; Lucia and Westman, 1984) be used. A brief description of their method follows.

The direct prediction Newton correction is given by a solution of the equations (F) linearized about the current estimate (X_k) of (X)

$$[J_k](X_{k+1} - X_k) = -(F_k) \tag{49}$$

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

$$J_{ij} = \partial F_i/\partial X_j \tag{50}$$

If a problem with Newton's method exists, it is the computation of $[J]$. For most engineering problems of reasonable complexity, complete derivative information is rarely available in analytic form. Thus, finite differences must be used to approximate all or part of $[J]$. In the present case, these "unavailable" derivatives include derivatives of K values with respect to composition, derivatives of the mass-transfer coefficients with respect to the molar fluxes, and so on. Finite difference approximations to these derivatives are very expensive since many more physical property calculations are required. Moreover, it is not always a good idea to simply ignore these derivatives as this can increase the number of iterations needed or even cause failure (Lucia and Machietto, 1983).

One way to avoid the repeated calculation of $[J]$ is to use one of the "quasi-Newton" methods (see Dennis and More (1977) for a recent review of these methods). The idea here is to approximate the Jacobian matrix in some way by using only an initial approximation to $[J]$ and some information on the changes in (X) and (F) from one iteration to the next. This can result in a very large reduction in the computational cost per iteration. Unfortunately, there may be a penalty for approximating the Jacobian using a quasi-Newton formula. If the initial approximation is poor, a (much) larger number of iterations may be required or, worse still, convergence may never be achieved. Also, quasi-Newton methods 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; if SI units are used in the calculations, then the numerical values of the variables and functions in (F) vary over 10 orders of magnitude (10^{-5}–10^5).

In the hybrid method of Lucia and co-workers, the Jacobian matrix is split into two parts, a computed part, $[C_k]$, and an approximated $[A_k]$:

$$[J_k] = [C_k] + [A_k] \tag{51}$$

$[C_k]$ contains all the partial derivatives of (F) which can be obtained from analytical expressions. $[A_k]$ is made up of any partial derivatives that are difficult or impossible to obtain from analytical expressions. $[C]$ is computed in each iteration while $[A]$ only is updated from an initial approximation using a quasi-Newton method. The correction to (X_k) is given by eq 49 with $[J]$ given by eq 51. A step-by-step procedure for implementing the hybrid method can be found in the aforementioned papers by Lucia and others. We had earlier described the use of the hybrid method to solve only the equilibrium and rate equations and found it to be a robust and efficient procedure (Taylor et al., 1983). Additional remarks pertaining to the use of the hybrid method to solve these equations can be found in that paper. We note here that including the material balance, or M, equations in the vector (F) only serves to increase the advantages of the hybrid method over all other methods that we have considered.

Calculation Procedure. We are now in a position to summarize our recommended calculation procedure. The conditions of the entering streams (V_0, v_{i0}, and T_0^V and the pressure must be specified (L_0 and l_{i0} must also be specified if they are non-zero—see part 2). The coolant temperature at the vapor entrance end of the condenser is required if the coolant temperature is to be included as a variable (or else specified if it is not). The number of sections, s, must be known in advance as well as the area of each section (this can be calculated from the geometry of the condenser and must be fixed prior to performing a simulation calculation).

The MERQ equations for step 1 are solved in order to obtain the conditions at the end of section 1 and at the beginning of section 2 and so on. If Newton's method or the hybrid approach are used, this will require the calculation of the function vector (F) at least once per iteration. A possible route is summarized below. Note that at any time, the discrepancy functions (F) are to be calculated by using the current values of the independent variables (X). This means that an initial guess of each quantity appearing in (X) must be supplied for section 1. Thereafter, good initial estimates of the unknowns for section j ($j = 2, ..., s$) become available from the solution to the equations for step $j - 1$.

(i) Using the current values of the component flows at the end of the section, v_{ij} and l_{ij}, calculate the compositions of the bulk vapor and liquid streams; any combination of the following may be used as desired

(a) inlet

$$\bar{y}_{ij}^{\mathrm{V}} = v_{i,j-1}/V_{j-1}; \quad \bar{x}_{ij}^{\mathrm{L}} = l_{i,j-1}/L_{j-1}$$

(b) average

$$\bar{y}_{ij}^{\mathrm{V}} = 0.5(v_{i,j-1}/V_{j-1} + v_{ij}/V_j); \quad \bar{x}_{ij}^{\mathrm{L}} = 0.5(l_{i,j-1}/L_{j-1} + l_{ij}/L_j)$$

(c) end

$$\bar{y}_{ij}^{\mathrm{V}} = v_{ij}/V_j; \quad \bar{x}_{ij}^{\mathrm{L}} = l_{ij}/L_j$$

(ii) In a similar way, calculate the bulk temperatures, $\bar{T}_j^{\mathrm{V}}$, $\bar{T}_j^{\mathrm{C}}$, and $\bar{T}_j^{\mathrm{L}}$.

(iii) Calculate all physical and transport properties at the required conditions. In some cases, film average temperatures and compositions may need to be used. These average conditions can easily be calculated with the information presently available.

(iv) Calculate the mass- and heat-transfer coefficients by using whatever method is preferred (see discussion above).

(v) Calculate K values and latent heats of vaporization at the current estimate of the interfacial conditions.

(vi) Complete the calculation of the MERQ equations (38)–(48).

Following the calculation of (F), the Jacobian matrix must be calculated as outlined above and the next estimate of (X) computed from the solution of the linear system (49). The calculations are then repeated until convergence of all functions has been obtained. In practice, this means converging the energy balances since these functions have numerical values far larger than any of the others. Once convergence has been obtained, the solution vector (X^*) is used to initialize the calculations for the next section. In this way, we proceed until the end of the condenser is reached.

Some Variations on a Theme. There are many instances in which the equation and variable sets presented above can be simplified somewhat. We consider several special cases below.

(i) One approximation that might be worth consideration is to set the condensate temperature to the arithmetic average of the wall and interface temperatures. If this is done, the liquid-temperature and liquid-phase energy balance can be removed from the set of independent varibles and equations, respectively. This leaves us with a total of $5n + 2$ independent equations and variables per section:

$$(F_j)^{\mathrm{T}} \equiv (\mathcal{M}_{1j}^{\mathrm{V}}, \mathcal{M}_{2j}^{\mathrm{V}}, ..., \mathcal{M}_{nj}^{\mathrm{V}}, \mathcal{M}_{1j}^{\mathrm{L}}, \mathcal{M}_{2j}^{\mathrm{L}}, ..., \mathcal{M}_{nj}^{\mathrm{L}}, \mathcal{E}_j^{\mathrm{V}}, \mathcal{E}_j^{\mathrm{C}}, \mathcal{E}_j^{\mathrm{W}}, \mathcal{R}_{1j}^{\mathrm{V}}, \mathcal{R}_{2j}^{\mathrm{V}}, ..., \mathcal{R}_{n-1,j}^{\mathrm{V}}, \mathcal{E}_j^{\mathrm{I}}, \mathcal{Q}_{1j}^{\mathrm{I}}, \mathcal{Q}_{2j}^{\mathrm{I}}, ..., \mathcal{Q}_{n-1,j}^{\mathrm{I}}, \mathcal{Q}_{nj}^{\mathrm{I}}, \mathcal{R}_{1j}^{\mathrm{L}}, \mathcal{R}_{2j}^{\mathrm{L}}, ..., \mathcal{R}_{n-1,j}^{\mathrm{L}})$$

$$(X_j)^{\mathrm{T}} \equiv (v_{1j}, v_{2j}, ..., v_{nj}, l_{1j}, l_{2j}, ..., l_{nj}, T_j^{\mathrm{V}}, T_j^{\mathrm{C}}, T_j^{\mathrm{W}}, N_{1j}, N_{2j}, ..., N_{n-1,j}, N_{nj}, y_{1j}^{\mathrm{I}}, y_{2j}^{\mathrm{I}}, ..., y_{n-1,j}, T_j^{\mathrm{I}}, x_{ij}^{\mathrm{I}}, x_{2j}^{\mathrm{I}}, ..., x_{n-1,j}^{\mathrm{I}})$$

It should be noted that this approximation is made in all the numerical simulations of multicomponent condensers described in this paper and in all the other special cases described below.

(ii) If we choose to approximate the mass-transfer process in the liquid phase by one of the two limiting cases (eq 25 and 26), then the rate equations $\mathcal{R}_{ij}^{\mathrm{L}}$ need to be replaced by the mixing equations, $\mathcal{X}_{ij}^{\mathrm{L}}$.

$$\mathcal{X}_{ij}^{\mathrm{L}} \equiv x_{ij}^{\mathrm{I}} - x_{ij}^{\mathrm{L}} = 0 \quad \text{(mixed)} \tag{52}$$

$$\mathcal{X}_{ij}^{\mathrm{L}} \equiv x_{ij}^{\mathrm{I}} - N_{ij}/N_{\mathrm{t}j} = 0 \quad \text{(unmixed)} \tag{53}$$

$$(F_j)^{\mathrm{T}} \equiv (\mathcal{M}_{1j}^{\mathrm{V}}, \mathcal{M}_{2j}^{\mathrm{V}}, ..., \mathcal{M}_{nj}^{\mathrm{V}}, \mathcal{M}_{1j}^{\mathrm{L}}, \mathcal{M}_{2j}^{\mathrm{L}}, ..., \mathcal{M}_{nj}^{\mathrm{L}}, \mathcal{E}_j^{\mathrm{V}}, \mathcal{E}_j^{\mathrm{C}}, \mathcal{E}_j^{\mathrm{W}}, \mathcal{R}_{1j}^{\mathrm{V}}, \mathcal{R}_{2j}^{\mathrm{V}}, ..., \mathcal{R}_{n-1,j}^{\mathrm{V}}, \mathcal{E}_j^{\mathrm{I}}, \mathcal{Q}_{1j}^{\mathrm{I}}, \mathcal{Q}_{2j}^{\mathrm{I}}, ..., \mathcal{Q}_{n-1,j}^{\mathrm{I}}, \mathcal{Q}_{nj}^{\mathrm{I}}, \mathcal{X}_{1j}^{\mathrm{L}}, \mathcal{X}_{2j}^{\mathrm{L}}, ..., \mathcal{X}_{n-1,j}^{\mathrm{L}})$$

$$(X_j)^{\mathrm{T}} \equiv (v_{1j}, v_{2j}, ..., v_{nj}, l_{1j}, l_{2j}, ..., l_{nj}, T_j^{\mathrm{V}}, T_j^{\mathrm{C}}, T_j^{\mathrm{W}}, N_{1j}, N_{2j}, ..., N_{n-1,j}, N_{nj}, y_{1j}^{\mathrm{I}}, y_{2j}^{\mathrm{I}}, ..., y_{n-1,j}^{\mathrm{I}}, T_j^{\mathrm{I}}, x_{ij}^{\mathrm{I}}, x_{2j}^{\mathrm{I}}, ..., x_{n-1,j}^{\mathrm{I}})$$

In either case, we might choose to delete the x_{ij}^{I} and l_{ij} from the set of variables and compute them directly from eq 52 and 53 which, therefore, would be removed from the set of independent equations.

$$(F_j)^{\mathrm{T}} \equiv (\mathcal{M}_{1j}^{\mathrm{V}}, ..., \mathcal{M}_{nj}^{\mathrm{V}}, \mathcal{E}_j^{\mathrm{V}}, \mathcal{E}_j^{\mathrm{C}}, \mathcal{E}_j^{\mathrm{W}}, \mathcal{R}_{1j}^{\mathrm{V}}, ..., \mathcal{R}_{n-1,j}^{\mathrm{V}}, \mathcal{E}_j^{\mathrm{I}}, \mathcal{Q}_{1j}^{\mathrm{I}}, ..., \mathcal{Q}_{n-1,j}^{\mathrm{I}}, \mathcal{Q}_{nj}^{\mathrm{I}})$$

$$(X_j)^{\mathrm{T}} \equiv (v_{1j}, ..., v_{nj}, T_j^{\mathrm{V}}, T_j^{\mathrm{C}}, T_j^{\mathrm{W}}, N_{1j}, ..., N_{n-1,j}, N_{nj}, y_{1j}^{\mathrm{I}}, ..., y_{n-1,j}^{\mathrm{I}}, T_j^{\mathrm{I}})$$

(iii) If one component in the vapor is truly noncondensable (or the calculations are to be made assuming that it is noncondensable), then the equations pertaining to that component (lets call it component n) will need to be modified. To start with, component n cannot, by definition, be present in the condensate which, therefore, contains $n - 1$ species. The set of mass-transfer rate equations in the liquid phase must be reduced in number by one, and the flux N_n dropped from the set of variables. Also, the equilibrium equation corresponding to component n and the liquid-phase composition x_{ij}^{I} must be removed from the set of equations and variables. If, in addition, the condensate is considered to be well-mixed or completely unmixed, we are left with the following vectors of equations and variables:

$$(F_j)^{\mathrm{T}} \equiv (\mathcal{M}_{1j}^{\mathrm{V}}, ..., \mathcal{M}_{nj}^{\mathrm{V}}, \mathcal{E}_j^{\mathrm{V}}, \mathcal{E}_j^{\mathrm{C}}, \mathcal{E}_j^{\mathrm{W}}, \mathcal{R}_{1j}^{\mathrm{V}}, ..., \mathcal{R}_{n-1,j}^{\mathrm{V}}, \mathcal{E}_j^{\mathrm{I}}, \mathcal{Q}_{1j}^{\mathrm{I}}, ..., \mathcal{Q}_{n-1,j}^{\mathrm{I}})$$

$$(X_j)^{\mathrm{T}} \equiv (v_{1j}, ..., v_{nj}, T_j^{\mathrm{V}}, T_j^{\mathrm{C}}, T_j^{\mathrm{W}}, N_{1j}, ..., N_{n-1,j}, T_j^{\mathrm{I}}, y_{1j}^{\mathrm{I}}, ..., y_{n-1,j}^{\mathrm{I}})$$

Notice that the interface temperature, T_j^{I}, now is paired with the interface energy balance function E_j^{I}, *not* the equilibrium equation Q_{nj}^{I} which has been dropped. As in all other cases, the interface mole fraction y_{nj}^{I} is computed from the requirement that the mole fractions sum to unity.

(iv) If the wall temperature profile is known, as is the case in some of the test condensers described in part 2, then it is convenient to remove the coolant temperature and coolant energy balance from the sets of variables and equations.

$$(F_j)^{\mathrm{T}} \equiv (\mathcal{M}_{1j}^{\mathrm{V}}, ..., \mathcal{M}_{nj}^{\mathrm{M}}, \mathcal{E}_j^{\mathrm{V}}, \mathcal{R}_{1j}^{\mathrm{V}}, ..., \mathcal{R}_{n-1,j}^{\mathrm{V}}, \mathcal{E}_j^{\mathrm{I}}, \mathcal{Q}_{1j}^{\mathrm{I}}, ..., \mathcal{Q}_{n-1,j}^{\mathrm{I}})$$

$$(X_j)^{\mathrm{T}} \equiv (v_{1j}, ..., v_{nj}, T_j^{\mathrm{V}}, N_{1j}, ..., N_{n-1,j}, T_j^{\mathrm{I}}, y_{1j}^{\mathrm{I}}, ..., y_{n-1,j}^{\mathrm{I}})$$

where we have also incorporated the simplifications that were made in (iii) above.

(v) The last (but by no means the least important) simplification that we sometimes make is to remove the vapor- and liquid-phase material balance equations ($\mathcal{M}_{ij}^{\mathrm{V}}$, $\mathcal{M}_{ij}^{\mathrm{L}}$) from the set of independent equations. These equations are linear if the fluxes N_{ij} are included in the set of variables (X) (which, of course, they must be if the rate equations are to be solved simultaneously with the other equations). Thus, the balance equations (38) and (39) can be solved directly for the component flow rates at the end of the jth section given estimates of the molar fluxes and the bulk conditions calculated as desired. The inclusion of linear equations in the vector of functions (F) does nothing to affect the rate of convergence since they are always satisfied on every iteration after the first. Including the linear equations in (F) increases the computational cost slightly but it does reduce the initial effort of deriving and coding expressions for the partial derivatives of (F) and, in our experience, can sometimes improve the stability of the hybrid method by allowing more complete expressions for the partial derivatives to be included in the computed part $[C]$ and fewer derivatives in the approximated part $[A]$.

The model presented above may also be used, with only two small changes, to describe a cocurrent separation process in, for example, an adiabatic wetted wall column. In this case, the energy balance equations for the coolant and at the wall (eq 42 and 47) are dropped from the set of model equations and T^{W} and T^{C} are dropped from the set of variables. The energy balance for the liquid phase, eq 7, must be included here but is simplified by deleting the heat flux q^{W} from the right-hand side. We shall, indeed, solve the resulting set of equations in our simulations of some experiments to be described in part 2.

Other ways to simplify the general model may also be derived.

Counterflow and Multiple Passes. Thus far, we have focused on the initial-value problem where we specified the coolant temperature at the vapor inlet end of the condenser. In a counterflow exchanger, we will know the coolant inlet temperature, not the exit temperature, and so the procedure discussed above needs to be modified. Two possible approaches come to mind. First, we can guess the coolant exit temperature by using the method exactly as described above to predict, among other things, the coolant inlet temperature. Any discrepancy between the specified and calculated values is used as a basis for choosing a new coolant exit temperature and the procedure repeated until reasonable agreement is reached. The second approach is to solve the total of $S(5c + 3)$ nonlinear equations for the entire device simultaneously (not just the equations for one section at a time). In this case, the Jacobian is block-tridiagonal in structure. This is precisely what is found when the equations used to model multistage separation processes are solved simultaneously. The linear system (49) that results from this approach is efficiently solved by using one of several numerical methods (Westerberg et al., 1979). Of these two approaches, the former is easier to implement given a code for solving the initial-value problem with exit temperature specified. The latter approach would be more efficient if a large number of sections were used to model the device. However, the problems being solved here are unlikely to be very large so we would advocate the former approach, particularly if a good initial estimate of the coolant exit temperature can be obtained.

Multiple pass exchangers pose interesting modeling and computational problems; here we encounter cocurrent and countercurrent flow in the same device. An exchanger in which the condensing vapor is cooled by a coolant stream that takes two passes through the device provides the basis for illustrating a possible computational procedure. We will denote the temperature of the coolant *leaving* the jth section by T_j^{C1} and T_j^{C2}, the second superscript denoting the pass number. For simplicity, we will *assume* here that the conditions in the vapor condensate side are uniform throughout the section. Thus, we need only one additional equation, an energy balance similar to eq 42 for the counterflow coolant pass, the surface area in each coolant energy balance reflects the area per pass. The energy balance at the wall also needs to be modified to allow for heat transfer to each pass. Thus, we have a total of $5c + 4$ independent equations and variables per section. The assumption of uniform interface and wall temperature is, no doubt, unrealistic and can be replaced if desired, the penalty being an increase (perhaps a large one) in the number of equations being solved.

Both of the procedures discussed above for the single-pass exchanger can be adapted for the multipass device. If the former procedure is used, the guessed variable is the coolant exit temperature *or* the coolant turn temperature depending on whether the coolant enters (and leaves) at the vapor inlet end or not.

Computational Results and Discussion

We have carried out a very large number of simulations of multicomponent condensers using the model and calculation procedure described above. Four example problems only, adapted from the literature on multicomponent condensation, must suffice to illustrate the features of the model and calculation procedure.

Problem 1 involves the condensation of methanol and water in the presence of air, a system studied earlier by Schrodt (1973) and by Krishna and Panchal (1977) and Krishna (1979). Problem 2 is similar to problem 1 but involves helium instead of air as the noncondensing species. This change serves to increase the importance of diffusional interaction effects which are quite considerable in this system (Krishna, 1979). Problem 3 involves the condensation of a mixture of straight-chain hydrocarbon vapors taken originally from Kern (1950) and reconsidered by Webb and McNaught (1980) who used an effective diffusivity model to calculate the vapor-phase mass-transfer rates. Problem 4 is a variation on a problem considered by Krishna et al. (1976); it involves the same hydrocarbons as problem 3 with the addition of hydrogen (which, in fact, has a significant effect on the results). Unlike Krishna et al., we do not consider hydrogen to be a noncondensing gas; it is, however, only sparingly soluble in the condensate. In all cases, physical and transport properties, K values, and enthalpies were calculated by the methods used by those who last considered the problems and, with appropriate modifications to out computer code, we are able to reproduce their results. The problem specifications are summarized in Table I. Figures 3–12 present our solutions to these problems; the percentage of the vapor condensed, the composition of selected species, the temperatures are plotted as a function of condenser surface area for each problem in turn. In our discussion of these figures, we focus attention on the following: (i) a comparison of the noninteractive film models (the effective diffusivity methods) with the film models that take multicomponent interaction effects into account (Krishna-Standart, Toor-Stewart-Prober, Krishna (1979), and Taylor-Smith), (ii) a comparison of the molar frame models that use the Chilton–Colburn analogy to obtain the heat- and mass-transfer coefficients with the mass frame models, (iii) the influence of the model used to approximate the mass-transfer behavior in the liquid phase (i.e. mixed, unmixed, and rate model), and (iv) the importance of step size and choice of bulk-phase conditions (i.e., inlet, outlet, or average) on the conservatism and accuracy of the calculation.

Significance of Interaction Effects. In considering very many condenser simulation and design calculations (not just those reported here), we have yet to find an application where the differences between any of the molar frame models that account for interaction effects (Krish-

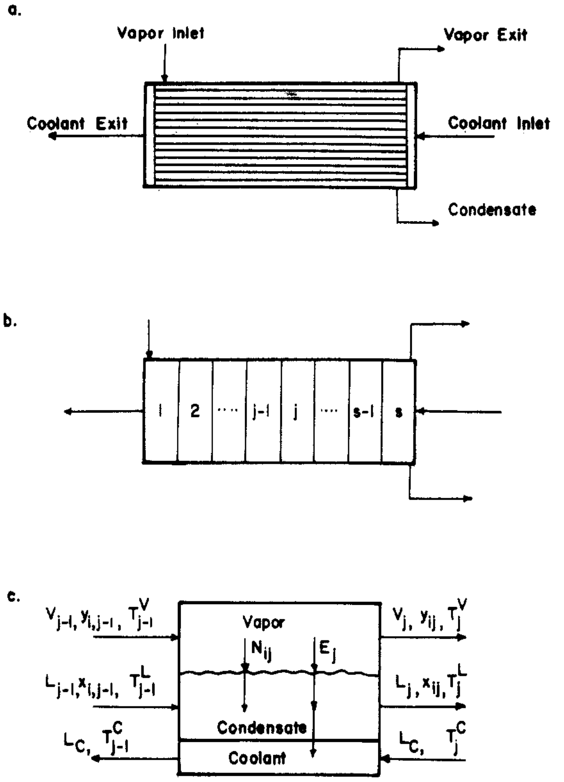

Figure 2. Model of a shell and tube condenser: (a) the entire condenser, (b) dividing the condenser into s sections, (c) a model of the jth section.

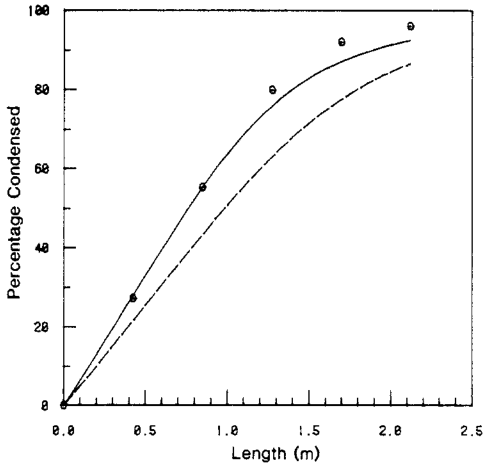

Figure 3. Percentage condensed as a function of condenser length—example 1. Key to Figures 3–8: (—) molar frame film model; (- - -) mass frame model (turbulent eddy diffusivity and Chilton–Colburn) if different from molar frame model; (– – –) effective diffusivity model. All lines are drawn through solutions obtained with condenser divided into 40 sections; (⊙) molar frame model with condenser divided into 5 sections.

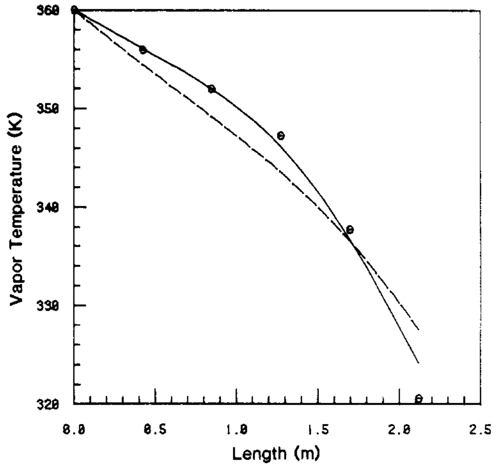

Figure 4. Vapor temperature as a function of condenser length—example 1.

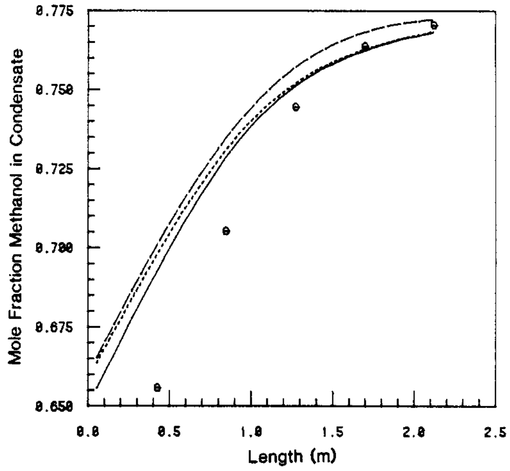

Figure 5. Condensate composition as a function of condenser length—example 1.

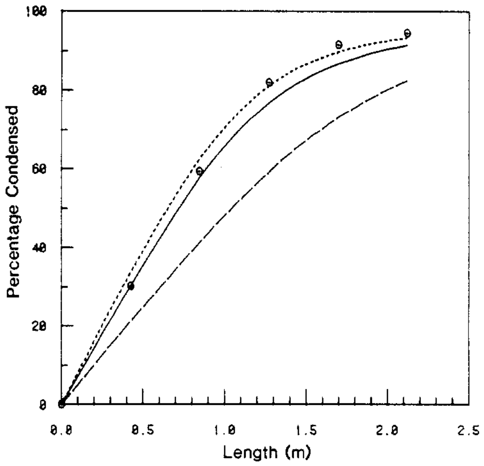

Figure 6. Percentage condensed as a function of condenser length—example 2.

na-Standart; Toor-Stewart-Prober; Krishna, 1979; Taylor-Smith) are really significant. However, effective diffusivity methods may yield results that can differ quite markedly from the results obtained by using an interactive model. Figures 5, 6, 9, and 11 can be used to determine the relative amounts of vapor that would condense in a device of given size. Consider problem 2 (for example): from Figure 6 we find that the tube length needed to condense 60% of the incoming vapor is 1.16 m predicted by using an interactive model but as much as 1.66 m predicted by using the effective diffusivity model, an increase in tube length of 43%! The temperature and composition of the vapor- and coolant-leaving condensers of either size (or and other size for that matter) can be determined directly from Figure 7. The condensate composition can be determined from Figure 8. For this particular example, we find that the molar frame and mass frame models that account for interaction effects are in good agreement on all these quantities but the effective diffusivity method predicts a mole fraction of methanol in the condensate quite different to that predicted by the interactive models (Figure 8). The large differences between the percentage condensed predicted by the interactive and noninteractive models is indicative of large

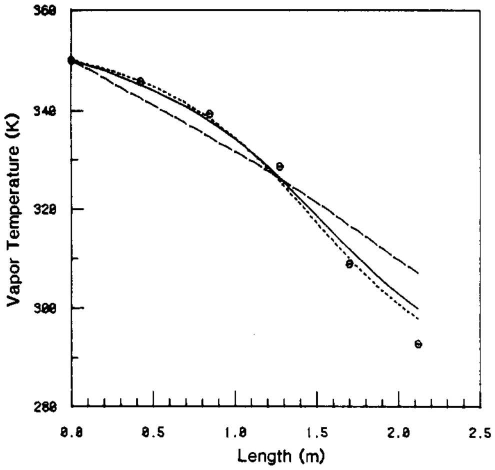

Figure 7. Vapor temperature as a function of condenser length—example 2.

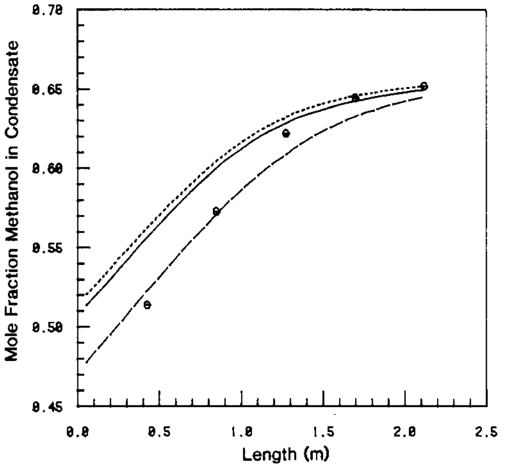

Figure 8. Condensate composition as a function of condenser length—example 2.

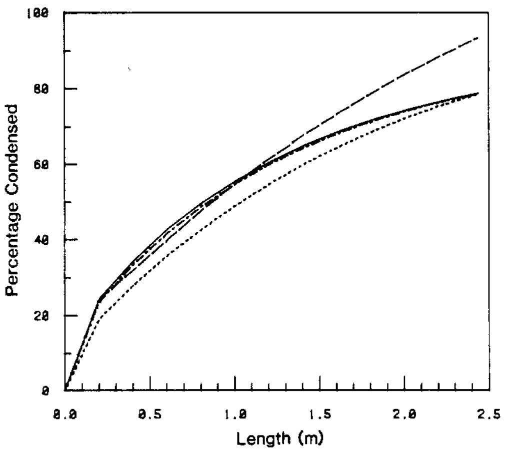

Figure 9. Percent condensed as a function of condenser length—example 3. Key to Figures 9–12: (---) molar frame film model with completely mixed condensate; (—) molar frame film model with condensate unmixed; (----) mass frame model with condensate unmixed; (···) effective diffusivity model with condensate unmixed.

differences between the respective predictions of the total fluxes; the disagreement between the two predictions of the condensate composition is a measure of the disagreement between the predictions of the component fluxes.

For example 1, we find that the interactive models suggest that tubes 1.41 m long will condense 65% of the incoming vapor, whereas the effective diffusivity method suggests that 1.84 m would be needed, a 30% larger condenser. The same relative difference in the size of device needed to condense 50% of the inlet vapor is found for example 3 (Figure 9).

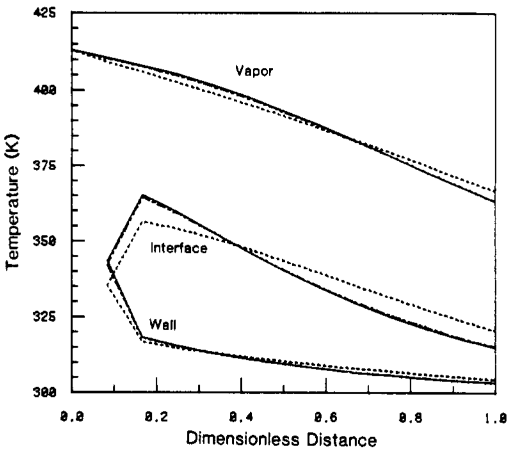

Figure 10. Temperature as a function of condenser length—example 3.

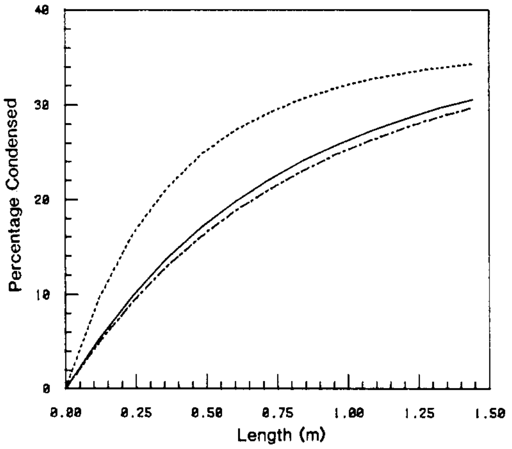

Figure 11. Percent condensed as a function of condenser length—example 4.

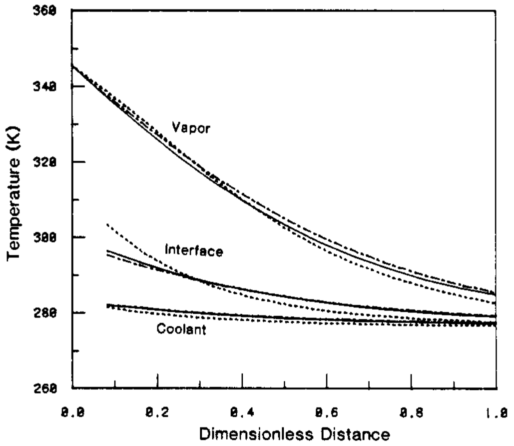

Figure 12. Temperature as a function of condenser length—example 4.

In each of these three examples, the effective diffusivity model gave the most conservative design (larger condenser surface area). That this is not always the case is demonstrated in example 4 where the effective diffusivity method requires some 44% *less* area to condense 30% of the inlet stream (Figure 11).

It is clear from these few results that the effective diffusivity methods may result in a *significantly* over- or underdesigned condenser. Further evidence of the influence of interaction effects in condensation can be found

Table I. Specification of Condenser Design Problems

problem	1	2	3	4
no. of components	3	3	5	6
components				
1	methanol	methanol	*n*-octane	*n*-octane
2	water	water	*n*-heptane	*n*-heptane
3	air	helium	*n*-hexane	*n*-hexane
4			*n*-butane	*n*-butane
5			propane	propane
6				hydrogen
tube orientation	vertical	vertical	vertical	vertical
tube diameter, m	0.0254	0.0254	0.0254	0.0254
surface area per m length of one tube, m^2	0.08	0.08	0.08	0.08
inlet vapor flow rates, kmol/s × 10^6 per tube				
component				
1	128.9	92.1	204.4	8.4
2	36.8	46.0	245.5	4.2
3	18.4	46.0	40.9	12.6
4			204.6	6.3
5			122.7	10.5
6				28.0
vapor inlet temp, K	360.0	350.0	413.06	345.4
coolant temp at top, K	308.15	308.15	300.0	283.15
coolant flow rate, kg/s	0.06	0.06		0.04376
coolant flow direction	counter	counter		counter
heat-transfer coeff (assumed const)				
h_o^L, W/(m^2 K)	1700	1700		1700
h^C, W/(m^2 K)			1700	

in the papers by Krishna et al. (1976), Krishna (1979a), and Röhm (1980). We shall return to this topic in part 2 where we provide some experimental support for our recommendation that an interactive model be used in design or simulation calculations. It is important to emphasize here that there are no computational advantages to using an effective diffusivity approach; if the calculations are done as we suggest, then all methods take roughly the same amount of time. Indeed, it is quite simple to devise problems in which the effective diffusivity methods require more computer time than the more rigorous methods.

Film Model or Turbulent Eddy Diffusivity Model. It must be stated at the outset that we have found that there is little to distinguish the mass frame models (turbulent eddy diffusivity and Chilton–Colburn) from the molar frame models (all of which use the Chilton–Colburn analogy) in these (and other) examples (see, however, part 2). Two ways of using the analogy need to be considered; the first in the molar frame of reference, the second in the mass frame of reference. First, there is very little difference between the turbulent eddy diffusivity model (which is necessarily based in the mass reference frame) and the Chilton–Colburn-based film model in the mass frame. Even at very high vapor flow rates, corresponding to inlet Reynolds numbers in the range of 60 000–100 000, we are unable to find situations where the turbulent eddy diffusivity models differ from the mass frame Chilton–Colburn methods to any extent. This is an important result for it indicates that the Chilton–Colburn analogy, widely used in design calculations, is perhaps unlikely to lead to large discrepancies when compared to the more sophisticated turbulent eddy diffusivity models. This is also important from the computational viewpoint; the Krishna–Standart, Toor–Stewart–Prober, and the explicit methods are somewhat less demanding of computer time than are the turbulent eddy diffusivity models. This is due to the necessity of computing the eigenvalues of $[D^0]$ and the matrix function in eq 19 using Sylvester's theorem. The matrix functions required in the Krishna–Standart and Toor–Stewart–Prober methods can be computed very much more efficiently (particularly if there are more than three or four components in the mixture) from a power series (Taylor and Webb, 1981; Taylor, 1982).

The differences between the mass reference frame and molar reference frame models are only a little more marked. In examples 1, 2, and 3, it is difficult, if not impossible, to distinguish between them. Only in example 4 is there a noticeable difference with the mass frame models, predicting that a condenser slightly larger than that given by the molar frame models is required.

A clue to the success of the Chilton–Colburn analogy can be found in the analysis carried out recently by Fletcher, Maskell, and Patrick (1982). Using a modified von-Driest mixing length model, Fletcher et al. showed that for Sc > 1, this model predicted a −2/3 power dependence of the Stanton number on the Schmidt number, in agreement with the Chilton–Colburn assumption. It is, however, pertinent to point out that the studies of Fletcher et al. also showed that for Sc < 1, the Stanton number varies inversely with the Schmidt number. One might expect from this result that for high molecular diffusivities of a particular binary pair the predictions of the Chilton–Colburn analogy are in error. Systems 2 and 4 of our study are of this kind and yet we find no serious disagreement using the Chilton–Colburn analogy. Why?

One reason for the close agreement between the molar frame models and the mass frame model is the tendency for different models to predict very similar total fluxes and fluxes of the major transferring species (with the same boundary conditions used for all models). Even the effective diffusivity models benefit from this. Serious discrepancies between the interactive models generally occur only for species whose fluxes are small relative to the major flux. In such cases, it is very likely that two different models will predict different directions of mass transfer for the minor transferring species; i.e., one model might predict that a species is evaporating while another may predict that the same species is condensing. The calculations made by Krishna (1982) are a case in point. There is, however, more to it; the close agreement between composition and temperature profiles is largely due also to the constraints of material and energy balance which we must impose on each section of the device. In order to illustrate this point, let us assume that two different mass-transfer models predict total fluxes and fluxes of the major transferring species that are in close agreement, with, say a 5% relative discrepancy (this is quite typical; see Smith and Taylor (1983)). Let us further assume that the two methods predict different directions of transfer for a minor transferring species and that the magnitude of this flux is about 10 times smaller than the major contribution to the total flux (in our experience, these are the only circumstances in which different interactive models can predict different directions of transfer for a species). It is easy to see with reference to the material balance equations (38) that the component flow rates (or the mole fractions) of *all* species will still be in reasonably good agreement at the end of the current section, even though one model has predicted a small increase in the flow rate of one component whereas another model predicted a small decrease. Moreover, it is also easy to check (with a few elementary calculations) that this conclusion is not affected by the relative amounts of the various species present in the vapor.

There is yet another reason why the various interactive models are usually in excellent agreement, also related to the requirements of mass and energy conservation. If one mass-transfer model predicts a high flux of one species in one section of the condenser, more of that component will condense in that section, leading to a lower driving force and, therefore, lower condensation rate in the next section. On the other hand, if another model predicts a lower condensation rate in one section of the condenser, not as much of that component is predicted to condense, leading to higher driving forces and condensation rates in the next section. In this way, overprediction in one section is compensated by underprediction in the next (or, of course, the opposite). To a very large extent, the effective diffusivity methods benefit from this as well; witness the relatively good predictions of the total amount condensed and of the total heat load in many of the experimental simulations in part 2 (although not in all the examples considered here).

Liquid-Phase Models. There is no significant difference between the two extremes of condensate mixing (i.e., completely mixed or completely unmixed) if there is a noncondensing or sparingly soluble gas present in the vapor stream (problems 1, 2, and 4). This conclusion was also reached by Krishna et al. (1976), Webb and Sardesai (1981), and Taylor and Noah (1982). However, in problem 3, in which all the components are condensable, there is a very considerable difference between these two extremes at the higher percentages of vapor condensed (Figure 7). McNaught (1983a) writes that it is common practice to assume complete mixing of the condensate when applying the Silver (1947) (equilibrium) method and "it is well-established that this can lead to underdesign if significant separation of the phases occurs" (as in a horizontal condenser). We find that the same thing can be said if complete mixing of the condensate is assumed in the nonequilibrium models described in this paper. A design based on the well-mixed condensate model might lead to a significant underdesign. We have also made some calculations for system 3 by using an effective diffusivity model for the mass-transfer process in the condensate. The use of a noninteracting model is justifiable in this case since the binary pair diffusivities are so close together. The low-flux mass-transfer coefficients were estimated from a penetration-type model of mass transfer (Bird et al., 1960, p 540) with the velocity of the liquid used as an adjustable parameter. Not surprisingly, we obtained results that were intermediate between the two extreme cases, eq 26 and 27; just how close the results are to one or other of the two extreme cases depends on the condensate velocity used in the calculations. Using a similar model for the liquid-phase transport in the other problems has a negligible effect on the results. We conclude from these and other results that we have obtained with similar systems that the more conservative design is, in general, obtained with the condensate assumed to be completely unmized. We would emphasize once more that there is no computational penalty for adopting either one of the two extreme cases. Interestingly enough, it is impossible to predict situations where some components condense while others evaporate, using the no-mixing option. It is quite possible to predict this situation with a rate model or with the well-mixed condensate; indeed, our computations indicate that this happens in problem 3 in some of the sections close to the vapor inlet.

Big Steps or Little Steps. The cost of a design calculation is directly proportional to the number of times the model equation set is to be solved. In turn, this number depends on the size of the area or length increment used in the calculations. Thus, a doubling of the length increment gives rise to about a 50% reduction in the computational cost. Krishna and Panchal (1977) and Krishna (1979) used the Euler method with steps only 5.3 cm in length. Webb and Sardesai (1981) used Merson's method of Runge-Kutta type to integrate over 1 m in five steps. This is *roughly* equivalent to a first-order method with steps of 4 cm. Is this the optimum size of length increment? The question we address now therefore is just exactly what size of area or length increment should be used in the calculations? The answer depends on the choice of bulk-phase conditions used in the rate equations. As noted above, there are three possibilities: using the inlet conditions, the outlet conditions, or some average of the two.

The shorter the length increment, the smaller is the discrepancy between the three averaging procedures. This, of course, is only to be expected since a large number of steps reduces the magnitude of the change in any particular quantity over any one length increment to the point where it does not matter much which conditions are used in the rate equations. Somewhat to our surprise, for a given number of steps, all three choices yield quite similar predictions of the total amount condensed and of the heat load. As expected, the use of the end-of-section conditions in the rate equations leads to the most conservative design (i.e., the lowest condensate flow). Also, the fewer the number of steps taken (or the longer the length increment), the more conservative the design and the cheaper the calculation.

It is in the prediction of the composition of the exit stream that leads to the largest discrepancies between the various alternatives. Using the *arithmetic* average of the mole fractions and temperatures at the beginning and at the end of the section in the rate equations for section j often gives good estimates of the composition and temperature of the exit stream with as few as *four* sections (or, sometimes, only two) if noncondensing or sparingly soluble gases are present. This is the case in all the example problems considered by Taylor and Noah (1982) (two of which are problems 1 and 2 in this paper) and in problem 4. In Figures 3–8, for example, the lines are drawn through 40 points (length increments of 5.3 cm—a little over 2 in.). However, a line drawn through 10 points (length increments of 21.2 cm) or even only 5 points (length increments of 41.4 cm—about 16 in.) would be virtually coincident with these lines (Figures 3 and 8). If all components condense (as in problem 3), it appears to be better to use the *end* of section conditions in the rate equations. It proved to be impossible to obtain solutions to problem 3 using either the beginning or average conditions with length increments as long as 61 cm (about 2 ft). This is due to the overprediction of the fluxes in the first sections of the condenser with the result that negative amounts of some species are present in downstream sections. This usually has disastrous consequences in the subroutines used to calculate the physical properties. With the end conditions used in the rate equations for problem 3, the predicted exit vapor composition does not change all that much as the size of each length increment is increased. Moreover, the results obtained with length increments as long as 61 cm are remarkably close to the results obtained using *much* smaller length increments (4 or 5 cm). The situation is completely different if the beginning conditions are used; with length increments of 30 cm (about 1 ft), the total amount condensed and heat load may be well enough predicted, but the mole fractions in the exit vapor may be in error by as much as an order of magnitude.

Based on all of our numerical computations, we find that condenser design or simulation calculations can be satisfactorily carried out with length increments in the range 25–50 cm (roughly 1–2 ft) provided that the appropriate bulk conditions are used in the rate equations. Such length increments are about 5–6 times longer than most of those used in the past; this results in a calculation that is about 5–6 times cheaper than those carried out previously.

Conclusions and Recommendations

We have reviewed in this paper a nonequilibrium model of multicomponent condensation. In particular, we have considered various approaches to calculating the rates of mass and energy transfer in the vapor and condensate, respectively. A new way of solving the model equations has been proposed, in which the differential conservation equations are approximated by finite differences and the resulting set of algebraic equations solved *simultaneously* with the nonlinear equations representing the processes of interphase transport and interfacial equilibrium. A number of special cases of the general model have also been identified.

With regard to the various models of vapor-phase mass transfer, we conclude the following:

1. Effective diffusivity models should not be used in the determination of the rates of mass transfer in the vapor phase. They are not justified on theoretical grounds nor, as we shall see in part 2, on experimental grounds, and their use offers no reduction in the cost of obtaining a solution or any increase in the ease by which that solution is obtained.

2. In agreement with earlier work in this area, we find that the film models that take interaction effects into account (Krishna–Standart, Toor–Stewart–Prober, Krishna (1979), Taylor–Smith) yield temperature and composition profiles that, for all practical purposes, are indistinguishable.

3. There is little to choose between the molar frame models that use the Chilton–Colburn analogy to obtain the heat- and mass-transfer coefficients and the mass frame methods (Chilton–Colburn and turbulent eddy diffusivity) when they are used to predict the performance of multicomponent condensers.

With regard to the liquid phase, we find (also in agreement with previous work) that there is very little to distinguish between the results obtained using the two extremes of condensate mixing if noncondensing or sparingly soluble gases are present in the vapor phase. There can be a very considerable different if all species condense. More conservative design is obtained with the liquid phase assumed to be completely unmixed.

We conclude from our calculations that the end-of-section conditions should be used in the determination of the rates of heat and mass transfer if all species condense. If noncondensing or sparingly soluble gases are present, the average of the beginning and end conditions should be used. The possibility of being able to complete a simulation calculation with fewer than ten sections (possibly with as few as two or four steps) or a design calculation with very long length increments, with a consequent large reduction in the computer time requirements (as compared to the numerical integration of the differential equations that we started with), overcomes one of the published objections to the use of the more realistic nonequilibrium models of condensation (Butterworth, 1983; McNaught, 1983a).

Acknowledgment

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Nomenclature

ΔA_j = interfacial area in the jth section of a condenser, m^2
$[A]$ = approximated part of Jacobian matrix, various
$[B^0]$ = transformation matrix
c_t = mixture molar dentisy, kmol m^{-3}
C_{pi} = molar heat capacity of component i, J kmol^{-1}
C_p = molar heat capacity of mixture, J kmol^{-1}
$[C]$ = computed part of Jacobian matrix, various
$\mathcal{D}_{ij}$ = diffusivity for pair $i - j$, m^2 s^{-1}
$D_{i\mathrm{eff}}$ = effective diffusivity of component i in multicomponent mixture, m^2 s^{-1}
$[D]$ = matrix of Fickian diffusion coefficients, m^2 s^{-1}
E = energy flux in stationary coordinate frame of reference, W m^{-2}
$\mathcal{E}$ = energy balance equation, W m^{-2}, W
f = Fanning friction factor
(F) = vector of independent equations, various
h = heat-transfer coefficient, W m^{-2} K^{-1}
$\bar{H}$ = partial molar enthalpy of component i, J kmol^{-1}
$[I]$ = identity matrix
j_D = Chilton–Colburn j factor for mass transfer
j_H = Chilton–Colburn j factor for heat transfer
$[J]$ = Jacobian matrix, various
$\mathcal{K}_{ij}$ = mass-transfer coefficient in a binary mixture, m s^{-1}
$[k]$ = matrix of multicomponent mass-transfer coefficients, m s^{-1}
$k_{i\mathrm{eff}}$ = pseudobinary (effective) mass-transfer coefficient of component i in a mixture, m s^{-1}
$[K]$ = matrix of multicomponent overall mass-transfer coefficients, m s^{-1}
K_i = equilibrium ratio [K value]
l_i = molar flow rate of component i in liquid phase, kmol s^{-1}
M_i = molecular weight of component i, kg kmol^{-1}
$[M]$ = symbol for a general matrix, various
$\mathcal{M}$ = material balance equation, kmol s^{-1}
n = number of components in the mixture
n_i = mass flux of component i referred to a stationary coordinate reference frame, kg m^{-2} s^{-1}
n_t = mixture total mass flux referred to a stationary coordinate reference frame, kg m^{-2} s^{-1}
N_i = molar flux of component i referred to a stationary coordinate reference frame, kmol m^{-2} s^{-1}
N_t = mixture molar flux of component i referred to a stationary coordinate reference frame, kmol m^{-2} s^{-1}
Pr = molecular Prandtl number
q = conductive heat flux, W m^{-2}
$\mathcal{Q}$ = equilibrium equation
Re = Reynolds number
$\mathcal{R}$ = mass-transfer rate equation, kmol m^{-2} s^{-1}, kmol s^{-1}
s = number of sections
Sc = Schmidt number
[Sc] = matrix of Schmidt number

St = Stanton number
T = temperature, K
V = molar flow rate of vapor mixture, kmol s^{-1}
v_i = molar flow rate of vapor component i, kmol s^{-1}
x_i = mole fraction of component i
(X) = matrix of independent variables, various
y_i = mole fraction of component i

Greek Letters

δ_{ik} = Kronecker delta, 1 if $i = k$, 0 if $i \neq k$
λ_i = molar heat of vaporization of component i, J kmol^{-1}
μ = molecular (dynamic) viscosity of mixture, Pa s
Ξ = correction factor for high fluxes in explicit methods
$\Xi_{i\text{eff}}$ = correction factor for high fluxes in pseudobinary (effective diffusivity) method
$[\Xi]$ = matrix of high flux correction factors
ρ_t = mixture mass density, kg m^{-3}
$\Phi_{i\text{eff}}$ = mass-transfer rate factor in pseudobinary (effective diffusivity) methods
$[\Phi]$ = matrix of mass-transfer rate factors
ϵ = heat transfer rate factor
ω_i = mass fraction of component i

Subscripts

eff = pseudobinary or "effective" parameter
I = referring to the interface
i = component i property or parameter
i, j, k = component indexes or section numbers, j only
m = refers to the mass reference frame
n = nth component
o = overall parameter
t = referring to total mixture

Superscripts

C = referring to the coolant
I = referring to the interface
L = referring to the liquid phase
0 = referring to the mass average velocity
V = referring to the vapor/gas phase
W = referring to the wall
• = denotes parameter under conditions of high transfer rates

Miscellaneous

$\bar{}$ = overbar denotes partial molar property; also averaged parameter

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