G = number of moles of A reacted
H = Heavyside's function
I = integral defined by Eq. 62
I_o = integral defined by Eq. 69
I_i = integral defined by Eq. 76
J_o = integral defined by Eq. 79
J_i = integral defined by Eq. 80
k = reaction rate constant
n = reaction order
$N(r)$ = molar flow rate of reaction mixture
N_{Bo} = Bodenstein number, ud_p/D
N_{Da} = Damköhler number, defined by Eq. 12
N^*_{Da} = Damköhler number defined by Eq. 17
N_{Pe} = Peclet number, u_2R_2/D_2
N^*_{Pe} = $u_1R_1^s/DR_2^{s-1}$
r = radial distance
s = geometry exponent, defined by Eq. 2
u = molar velocity of reaction mixture
$w(\xi)$ = mole fraction of species A for inward flow
$y(\xi)$ = mole fraction of species A for outward flow

Greek Letters

δ = quantity defined by Eq. 71
Δ = quantity defined by Eq. 67
ϵ = $y(1) - w(\xi_1)$
$\bar{\epsilon}$ = quantity defined by Eq. 57
τ = space time (volume of reactor/feed flow rate)
ξ = dimensionless radial distance, r/R_2
ν = stoichiometric coefficient describing change in total mole number

Subscripts

f = feed conditions
i = inward flow
o = outward flow
p = plug flow
1 = interior surface of the reactor
2 = exterior surface of the reactor

LITERATURE CITED

Burghart, A., and T. Zaleski, "Longitudinal Dispersion at Small and Large Peclet Numbers in Chemical Flow Reactors," *Chem. Eng. Sci.*, **26**, 1361 (1971).

Calo, J. M., and H. C. Chang, "Two Dimensional Non-Isothermal Cell Model of a Radial Flow Fixed Bed Reactor," CHISA '78, Prague, Czechoslovakia (1978).

Calo, J. M., "Cell Model Studies of Radial Flow Fixed Bed Reactors," ACS Symp. Ser., **65**, 550 (1978).

Duduković, M. P., and H. S. Lamba, "Analysis of the Radial Flow Fixed Bed Reactor," 80th AIChE National Meeting, Boston, MA (1975).

Himmelblau, D. M., and K. B. Bischoff, *Process Analysis and Simulation, Deterministic Systems*, John Wiley & Sons, New York (1968).

Hlavacek, V., and M. Kubicek, "Modelling of Chemical Reactors—XXV: Cylindrical and Spherical Reactor with Radial Flow," *Chem. Eng. Sci.*, **27**, 177 (1972).

Levenspiel, O., *Chemical Reaction Engineering*, 2nd ed., John Wiley & Sons, New York (1972).

Luss, D., "Sufficient Conditions for Uniqueness of the Steady State Solutions in Distributed Parameter Systems," *Chem. Eng. Sci.*, **23**, 1249 (1968).

Mears, D. E., "The Role of Axial Dispersion in Trickle-Flow Laboratory Reactors," *Chem. Eng. Sci.*, **26**, 1361 (1971).

Nayfeh, A. H., *Perturbation Methods*, Wiley, New York (1973).

Ponzi, P. R., and L. A. Kaye, "Effect of Flow Maldistribution on Conversion and Selectivity in Radial Flow Fixed Bed Reactors," *AIChE J.*, **25**, 108 (1978).

Raskin, A. Ya., Yu. A. Sokolinskii, V. I. Mukosei, and M. E. Aerov, "Mathematical Model and Calculation Algorithm for Radial Adiabatic Reactors," *Theor. Found. Chem. Tech.*, **2**, 220 (1968).

Strauss, A., and K. Budde, "Die Anwendung von Radial Stormreaktoren fiir Heterogen-Katalytiche Prozesse," *Chem. Techn.*, **30**, 73 (1978).

Trambouze, P., "Scale-Up Procedures for Refining and Petrochemical Processes," Euchem Conference, Santander, Spain (1978).

Van Dyke, M., *Perturbation Methods in Fluid Dynamics*, Academic Press, New York (1964).

Villadsen, J., and M. L. Michelsen, *Solution of Differential Equation Models by Polynomial Approximation*, Prentice-Hall, Inc. (1978).

Zwietering, Th.N., "The Degree of Mixing in Continuous Flow Systems," *Chem. Eng. Sci.*, **11**, 1 (1959).

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Minimum Reflux Conditions

Part I: Theory*

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This paper presents a new formulation of the infinite plate or minimum reflux limit of a multicomponent distillation column. Based on this model, two new calculation methods are developed. The first is a short-cut method which extends Underwood's classic minimum reflux treatment to variable molar overflow situations. The second is a rigorous method which is similar to a multicomponent flash calculation and represents a significant computational advance over other rigorous methods.

SCOPE

Accurate plate-by-plate simulations of multistage, multicomponent distillation columns require substantial computational effort. Consequently, simpler, limiting descriptions are useful to guide process synthesis decisions and optimum column design. This investigation focuses on the infinite plate or minimum reflux limit.

The calculation of minimum reflux conditions for a specified separation has often been the subject of theoretical study. Underwood (1946, 1948), Shiras et al. (1950), Bachelor (1957), McDonough and Holland (1962), Erbar and Maddox (1962), Lee (1974), Chien (1978), and Tavana and Hanson (1979) have all considered this problem. These authors approximate the infinite stage column by increasingly larger finite columns. Except in the case where relative volatilities and molar over-

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flows are constant (Underwood, 1948) or where all components of the feed are distributed (Shiras et al. 1950), such calculations, because of their large size, prove both difficult and expensive.

The present investigation differs from previous work in that it is based on a continuum model for the infinite stage column. Two calculation methods are developed using this model. The first is a short-cut method which assumes ideal solution behavior, constant relative volatilities, and temperature independent partial molar enthalpies. This calculation closely resembles Underwood's classic minimum reflux algorithm. The second is a rigorous method which incorporates non-ideal equilibrium and enthalpy behavior. This calculation requires simultaneous solution of a set of algebraic equations whose dimension equals the number of chemical species in the feed plus twice the number of non-distributed species in the column plus five.

Sample results obtained using these new calculation methods are presented and compared with Underwood's solution and with plate-by-plate simulation. Numerical solution of the new equations is discussed and illustrated in detail in a companion paper (Nandakumar and Andres, 1981).

CONCLUSIONS AND SIGNIFICANCE

The theoretical model for an infinite plate, multicomponent, distillation column that is developed in this work leads to new insight into steady-state minimum reflux behavior. This insight is developed by use of the model to rederive Underwood's classic minimum reflux equations and to derive two original calculation methods, which assume progressively less restrictive equilibrium and enthalpy behavior.

A short-cut method is derived based on the assumptions of ideal solution behavior, constant relative volatilities, and temperature independent partial molar enthalpies. This method incorporates the important effects of variable molar overflow, however, it is formally similar to Underwood's constant molar overflow algorithm and is as simple to use.

A rigorous calculation method is also derived. These equations can be used whenever there is an invariant relative volatility ordering among the non-distributed chemical species and when a "shock model" for the infinite stage column is valid. Within these restrictions the method is general. The vapor-liquid equilibrium relationship may be represented by any nonideal model, any nonideal enthalpy model may be assumed for the vapor or liquid phases, nonadjacent key components are permitted, and the exact infinite plate limit is obtained. Solution of the new equations is similar in computational complexity to the solution of the equations describing a multicomponent flash separation. In most cases, the method requires much less computation than is required either by a plate-by-plate simulation or by other rigorous minimum reflux methods.

Most distillation columns are "simple", having a single feed, single distillate product, and single bottoms product. Such columns are used to separate two chemical species in a multicomponent feed. When the number of plates in a simple column is varied, the specified separation often can be maintained by simultaneously adjusting reflux rate. Two limiting conditions arise: (1) "minimum reflux" corresponding to an infinite number of plates; and (2) "total reflux" corresponding to a minimum number of plates. These limits are important design constraints. In particular, the minimum reflux or minimum flows solution provides the minimum energy requirements for the separation.

Calculation of the minimum stage requirement for a distillation separation is straightforward and relatively simple (Fenske, 1932; Underwood, 1932). Minimum reflux calculations, however, are more difficult.

An infinite stage column is usually characterized by two "pinch" regions, one above and one below the feed. A pinch region is a section of the column containing an infinite number of stages having identical compositions, temperature, and molar overflows. When all of the components in the feed are distributed, i.e., they are present in both distillate and bottoms, the compositions and temperatures of the two pinch regions are the same. In such cases the column is sometimes said to exhibit a single pinch. When there are nondistributed species, the pinch regions have different compositions and temperatures. The product flows from each section of the column are determined by the corresponding pinch region. Thus, the critical task in a minimum reflux calculation is to relate the pinch conditions above and below the feed.

There are two special cases for which the minimum flows solution is easily obtained. The first is when relative volatilities and total molar overflows are constant. Underwood (1946, 1948) derived an elegant infinite stage algorithm for this situation. The usefulness of this treatment is limited unfortunately by its restrictive assumptions. The second special case is when all components of the feed are distributed. Minimum reflux conditions for such a separation are defined by a set of algebraic equations whose dimension equals the number of components in the feed plus five. Such a calculation is modest in size when compared to plate-by-plate simulation.

All rigorous calculation methods, for separations in which some species are nondistributed, determine the relationship between the two pinch zones by plate-by-plate simulation of increasingly larger finite columns. Aside from the fact that it introduces a certain degree of approximation, the serious drawback of this approach is the large size of such calculations.

A different formulation of the minimum reflux problem is proposed in the present investigation. The infinite stage limit is incorporated into the theoretical model at the outset. Both rectifying and stripping sections of the column are treated as continuous countercurrent exchangers with negligible axial dispersion. Investigation of each section's transient behavior then leads to a steady-state description of the column. The advantages of this approach are twofold: (1) the formalism sheds new light on minimum reflux behavior; and (2) this mathematical description substantially simplifies minimum reflux calculations.

Continuum Model of Minimum Reflux Column

A simple distillation column can be broken down for purposes of analysis into three sections: (1) a feed stage, (2) a top or rectifying section, and (3) a bottom or stripping section. First, we will develop differential material and energy balances for the rectifying and stripping sections.

A material balance on the ith species taken around the nth stage in either section gives:

$$\frac{d}{dt}(\bar{l}x_{i,n} + \bar{v}y_{i,n}) = \bar{L}(\bar{x}_{i,n-1} - \bar{x}_{i,n})$$
$$+ \bar{L}f(\bar{x}_{i,n-1} - 2\bar{x}_{i,n} + \bar{x}_{i,n+1}) + \bar{V}(\bar{y}_{i,n+1} - \bar{y}_{i,n})$$
$$+ \bar{V}s(\bar{y}_{i,n+1} - 2\bar{y}_{i,n} + \bar{y}_{i,n-1})(i = 1,2, \ldots ,C) \quad (1)$$

Here, f and s represent backmixing parameters (Hartland and Mecklenburgh, 1966; Mecklenburgh and Hartland, 1975). Eq. 1 reduces to the usual countercurrent ideal stage model when f and s are zero. Note that the direction of increasing n is the direction of liquid flow.

The total flows in Eq. 1 are expressed as volumetric rates and $\bar{x}_i$ and $\bar{y}_i$ correspond to molar concentrations. It is assumed that the total volumetric flows and volumetric holdups in each section of the column are constant. While these assumptions greatly simplify our analysis, they do not restrict the final minimum reflux model. Holdup has no effect on steady-state behavior, and the final equations will be rewritten in terms of total molar flows which need not remain constant.

Define continuous variables:

$$\bar{x}_i(\tau,z),\ \bar{y}_i(\tau,z),\ \tau = \frac{t}{N}\frac{\bar{L}}{\bar{l}},\ z = \frac{n}{N}$$

Here N is the total number of stages in the section of interest. Next, introduce Taylor series expressions for $\bar{x}_{i,n}$, $\bar{x}_{i,n-1}$, $\bar{x}_{i,n+1}$, etc.

$$\bar{x}_{i,n} = \bar{x}_i(\tau,z)$$

$$\bar{x}_{i,n-1} \approx \bar{x}_i(\tau,z) - \Delta z\frac{\partial \bar{x}_i}{\partial z} + \frac{(\Delta z)^2}{2!}\frac{\partial^2 \bar{x}_i}{\partial z^2}$$

$$\bar{x}_{i,n+1} \approx \bar{x}_i(\tau,z) + \Delta z\frac{\partial \bar{x}_i}{\partial z} + \frac{(\Delta z)^2}{2!}\frac{\partial \bar{x}_i}{\partial z^2}$$

where $\Delta z = 1/N$. Upon substitution, Eq. 1 becomes:

$$\frac{\partial}{\partial \tau}(\bar{x}_i + \frac{\bar{v}}{\bar{l}}\bar{y}_i) = -\frac{\partial \bar{x}_i}{\partial z} + \frac{\bar{V}}{\bar{L}}\frac{\partial \bar{y}}{\partial z}$$
$$+ \left(\frac{2N}{1+2f}\right)^{-1}\frac{\partial^2 \bar{x}_i}{\partial z^2} + \left(\frac{2N}{1+2s}\right)^{-1}\frac{\bar{V}}{\bar{L}}\frac{\partial^2 \bar{y}_i}{\partial z^2} \quad (i = 1,2, \ldots C) \qquad (2)$$

In the infinite plate limit, $N \rightarrow \infty$, the Peclet numbers $(2N/1 + 2f)$ and $(2N/1 + 2s)$ in Eq. 2 become infinite and both axial dispersion terms drop out. Eq. 2 becomes:

$$\frac{\partial}{\partial \tau}(\bar{x}_i + \frac{\bar{v}}{\bar{l}}\bar{y}_i) + \frac{\partial}{\partial z}(\bar{x}_i - \frac{\bar{V}}{\bar{L}}\bar{y}_i) = 0 \quad (i = 1,2, \ldots C) \quad (3a)$$

Both the rectifying and the stripping sections of an infinite column can thus be modelled as continuous countercurrent exchangers with negligible axial dispersion.

Eq. 3a represents a set of differential material balances written for each component of the feed. A similar differential energy balance, assuming the column is adiabatic, yields

$$\frac{\partial}{\partial \tau}\left(\bar{h} + \frac{\bar{v}}{\bar{l}}\bar{H}\right) + \frac{\partial}{\partial z}\left(\bar{h} - \frac{\bar{V}}{\bar{L}}\bar{H}\right) = 0 \qquad (3b)$$

The compositions and temperatures of the two phases are in equilibrium at each point. Hence,

$$\bar{y}_i = \bar{y}_i(\bar{x}_1,\bar{x}_2, \ldots \bar{x}_C,\bar{h}) \quad (i = 1,2, \ldots C) \qquad (4a)$$

and

$$\bar{H} = \bar{H}(\bar{x}_1,\bar{x}_2, \ldots \bar{x}_C,\bar{h}) \qquad (4b)$$

Eqs. 3 and 4 represent a quasilinear system of $C + 1$ partial differential equations of first order. If these equations are totally hyperbolic and the initial and entry conditions for a section are constant, we have Riemann's problem (Rhee et al., 1970a; Aris and Amundson, 1973). The solution to this problem has an image in the $C + 1$ dimensional concentration and enthalpy space which lies on a single curve, $\Gamma(w)$. Plotted as a function of z, the solution at any instant in time consists typically of plateau regions of constant concentration and enthalpy which are joined by transition regions in which the concentrations and enthalpy vary in the coherent manner described by $\Gamma(w)$.

Introducing differentiation along the curve $\Gamma(w)$, we deduce from Eqs. 3 and 4 that both

$$\frac{D\bar{y}_1}{D\bar{x}_1} = \frac{D\bar{y}_2}{D\bar{x}_2} = \ldots = \frac{D\bar{y}_C}{D\bar{x}_C} = \lambda(w) \qquad (5a)$$

$$\frac{D\bar{H}}{D\bar{h}} = \lambda(w) \qquad (5b)$$

and

$$\sigma(w) = \left(\frac{dz}{d\tau}\right)_w = \frac{1 - \frac{\bar{V}}{\bar{L}}\lambda(w)}{1 + \frac{\bar{v}}{\bar{l}}\lambda(w)} \qquad (6)$$

where

$$\frac{D\bar{y}_i}{D\bar{x}_i} = \sum_{j=1}^{C}\frac{\partial \bar{y}_i}{\partial \bar{x}_j}\frac{d\bar{x}_j}{d\bar{x}_i}\bigg|_\Gamma + \frac{\partial \bar{y}_i}{\partial \bar{h}}\frac{d\bar{h}}{d\bar{x}_i}\bigg|_\Gamma$$

$$\frac{D\bar{H}}{D\bar{h}} = \sum_{j=1}^{C}\frac{\partial \bar{H}}{\partial \bar{x}_j}\frac{d\bar{x}_j}{d\bar{h}}\bigg|_\Gamma + \frac{\partial \bar{H}}{\partial \bar{h}}.$$

Eq. 5, the coherence condition, is the fundamental differential equation of the problem, the solution of which generates $\Gamma(w)$. Eq. 6 defines the characteristic velocity in physical space of a point on $\Gamma(w)$. Transition regions traveling into a section from its $z = 0$ boundary are characterized by $\sigma(w) > 0$; those propagating from $z = 1$ have $\sigma(w) < 0$.

Along each continuous or smooth transition,

$$\frac{\partial \sigma(w)}{\partial z} = \frac{d\sigma}{dw}\frac{\partial w}{\partial z} > 0 \qquad (7)$$

If this inequality is not satisfied, the transition described by Eq. 6 is unstable and is replaced by a step discontinuity (Rhee et al., 1970a). Such a step or shock transition satisfies the relations

$$\frac{[\bar{y}_1]}{[\bar{x}_1]} = \frac{[\bar{y}_2]}{[\bar{x}_2]} = \ldots = \frac{[\bar{y}_C]}{[\bar{x}_C]} = \lambda \qquad (8a)$$

$$\frac{[\bar{H}]}{[\bar{h}]} = \lambda \qquad (8b)$$

and

$$\sigma = \frac{dz}{d\tau} = \frac{1 - \frac{\bar{V}}{\bar{L}}\lambda}{1 + \frac{\bar{v}}{\bar{l}}\lambda} \qquad (9)$$

Here, the square bracket [ ] denotes the difference in the enclosed quantity across the discontinuity.

Eq. 8 is a discrete form of the coherence condition. These algebraic equalities relate the plateau concentrations and enthalpy on either side of a step transition. Eq. 9 defines the characteristic velocity of the shock. As before, transitions traveling into a section from its $z = 0$ boundary have $\sigma > 0$; those traveling from $z = 1$ have $\sigma < 0$. Given the state on one side of a shock, the state on the other side can be calculated from Eq. 8 if one of the concentrations or the enthalpy on the other side of the shock is known or if the velocity of the shock is known.

Rhee, Aris and Amundson (1970a, b, c, 1971, 1972) and Helfferich and Klein (1970) have successfully applied to multicomponent chromatography and multicomponent adsorption

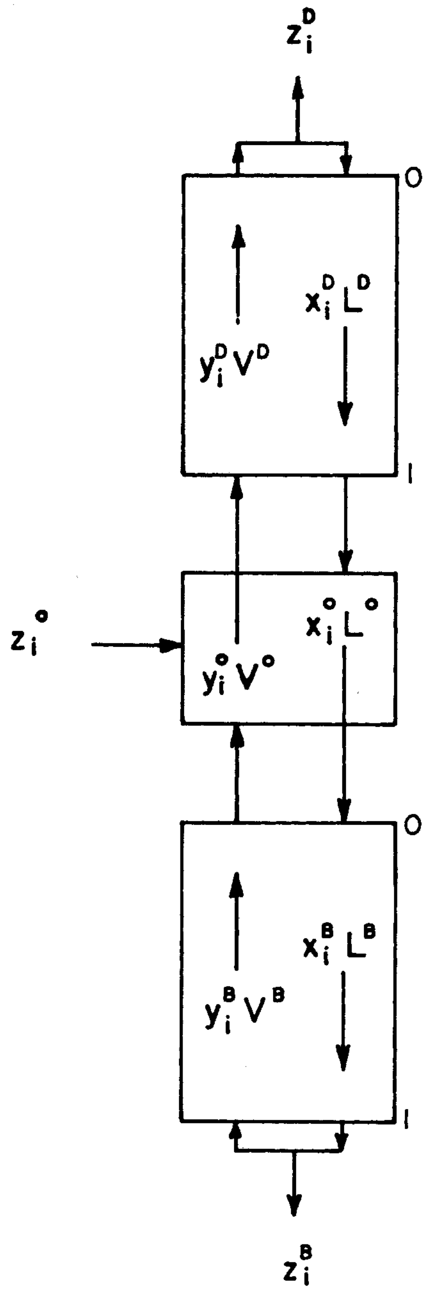

Figure 1. Schematic diagram of minimum reflux column.

the concepts exemplified by Eqs. 5-9. These relations can also be used to deduce the steady-state behavior of an infinite stage distillation column.

A schematic diagram of a simple infinite stage column is shown in Figure 1. The column is taken to consist of an equilibrium feed stage and two ideal continuous countercurrent exchangers. Important features to note are the reflux boundary conditions imposed at the far end of each continuous section. The reflux rate defines the critical $\overline{V}/\overline{L}$ ratio throughout a section. More importantly, because of these boundary conditions, each continuous section behaves at steady state as if it were a finite portion of a semi-infinite domain. Only the transitions which interconnect the concentration and enthalpy state of the feed stage with the respective pinch states need be considered.

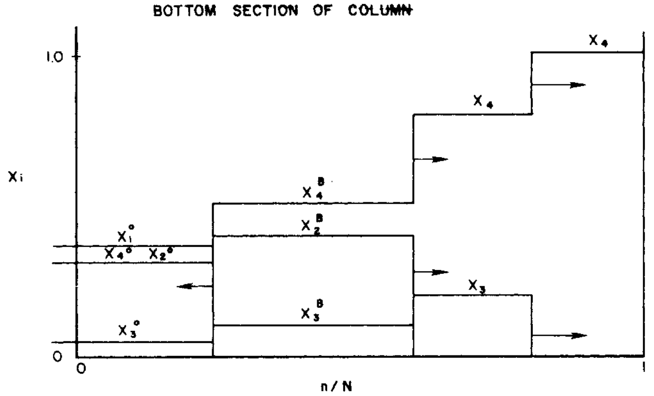

Figure 2. Bottom section of column.

Steady-state operating conditions for the column in Figure 1 can be determined as follows. Concentrations and enthalpy at the feed stage are assumed and are taken to be constant with time (i.e., constant entry conditions), and uniform initial concentrations and enthalpy in each continuous section are chosen (i.e., uniform initial conditions). Once the total volumetric flows, the state of the feed stage, and the initial state of a section are fixed, the transient evolution of the section is a well defined Riemann problem. The solution to this problem is determined by means of Eqs. 5-9. The steady-state pinch conditions obtained by this analysis define the product flows of every chemical species and of enthalpy. Setting each of the feed inflows equal to the corresponding sum of top and bottom product outflows then establishes the minimum reflux solution.

Eqs. 5 and 8 define a unique composition profile which interconnects the fixed state at the feed stage with the uniform initial conditions in the top and the bottom sections of the column. Whatever the volumetric flows, if initially the top section contains only the most volatile component of the feed and the bottom section only the least volatile, then both top and bottom pinch states lie on this $\Gamma(w)$ curve.

The $\Gamma(w)$ curve during its transient evolution consists of a series of plateaus of constant composition joined by coherent transition segments, $\Gamma^i(w)$. Each point on these $\Gamma^i(w)$ segments has a characteristic velocity, $\sigma^i(w)$, given by Eq. 6 or 9. Thus, the pinch composition either is a plateau composition bracketed by $\Gamma^i(w)$ and $\Gamma^{i+1}(w)$ where $\sigma^i(w)$ is less than zero and $\sigma^{i+1}(w)$ is greater than zero or is a point on a continuous transition $\Gamma^i(w)$ at which $\sigma^i(w)$ is zero. All other compositions have finite velocities and are swept through the column. In most cases the $\Gamma^i(w)$ are all discontinuous (see Eq. 7), and the pinch is a plateau bracketed by shock transitions.

The transient evolution of $\Gamma(w)$ in the stripping section of a column is shown schematically in Figure 2. In order to portray the entire profile, the location of the initial step discontinuity from the composition of the feed-stage to a uniform state in which only the least volatile species is present has been shifted in this figure from $z = 0$ to $z = 0.5$. At steady state the composition throughout the stripping section is $\{x_i^B\}$.

A critical difference between the composition in a pinch region and the composition at the feed stage is the usual absence at the pinch of one or more components of the feed. The reason for this absence becomes apparent if one writes an equation for the steady-state flux in a pinch region. For example, the flux of the ith component at the bottom pinch is:

$$Z_i^B = \bar{L}^B \bar{x}_i^B - \bar{V}^B \bar{y}_i^B \tag{10}$$

Express the vapor-liquid equilibria in terms of a set of relative volatilities, α_i,

$$\frac{y_i}{x_i} = \alpha_i K \quad (i = 1,2,\ldots,C) \tag{11}$$

Thus,

$$\frac{\overline{Vy_i}}{\overline{Lx_i}} \equiv \frac{Vy_i}{Lx_i} = \alpha_i\left(\frac{KV}{L}\right) \quad (i = 1,2,\ldots,C) \tag{12}$$

Here, K is the equilibrium constant of a reference species and KV/L is a stripping factor for the same reference component. In what follows all components will be ordered in ascending order from most volatile to least volatile so that

$$\alpha_1 > \alpha_2 > \ldots \alpha_C \tag{13}$$

Substitution of Eq. 12 into Eq. 10 yields:

$$Z_i^B = \left[1 - \alpha_i\left(\frac{K^B V^B}{L^B}\right)\right]\bar{L}^B \bar{x}_i^B \tag{14}$$

All the variables in this equation must be positive or zero. Thus, species i is excluded from the bottom pinch whenever

$$\alpha_i\left(\frac{K^B V^B}{L^B}\right) \geq 1 \tag{15}$$

The bottom pinch composition can easily be altered by varying V^B/L^B. In the limit of large $V^B L^B$ (i.e., $V^B/L^B \rightarrow 1$) only the least volatile component, species C, is present at the pinch. As V^B/L^B is decreased, first species C-1, then species C-2, and so on are allowed in the pinch region. Finally, as V^B/L^B approaches zero, none of the feed components are excluded from the bottom pinch.

A similar treatment of the rectifying section yields the result that species i is excluded from the top pinch whenever

$$\alpha_i\left(\frac{K^D V^D}{L^D}\right) \leq 1 \tag{16}$$

Thus, in the limit of small V^D/L^D(i.e., $V^D/L^D \rightarrow 1$) only the most volatile component, species 1, is present at the top pinch. As V^D/L^D is increased, first species 2, then species 3, and so on are allowed in the pinch region.

Another way of understanding this phenomenon is to look at the dependence of $\sigma(w)$ on $\overline{V}/\overline{L}$. Once $\Gamma(w)$ is fixed, the effect of increasing $\overline{V}/\overline{L}$ is to decrease $\sigma(w)$ (see Eqs. 6 and 9). Thus, increasing $\overline{V}/\overline{L}$ in the bottom section of the column moves the pinch point *closer* to the condition at which only the least volatile component is present. Increasing $\overline{V}/\overline{L}$ in the top section moves the pinch point *away* from the condition at which only the most volatile component is present.

The order in which components disappear along $\Gamma(w)$ is determined by their relative volatilities (see Eqs. 15 and 16 and the ensuing discussion). Defining a light key lk, the components, $1,2, \ldots, lk - 1$ disappear in the stripping section in ascending order from 1 to $lk - 1$ (Figure 2). Defining a heavy key hk, the species $hk + 1, hk + 2, \ldots, C$ disappear in the rectifying section in descending order from C to $hk + 1$. As long as the relative volatility ordering of the nondistributed components is invariant in the column, each nondistributed species must disappear in a separate $\Gamma^i(w)$ transition. Thus, the $\Gamma^i(w)$'s connecting the feedstage and each pinch region can be identified and numbered according to the component that disappears in the transition.

Minimum reflux calculations are greatly simplified when all the $\Gamma^i(w)$ are discontinuous. In such cases the pinches must be plateau compositions and the algebraic relations of Eq. 8 can be used to calculate composition and enthalpy jumps across the $\Gamma^i(w)$'s connecting the pinch states. As Eq. 8 is valid not only as a discrete coherence condition but also as an integral form of Eq. 5, the pinches can be related in this manner whenever both are plateau states. We have termed the case, when Eq. 8 can be used recursively to relate the pinch regions above and below the feed the shock model for a minimum reflux column. It is for this situation that we develop two new calculation methods. When one or both of the pinches lie on a continuous transition, minimum reflux calculations are much more difficult.

Generalized Underwood Calculation

Underwood's classic minimum reflux equations have been derived in a number of ways (Underwood, 1948); Acrivos and Amundson, 1955); Ramkrishna and Amundson, 1973). It is instructive to derive these equations again using the approach outlined in the previous section.

The critical assumption in the Underwood treatment is that the relative volatilities defined by Eq. 11 are all constant. Introducing this assumption and making use of the fact that $\Sigma_i y_i = 1$, K becomes

$$K = \left(\sum_i \alpha_i x_i\right)^{-1} \tag{17}$$

and the mean stripping factor in a section becomes

$$\frac{KV}{L} = \frac{V}{L}\left(\sum_i \alpha_i x_i\right)^{-1} \tag{18}$$

We will find that for fixed feed state composition and uniform initial conditions the composition throughout a section can be expressed as a unique function of this mean stripping factor.

Let

$$\psi_i(w) = \alpha_i \overline{Lx}_i = \alpha_i L x_i \tag{19}$$

and

$$w = \left(\frac{KV}{L}\right)^{-1} = \frac{1}{V} \sum_i \psi_i(w) \tag{20}$$

Therefore,

$$\bar{x}_i = \psi_i/\alpha_i \bar{L} \quad (i = 1,2, \ldots, C) \tag{21}$$

and

$$\bar{y}_i = \psi_i / w\bar{V} \quad (i = 1,2, \ldots, C) \tag{22}$$

The second assumption in Underwood's treatment is that the total molar flows in each section of the column are constant. Instead, we will assume the partial molar enthalpies of both phases to be temperature independent. Hence,

$$\bar{h} = \sum_i \bar{x}_i h_i \tag{23}$$

and

$$\bar{H} = \sum_i \bar{y}_i H_i = \sum_i \bar{y}_i (h_i + \Delta H_i) \tag{24}$$

This is a useful generalization which accounts for variable molar flows. The classic Underwood equations can be recovered by setting

$$\Delta H_i = 1 \quad (i = 1,2, \ldots, C) \tag{25}$$

The coherence equations (Eq. 5) now become

$$\frac{\frac{1}{w}\frac{d\psi_i}{dw} - \frac{\psi_i}{w^2}}{\frac{1}{\alpha_i}\frac{d\psi_i}{dw}} = \frac{\bar{V}}{\bar{L}}\lambda(w) \quad (i = 1,2, \ldots, C) \tag{26a}$$

and

$$\frac{\sum_i (h_i + \Delta H_i)\left(\frac{1}{w}\frac{d\psi_i}{dw} - \frac{\psi_i}{w^2}\right)}{\sum_i (h_i)\left(\frac{1}{\alpha_i}\frac{d\psi_i}{dw}\right)} = \frac{\bar{V}}{\bar{L}}\lambda(w) \tag{26b}$$

Eqs. 26a and 26b can be satisfied only if

$$\sum_i (\Delta H_i)\left(\frac{1}{w}\frac{d\psi_i}{dw} - \frac{\psi_i}{w^2}\right) \equiv \sum_i (\Delta H_i)\left(\frac{d\bar{y}_i}{dw}\right) = 0 \tag{27}$$

Thus

$$\bar{V}\sum_i \bar{y}_i \Delta H_i \equiv V \sum_i y_i \Delta H_i = V\Delta H \tag{28}$$

where $V\Delta H$ is constant in each section of the column. This condition is the result of coherence and adiabatic constraints. As the mean heat of vaporization, ΔH, increases (decreases) with the composition changes involved in going from the feed state to a pinch, the molar vapor flow rate must decrease (increase) to maintain $V\Delta H$ constant. Thus, the vapor flow rate at the bottom pinch is typically less than the vapor flow rate directly below the feed stage. This is due to the absence of the more volatile components of the feed which usually have smaller heats of vaporization. In the rectifying section the reverse holds true.

Multiplying Eq. 27 by w^2 and differentiating with respect to w yields:

$$\sum_i (\Delta H_i)\left(\frac{d^2\psi_r}{dw^2}\right) = 0 \qquad (29)$$

Performing the same operation on Eq. 26a yields

$$\frac{d^2\psi_1/dw^2}{\dfrac{1}{\alpha_1\psi_1}\left(\dfrac{d\psi_1}{dw}\right)^2} = \frac{d^2\psi_2/dw^2}{\dfrac{1}{\alpha_2\psi_2}\left(\dfrac{d\psi_2}{dw}\right)^2} = \ldots = \frac{d^2\psi_C/dw^2}{\dfrac{1}{\alpha_C\psi_c}\left(\dfrac{d\psi_C}{dw}\right)^2} \qquad (30)$$

Eqs. 29 and 30 can be satisfied only if

$$\frac{d^2\psi_i}{dw^2} = 0 \quad (i = 1,2, \ldots, C) \qquad (31)$$

Integration of Eq. 31 gives

$$\psi_i = \alpha_i\overline{Lx}_i = \alpha_i\overline{Lx}_i^o + J_i(w - w^o) \ (i = 1,2, \ldots, C) \qquad (32)$$

Substitution of Eq. 32 into Eq. 26a yields

$$\frac{J_i - \dfrac{\psi_i}{w}}{\dfrac{1}{\alpha_i}J_i} = \frac{\overline{V}}{\overline{L}}\, w\lambda(w) = \phi \ (i = 1,2, \ldots, C) \qquad (33)$$

or

$$J_i = \frac{\alpha_i\psi_i/w}{\alpha_i - \phi} = \frac{\alpha_i\overline{Vy}_i}{\alpha_i - \phi} \quad (i = 1,2, \ldots, C) \qquad (34)$$

Combining Eqs. 22, 27, and 28 yields

$$\sum_i \Delta H_i J_i \equiv V\Delta H \qquad (35)$$

Thus, given a composition in the column such as the feed stage composition, ϕ can be obtained by solving either

$$\sum_i \frac{\Delta H_i\alpha_i\overline{Vy}_i^o}{\alpha_i - \phi} \equiv \sum_i \frac{\Delta H_i\alpha_i V y_i^o}{\alpha_i - \phi} = V\Delta H \qquad (36)$$

or, since

$$\sum_i \Delta H_i\overline{Vy}_i = V\Delta H,$$

$$\sum_i \frac{\Delta H_i\overline{Vy}_i^o}{\alpha_i - \phi} \equiv \sum_i \frac{\Delta H_i V y_i^o}{\alpha_i - \phi} = 0 \qquad (37)$$

or, since

$$\overline{Vy}_i = \alpha_i\, \overline{Lx}_i/w$$

$$\sum_i \frac{\Delta H_i\alpha_i\overline{Lx}_i^o}{\alpha_i - \phi} \equiv \sum_i \frac{\Delta H_i\alpha_i L x_i^o}{\alpha_i - \phi} = 0 \qquad (38)$$

These equations have C-1, real, positive, distinct, common roots which are ordered as follows

$$\alpha_C \le \phi_{C-1} \le \alpha_{C-1} \le \ldots \le \phi_1 \le \alpha_1 \qquad (39)$$

Corresponding to each ϕ_k there is a unique $\Gamma^k(w)$. This possible solution is defined by a set of direction constants J_i^k (i = 1,2, . . . C) and a characteristic velocity $\sigma^k(w)$. The J_i^k are found by back substituting ϕ_k into Eq. 34. The characteristic velocity, defined by Eq. 6, is simply

$$\sigma^k(w) = \frac{1 - \dfrac{\phi_k}{w}}{1 + \dfrac{\bar{v}}{\bar{l}}\cdot\dfrac{\overline{L}}{\overline{V}}\left(\dfrac{\phi_k}{w}\right)} \qquad (40)$$

Along $\Gamma^k(w)$, $\phi_k w$ is constant (Ree et al., 1970a); thus,

$$\frac{d\sigma^k(w)}{dw} > 0 \qquad (41)$$

The σ^k's are ordered in a reverse sequence to that of the ϕ_k's, i.e.

$$\sigma^1(w) < \sigma^2(w) < \ldots \sigma^{C-1}(w) \qquad (42)$$

Eq. 37 or 38 defines a one-to-one mapping between a given composition and the set $\{\phi_i\}$. When $\Delta H_i = 1$, this is the h-transformation introduced by Helfferich and Klein (1970). Transformation of a fixed composition state into its $\{\phi_i\}$ representation greatly simplifies Riemann calculations. This simplification arises because only ϕ_k varies along a $\Gamma^k(w)$ transition, all the other ϕ_i remain constant.

The fixed composition state at the feed stage is connected to the steady-state composition state in each continuous section of the column by a unique $\Gamma(w)$ curve. This $\Gamma(w)$ curve is composed of a sequence $\Gamma^k(w)$ segments that are ordered by their respective characteristic velocities. Thus, the sequence in the stripping section is in ascending order in the index k; while the order in the rectifying section is in descending order in the index k. Remember, the steady-state pinch conditions are determined by the criteria that either the pinch state lie on a continuous transition $\Gamma^i(w)$ at a point where $\sigma^i(w)$ equals zero or the pinch state be the plateau composition interconnecting adjacent transitions $\Gamma^i(w)$ and $\Gamma^j(w)$ where $\sigma^i(w)$ is less than zero and $\sigma^j(w)$ is greater than zero.

We are now in a position to determine the steady-state behavior of the column. We shall find that $\partial\sigma(w)/\partial z < 0$ along $\Gamma(w)$ at steady-state. Thus, all transitions between the top and bottom pinches are discontinuous, and the "shock model" can be used to describe the column. This greatly simplifies minimum reflux calculations.

The bottom pinch is characterized by a larger mean stripping factor and a higher temperature than exist at the feed stage. This is because the most volatile species are absent at the pinch (Eq. 18). Thus, w decreases between the feed stage and the bottom pinch. Since $d\sigma(w)/dw > 0$ (Eq. 41), $\partial\sigma/\partial z < 0$, and all transitions between the feed stage and the pinch are discontinuous shocks. Thus, the pinch state is a plateau composition. Because of the absence of the least volatile species, the top pinch has a smaller mean stripping factor and a lower temperature than the feed stage. As a result, w increases between the feed stage and the top pinch. Again $\partial\sigma/\partial z < 0$ along $\Gamma(w)$, all transitions are discontinuous, and the pinch state is a plateau composition.

The discrete coherence conditions, Eqs. 8 and 9, can be used in a recursive manner to calculate the composition jumps across each shock transition. However, in the present case an even simpler formulation is possible. In the stripping section $\phi_i \rightarrow \alpha_i$ as $x_i \rightarrow 0$ across a $\Gamma^i(w)$ transition. In the rectifying section $\phi_i \rightarrow \alpha_{i+1}$ as $x_{i+1} \rightarrow 0$ across a $\Gamma^i(w)$ transition. Thus, given the feed stage composition $\{x_i^o\}$, the pinch compositions can be calculated as follows:

1. Calculate the $C-1$ values of ϕ_k by means of Eq. 38

$$\sum_{i=1}^{C} \frac{\Delta H_i\alpha_i x_i^o}{\alpha_i - \phi_k} = 0 \quad (k = 1,2, \ldots C-1) \qquad (43)$$

2. Calculate the bottom pinch composition $\{x_i^B\}$ by means of the equation set

$$\sum_{i=lk}^{C} \frac{\Delta H_i\alpha_i x_i^B}{\alpha_i - \phi_k} = 0 \quad (k = lk, lk + 1, \ldots C-1) \qquad (44)$$

3. Calculate the top pinch composition $\{x_i^D\}$ by means of the equation set

$$\sum_{i=1}^{hk} \frac{\Delta H_i\alpha_i x_i^D}{\alpha_i - \phi_k} = 0 \quad (k = 1,2, \ldots hk - 1) \qquad (45)$$

An overall material balance on the column gives

$$Z_i^0 = Z_i^B + Z_i^D \qquad (46)$$

where

$$Z_i^B = L^B x_i^B - V^B y_i^B \qquad (47)$$

and

$$Z_i^D = -L^D x_i^D + V^D y_i^D \qquad (48)$$

Multiplying Eq. 47 and Eq. 48 by $\Delta H_i \alpha_i / (\alpha_i - \phi_k)$ and summing (Eqs. 36 and 38) yields

$$\sum_{i=lk}^{C} \frac{\Delta H_i \alpha_i Z_i^B}{\alpha_i - \phi_k} = -V\Delta H^B \quad (k = lk,\, lk+1, \ldots C-1) \qquad (49)$$

and
$$\sum_{i=1}^{hk} \frac{\Delta H_i \alpha_i Z_i^D}{\alpha_i - \phi_k} = V\Delta H^D \quad (k = 1,2, \ldots ,hk-1) \qquad (50)$$

Finally, combining Eqs. 46, 49, and 50 gives

$$\sum_{i=1}^{C} \frac{\Delta H_i \alpha_i Z_i^0}{\alpha_k - \phi_k} = V\Delta H^D - V\Delta H^B = Z\Delta H^o$$
$$(k = lk,\, lk+1, \ldots ,hk-1) \qquad (51)$$

Eqs. 49-51 constitute a valuable generalization of the Underwood minimum reflux algorithm. The new equations are based on assumptions of constant relative volatility and of temperature independent partial molar enthalpy. As long as the system is not so nonideal as to give the multicomponent equivalent of a tangent pinch (King 1971), deviations from assumed behavior above the top pinch and below the bottom pinch do not affect the accuracy of the solution. The new equations account for variable molar flows in the column. They should be used in place of Underwood's equations for short cut calculation of minimum reflux behavior. If all the ΔH_i's are set equal to unity in Eqs. 49-51 (constant molar overflow assumption), one recovers the classic Underwood equations.

Rigorous Minimum Reflux Calculation Based on Shock Model

In this section we derive a rigorous method for calculating minimum reflux behavior that can be used whenever the nondistributed components exhibit invariant relative volatility ordering and the key components disappear by means of shock transitions. If the key components disappear by means of shock transitions, the pinch states are plateau compositions, and Eq. 8 can be used recursively to relate the pinch regions above and below the feed. This is the shock model for a minimum reflux column.

It is difficult to establish the general validity of the shock model when a system's equilibrium and enthalpy relations are nonideal. One must show first that Eqs. 3 and 4 are totally hyperbolic or equivalently that they exhibit coherent behavior and then that the pinches are plateau states.

It is of course possible to prove that specific equilibrium models yield a hyperbolic system. For example, Nandakumar (1979) has accomplished this proof for the ideal solution case. An answer to the question of whether all thermodynamically consistent equilibrium models produce coeherent behavior has not been found. On the other hand, coherent behavior is almost synonymous with physical behavior. We will assume coherence as a postulate. We will also assume invariant relative volatility ordering among all nondistributed components of the feed.

When the relative volatility ordering of all components is invariant and the system equations are totally hyperbolic, a nonlinear transformation exists for an adiabatic column

$$x_i^0 = x_i^0(\phi_1, \phi_2, \ldots \phi_{C-1}) \quad (i = 1,2, \ldots C) \qquad (52)$$

This transformation is analogous to that introduced in the previous section. In the stripping section the kth species can disappear only across a coherent transition, Γ^k, which is associated with the coordinate ϕ_k. In the rectifying section the kth species can disappear only across a coherent transition, Γ^{k-1}, which is associated with the coordinate ϕ_{k-1}.

The steady-state temperature distribution in a continuous column is constrained by the Second Law of Thermodynamics to vary in a monotonic fashion from a high temperature at the bottom of the column to a low temperature at the top. Using T to parameterize Γ^{lk}, the shock criterion in the stripping section becomes

$$\frac{d}{dT}\left(\frac{d\bar{y}_{lk}}{d\bar{x}_{lk}}\right)_{\Gamma^{lk}} > 0 \qquad (53)$$

In the rectifying section this criterion becomes

$$\frac{d}{dT}\left(\frac{d\bar{y}_{hk}}{d\bar{x}_{hk}}\right)_{\Gamma^{hk-1}} > 0 \qquad (54)$$

Violation of either inequality introduces pinch states which lie on a continuous transition. Obtaining minimum reflux conditions in such cases is difficult. These situations are the multicomponent equivalents of what, for a binary separation, would be called a tangent pinch (King, 1971). A tangent pinch occurs when the operating line for a binary column becomes tangent to the equilibrium line as plotted on a McCabe-Thiele diagram.

Ideal solution equilibrium constants and partial molar enthalpies are functions of temperature alone. Since the heat of vaporization of a pure component is positive and decreases in a monotonic fashion to zero at the critical temperature, ideal solution equilibrium constants all increase with increasing temperature and have second derivatives with respect to temperature that are negative. Thus, Eqs. 53 and 54 always are satisfied for ideal solutions, and the shock model equations outlined below are valid as long as there is invariant relative volatility ordering among the nondistributed components. The constant relative volatility example of the previous section is a special case of this general ideal solution result.

In the case of nonideal solutions it is often difficult to ascertain apriori whether Eqs. 53 and 54 are satisfied. In such cases the approach suggested is: (1) assume that the key transitions are discontinuous; (2) calculate minimum reflux conditions using the equations outlined below; and (3) test that the steady-state shock model is valid a posteriori by numerical integration of the fundamental differential equation or by plate-by-plate simulation.

Minimum reflux conditions are easy to calculate for distillation separations in which invariant relative volatility ordering exists between the pinches and in which the keys disappear by means of shock transitions. The pinch condition in the stripping section is defined by the relations

$$\sigma B^{lk-1} = \frac{1 - \left(\frac{\overline{VB}}{\overline{LB}}\right)\left(\frac{\overline{yB}_{lk-1}^{lk-1}}{\overline{xB}_{lk-1}^{lk-1}}\right)}{1 + \left(\frac{\overline{vB}}{\overline{lB}}\right)\left(\frac{\overline{yB}_{lk-1}^{lk-1}}{\overline{xB}_{lk-1}^{lk-1}}\right)} < 0 \qquad (55a)$$

and

$$\sigma B^{lk} = \frac{1 - \left(\frac{\overline{VB}}{\overline{LB}}\right)\left(\frac{\overline{yB}_{lk}^{lk}}{\overline{xB}_{lk}^{lk}}\right)}{1 + \left(\frac{\overline{vB}}{\overline{lB}}\right)\left(\frac{\overline{yB}_{lk}^{lk}}{\overline{xB}_{lk}^{lk}}\right)} > 0 \qquad (55b)$$

Here the superscripts denote either the transition in which the species designated by the superscript disappears or the plateau just prior to this transition.

Given the composition and enthalpy in the feed zone, the various virtual states (plateau compositions) interconnecting the feed zone and the pinch can be found by recursive use of Eq. 8. Thus,

$$\frac{\overline{yB}^k_i - \overline{yB}^{k-1}_i}{\overline{xB}^k_i - \overline{xB}^{k-1}_i} = \frac{\overline{yB}^{k-1}_{k-1}}{\overline{xB}^{k-1}_{k-1}} \quad \begin{array}{l}(i = k,\ k+1, \ldots .C)\\(k = 2, \ldots .b)\end{array} \tag{56a}$$

and

$$\frac{\overline{HB}^k - \overline{HB}^{k-1}}{\overline{hB}^k - \overline{hB}^{k-1}} = \frac{\overline{yB}^{k-1}_{k-1}}{\overline{xB}^{k-1}_{k-1}} \quad (k = 2, \ldots .b) \tag{56b}$$

where $b = lk$, $\overline{yB}^1_i = \bar{y}^o_i$, $\overline{xB}^1_i = \bar{x}^o_i$, $\overline{HB}^1 = \bar{H}^o$, and $\overline{hB}^1 = \bar{h}^o$. Eq. 56 represents material and energy balances for each virtual composition state interconnecting the feed zone and the pinch. It is interesting to note that there are only $(b-1)$ of these states as compared to the large number $(N \rightarrow \infty)$ of plates joining the feed stage and the pinch in conventional minimum reflux treatments.

Introduction of the identities

$$\overline{LB}\ \overline{xB}^k_i = LB^k\, xB^k_i \tag{57}$$

$$\overline{VB}\ \overline{yB}^k_i = VB^k\, yB^k_i \tag{58}$$

$$\overline{VB}\ \overline{HB}^k = VB^k\, HB^k \tag{59}$$

$$\overline{LB}\ \overline{hB}^k = LB^k\, hB^k \tag{60}$$

and the equilibrium expression

$$yB^k_i = KB^k_i\, xB^k_i \tag{61}$$

permits explicit solution of Eq. 56a to yield

$$xB^k_i = x^o_i \prod_{j=2}^{k} AB^j_i \quad \begin{array}{l}(i = k, k+1, \ldots .C)\\(k = 2, \ldots .b)\end{array} \tag{62}$$

where

$$AB^j_i = \frac{VB^{j-1}(KB^{j-1}_i - KB^{j-1}_{j-1})}{VB^j(KB^j_i - 1) - VB^{j-1}(KB^{j-1}_{j-1} - 1)}$$

In the ideal solution case KB^j_i is a function only of TB^j and consequently AB^j_i is a function only of VB^j, VB^{j-1}, TB^j, and TB^{j-1}. Introducing the constraint $\Sigma_i\, yB^k_i = 1$, Eq. 56 can in this case be rewritten as a "bubble point" relation and an "energy balance" relation for each of the $(b-1)$ virtual states:

$$\sum_{i=k}^{C} KB^k_i x^o_i \prod_{j=2}^{k} AB^j_i - 1 = 0 \quad (k = 2, \ldots .b) \tag{63}$$

and

$$VB^k(HB^k - hB^k) + VB^{k-1}(1 - KB^{k-1}_{k-1})hB^k$$
$$+ VB^{k-1}(KB^{k-1}_{k-1}hB^{k-1} - HB^{k-1}) = 0 \quad (k = 2, \ldots .b) \tag{64}$$

where

$$HB^j = \sum_{i=j}^{C} HB^j_i KB^j_i x^o_i \prod_{k=2}^{j} AB^k_i$$

and

$$hB^j = \sum_{i=j}^{C} hB^j_i x^o_i \prod_{k=2}^{j} AB^k_i$$

A parallel treatment of the rectifying section yields the relations

$$\sigma D^{C+1-hk} = \frac{1 - \left(\dfrac{\overline{VD}}{\overline{LD}}\right)\left(\dfrac{\overline{yD}^{C+1-hk}_{hk}}{\overline{xD}^{C+1-hk}_{hk}}\right)}{1 + \left(\dfrac{\overline{vD}}{\overline{lD}}\right)\left(\dfrac{\overline{yD}^{C+1-hk}_{hk}}{\overline{xD}^{C+1-hk}_{hk}}\right)} < 0 \tag{65a}$$

$$\sigma D^{C-hk} = \frac{1 - \left(\dfrac{\overline{VD}}{\overline{LD}}\right)\left(\dfrac{\overline{yD}^{C-hk}_{hk+1}}{\overline{xD}^{C-hk}_{hk+1}}\right)}{1 + \left(\dfrac{\overline{vD}}{\overline{lD}}\right)\left(\dfrac{\overline{yD}^{C-hk}_{hk+1}}{\overline{xD}^{C-hk}_{hk+1}}\right)} > 0 \tag{65b}$$

where the superscripts denote either the transition in which the species, designated by $C + 1$ minus the superscript, disappears or the plateau just prior to this transition, and

$$\frac{\overline{yD}^k_i - \overline{yD}^{k-1}_i}{\overline{xD}^k_i - \overline{xD}^{k-1}_i} = \frac{\overline{yD}^{k-1}_{C+2-k}}{\overline{xD}^{k-1}_{C+2-k}} \quad \begin{array}{l}(i = k,\ k+1. \ldots C)\\(k = 2, \ldots d)\end{array} \tag{66a}$$

$$\frac{\overline{HD}^k - \overline{HD}^{k-1}}{\overline{hD}^k - \overline{hD}^{k-1}} = \frac{\overline{yD}^{k-1}_{C+2-k}}{\overline{xD}^{k-1}_{C+2-k}} \quad (k = 2, \ldots d) \tag{66b}$$

where $d = C + 1 - hk$, $\overline{yD}^1_i = \bar{y}^o_i$, $\overline{xD}^1_1 = \bar{x}^o_i$, $\overline{HD}^1 = \bar{H}^o$, and $\overline{hD}^1 = \bar{h}^o$.

Finally,

$$xD^k_i = x^o_i \prod_{j=2}^{k} AD^j_i \quad \begin{array}{l}(i = 1,2, \ldots C + 1 - k)\\(k = 2, \ldots d)\end{array} \tag{67}$$

where

$$AD^j_i = \frac{VD^{j-1}(KD^{j-1}_i - KD^{j-1}_{C+2-j})}{VD^j(KD^j_i - 1) - VD^{j-1}(KD^{j-1}_{C+2-j} - 1)}$$

$$\sum_{i=1}^{C+1-k} KD^k_i x^o_i \prod_{j=2}^{k} AD^j_i - 1 = 0 \quad (k = 2, \ldots d) \tag{68}$$

and

$$VD^k(HD^k - hD^k) + VD^{k-1}(1 - KD^{k-1}_{C+2-k})hD^k$$

$$+ VD^{k-1}(KD^{k-1}_{C+2-k}\ hD^{k-1} - HD^{k-1}) = 0 \quad (k = 2, \ldots d) \tag{69}$$

where

$$HD^j = \sum_{i=1}^{C+1-j} HD^j_i KD^j_i x^o_i \prod_{k=2}^{j} AD^k_i$$

and

$$hD^j = \sum_{i=1}^{C+1-j} hD^j_i x^o_i \prod_{k=2}^{j} AD^k_i$$

A set of $C + 5$ equations that couple the upper and lower pinches completes the new minimum reflux description

$$(VD^d KD^d_i - LD^d) \prod_{j=2}^{d} AD^j_i x^o_i - Z^o_i = 0 \quad (i < lk) \tag{70}$$

$$\Big\{[VD^d KD^d_i - LD^d] \prod_{j=2}^{d} AD^j_i + [LB^b$$
$$- VB^b KB^b_i] \prod_{j=2}^{b} AB^j_i\Big\} x^o_i - Z^o_i = 0 \ (lk \le i \le hk) \tag{71}$$

$$(LB^b - VB^b KB^b_i) \prod_{j=2}^{b} AB^j_i x^o_i - Z^o_i = 0 \ (i > hk) \tag{72}$$

$$\sum_{i=1}^{C} KO_i x^o_i - 1 = 0 \tag{73}$$

$$VD^d - LD^d - VB^b + LB^b - \sum_{i=1}^{C} Z^o_i = 0 \tag{74}$$

$$VD^d HD^d - LD^d hD^d - VB^b HB^b + LB^b hB^b - ZH^o = 0 \tag{75}$$

$$(VD^d KD^d_{hk} - LD^d) \prod_{j=2}^{d} AD^j_{hk}$$
$$- ZD_{hk}(LB^b - VB^b KB^b_{hk}) \prod_{j=2}^{b} AB^j_{hk} = 0 \tag{76}$$

and

$$(VD^d KD^d_{lk} - LD^d) \prod_{j=2}^{d} AD^j_{lk}$$

TABLE 1. COMPARISON BETWEEN UNDERWOOD AND GENERALIZED UNDERWOOD SOLUTIONS

Components: Ethane, Propane, n-Butane, n-Pentane, Octane
Z_i^o: [0.1 0.2 0.4 0.2 0.1]
α_i: [183.26 74.85 30.99 12.96 1.0]

	Underwood	Generalized Underwood	Generalized Underwood
	$LK = 3$, $ZD_3 = 10$ $HK = 4$, $ZD_4 = 0.005$	$LK = 3$, $ZD_3 = 10$ $HK = 4$, $ZD_4 = 0.005$	$\Sigma Z_i^d = 0.6646$ $V^d \Delta H^d = (6560) \times 2326$
Top Pinch:			
Vapor Flow	1.0697	1.0818	1.0658
Liquid Flow	0.4051	0.4172	0.4011
Bottom Pinch:			
Vapor Flow	1.0697	0.9338	0.9182
Liquid Flow	1.4051	1.2692	1.2536
Distillate Rate:			
1	0.1	0.1	0.1
2	0.2	0.2	0.2
3	0.3636	0.3636	0.3614
4	0.995×10^{-3}	0.995×10^{-3}	0.322×10^{-2}
5	0.0	0.0	0.0

$$- ZD_{lk}(LB^b - VB^b KB_{lk}^b) \prod_{j=2}^{b} AB_{lk}^j = 0 \qquad (77)$$

Eqs. 62-64 and 67-77 form a set of coupled algebraic equations which define the minimum reflux column. They have been used to construct an efficient algorithm for calculating minimum reflux conditions (Nandakumar and Andres, 1981). This new mathematical description, while rigorous, is much simpler than the description required by other approaches, e.g., Chien (1978) and Tavana and Hanson (1979). In the ideal solution case, $C + 2(d + b - 2) + 5$ equations define the column. Thus the minimum reflux calculation is reduced to something more analogous to a multicomponent flash calculation than to a typical multiplate, multicomponent, distillation calculation.

Sample Results and Discussion

Details of the numerical solution of the new equations we have derived above are presented in Part II (Nandakumar and Andres, 1981). In this section we merely present sample results obtained with each method and compare these results with minimum reflux conditions obtained by Underwood's algorithm and by plate-by-plate simulation.

The first example is designed to illustrate the sensitivity of minimum reflux behavior to the molar overflow distribution in a column, i.e., the differences between an Underwood solution (constant molar overflow) and a Generalized Underwood solution (variable molar overflow). In this example a liquid feed stream containing ethane, propane, N-butane, N-pentane, and octane $[\{x_i\} = \{0.1, 0.2, 0.4, 0.2, 0.1\}]$ is to be separated so that $lk = 3$ (N-butane) and $hk = 4$ (N-pentane). The desired distillate/bottoms splits are $ZD_3 = 10$ and $ZD_4 = 0.005$. The equilibrium and enthalpy data used in the calculation are taken from Tables A-4 and A-8 in Holland (1963). Evaluation of the relative volatilities and molar heats of vaporization of the feed yields:

$$\{\alpha_i\} = \{183.26, 74.85, 30.99, 12.96, 1\}$$

$$\{\Delta H_i\} = \{3{,}004, 4{,}622, 6{,}750, 9{,}302, 15{,}934\} \times 2326 \text{ J/kg} \cdot \text{mol}$$

An Underwood calculation yields the specifications presented in the first column of Table 1. A Generalized Underwood calculation gives the specifications presented in the second column of

TABLE 2. COMPARISON BETWEEN PLATE-BY-PLATE SIMULATION AND SHOCK MODEL SOLUTION

Components: $[C_3, i\text{-}C_4, n\text{-}C_4, i\text{-}C_5, n\text{-}C_5]$
$Z_i = [0.2\ 0.2\ 0.2\ 0.2\ 0.2]$

Equilibrium and Enthalpy Data from Holland (1963)

	Shock Model Calculation	Plate-by-Plate Simulation
	$HK = 3$, $ZD_3 = 0.37214$ $LK = 2$, $ZD_2 = 2.68715$	120 Plates
Distillate:		
Total rate	0.4000	0.4000
Component rate	(0.2, 0.1458, 0.0542, 0.0, 0.0)	(0.2, 0.1458, 0.0542, 0.0, 0.0)
Top Pinch:		
Temperature (°K)	391.51	391.42
Vapor Flow	1.503	1.514
Liquid Flow	1.103	—
Feed Zone, T (°K)	406.62	406.51
Bottom Pinch:		
Temperature (°K)	416.59	416.44
Vapor Flow	1.517	1.514
Liquid Flow	2.117	—
Bottoms:		
Total Rate	0.60000	0.60000
Component Rate	(0, 0.0542, 0.1458, 0.2, 0.2)	(0, 0.0542, 0.1458, 0.2, 0.2)

Table 1. Finally, results of a Generalized Underwood calculation, in which the distillate product rate and condenser load are those specified by the Underwood calculation, are shown in the third column.

The most interesting comparisons are between columns one and three. Column one represents the idealized constant molar overflow situation; while column three represents a variable molar overflow column with the same external specifications as in the idealized case. The "real" column has a vapor flow at the bottom pinch that is 14 percent less than the "ideal" prediction. The difference in product purity is even more significant. The distillate flow of *n*-pentane is 3.2 times greater in the "real" column. Such differences are of course the reason for making rigorous minimum reflux calculations.

A second example illustrates the agreement between predictions obtained using the rigorous shock model equations and predictions obtained by plate-by-plate simulation of large finite columns. This example is taken directly from Holland (1963) (Example 10.1). The results of the two calculations are considered to be indistinguishable. It is important to note, however, that the shock model calculation is almost trivial while the plate-by-plate calculation takes substantial computational effort. Furthermore, the shock model algorithm permits direct incorporation of a split specification and thereby eliminates the usual secondary iteration procedure required by any method which requires specification of external flows.

NOTATION

AB_i^j = defined in Eq. 62
AD_i^j = defined in Eq. 67
C = total number of components in feed
f = backmixing parameter for liquid phase
$H(\overline{H})$ = enthalpy of vapor phase defined on molar (volumetric) basis
$h(\overline{h})$ = enthalpy of liquid phase defined on molar (volumetric) basis
H_i = partial molar enthalpy of component *i* in vapor
h_i = partial molar enthalpy of component *i* in liquid
(ΔH_i) = latent heat of vaporization of component *i*
hk = heavy key component (heaviest component in distillate)
J_i = Riemann invariants, defined in Eq. 32
K = vapor-liquid equilibrium constant of reference component
$L(\overline{L})$ = liquid flow rate defined on molar (volumetric) basis
$l(\overline{l})$ = liquid hold up per unit length defined on molar (volumetric) basis
lk = light key component (lightest component in bottom product)
N = total number of stages
s = backmixing parameter for vapor phase
t = time variable
T = absolute temperature
$V(\overline{V})$ = vapor flow rate defined on molar (volumetric) basis
$v(\overline{v})$ = vapor hold up per unit length defined on molar (volumetric) basis
w = a parameter running along the solution curve $\Gamma(w)$
$x_i(\overline{x}_i)$ = liquid mole fraction (molar concentration) of component *i*
$y_i(\overline{y}_i)$ = vapor mole fraction (molar concentration) of component *i*
z = distance variable
Z = total molar rate
Z_i = molar rate of component *i*
ZH = total enthalpy rate
ZD_i = product specification defined as split of component *i* between distillate and bottom product (Z_i^D/Z_i^B)
$Z\Delta H^\circ$ = difference between enthalpy of feed and enthalpy of a saturated liquid feed

Greek Letters

α_i = relative volatility of component *i*
λ = eigenvalue defined in Eq. 5a
ϕ_i = Underwood roots defined in Eq. 36, 37, or 38
ψ_i = $\alpha_i \overline{L} \overline{x}_i$, defined in Eq. 19
$\Gamma(w)$ = solution curve in composition-enthalpy space
$\sigma(w)$ = characteristic velocity of a point on $\Gamma(w)$
τ = scaled time variable, $t/N(\overline{L}/\overline{l})$

Subscripts

hk = heavy key component
i = component identification number
lk = light key
n = stage identification number

Superscripts

B = a quantity defined for the stripping section
b = a quantity defined at the stripping pinch ($b = lk$)
D = a quantity defined for the rectifying section
d = a quantity defined at the rectifying pinch ($d = C - hk + 1$)
j, k = define transitions and plateau compositions
o = quantities defined for the feed zone

Note

Variables like temperature, flow rates, etc., are defined in the rectifying section, feed state, and stripping section by appending the letters *D*, *O*, and *B*, respectively.

LITERATURE CITED

Acrivos, A., and N. R. Amundson, "On the Steady State Fractionation of Multicomponent and Complex Mixtures in an Ideal Cascade," Parts I and II, *Chem. Eng. Sci.*, **4**, 29 (1955).
Aris, R., and N. R. Amundson, ***Mathematical Methods in Chemical Engineering***, **2**, Prentice Hall, Englewood Cliffs, NJ (1973).
Bachelor, J. B., "How to Figure Minimum Reflux," *Pet. Refiner*, **36**, 161 (1957).
Chien, H. H. Y., "A Rigorous Method for Calculating Minimum Reflux Ratios in Distillation," *AIChE J.*, **24**, 605 (1978).
Erbar, R. C., and R. N. Maddox, "Minimum Reflux Rate for Multicomponent Distillation Systems by Rigorous Plate Calculation," *Can. J. Chem. Eng.*, **40**, 25 (1962).
Fenske, M. R., "Fractionation of Straight-Run Pennsylvania Gasoline," *Ind. Eng. Chem.*, **24**, 482 (1932).
Hartland, S., and J. C. Mecklenburgh, "A Comparison of Differential and Stagewise Counter Current Extraction with Backmixing," *Chem. Eng. Sci.*, **21**, 1209 (1966).
Helfferich, F., and G. Klein, ***Multicomponent Chromatography***, Marcel Dekker, NY (1970).
Holland, C. D., ***Multicomponent Distillation***, Prentice Hall, Englewood Cliffs, NJ (1963).
King, C. J., *Separation Processes*, McGraw-Hill, NY (1971).
Lee, E. S., "Estimation of Minimum Reflux in Distillation and Multipoint Boundary Value Problems," *Chem. Eng. Sci.*, **29**, 871 (1974).
McDonough, J. A., and C. D. Holland, "Figure Separations this New Way," Part 9, *Petroleum Refiner*, **41**, 153 (1962).
Mecklenburgh, J. C., and S. Hartland, *The Theory of Backmixing*, John Wiley & Sons, NY (1975).
Nandakumar, K., "Simulation of High Dimensional Systems," Ph.D. Thesis, Princeton University, Princeton, NJ (1979).
Nandakumar, K., and R. P. Andres, "Minimum Reflux Conditions: Part II: Numerical Solution," *AIChE J.*, **27**, 460 (1981).
Ramakrishna, D., and N. R. Amundson, "Self Adjoint Operators from Selected Non-Symmetric Matrices: Application to Kinetics and Rectification," *Chem. Eng. Sci.*, **28**, 601 (1973).
Rhee, H. K., R. Aris, and N. R. Amundson, "On the Theory of Multicomponent Chromatography," *Phil. Trans. Roy. Soc. London*, **A267**, 419 (1970a).
Rhee, H. K., and N. R. Amundson, "An Analysis of an Adiabatic Adsorption Column," Parts I and II, *The Chem. Eng. J.*, **1**, 241, 279 (1970b, c).

Rhee, H. K., R. Aris, and N. R. Amundson, "Multicomponent Adsorption in Continuous Countercurrent Exchangers," *Phil. Trans. Roy. Soc. London*, **A267**, 187 (1971).

Rhee, H. K., R. Aris, and N. R. Amundson, "An Analysis of an Adiabatic Adsorption Column," Parts III and IV, *The Chem. Eng. J.*, 3, 22, 121 (1972).

Shiras, R. N., D. N. Hanson, and C. H. Gibson, "Calculation of Minimum Reflux in Distillation Columns," *Ind. Eng. Chem.*, **42**, 871 (1950).

Tavana, M., and D. N. Hanson, "The Exact Calculation of Minimum Flows in Distillation Columns," *Ind. Eng. Chem. Process Design Develop.*, **18**, 154 (1979).

Underwood, A. J. V., "The Theory and Practice of Testing Stills," *Trans. Inst. Chem. Engr.*, **10**, 112 (1932).

Underwood, A. J. V., "Fractional Distillation of Multicomponent Mixtures—Calculation of Minimum Reflux Ratio," *J. Inst. Petrol.*, **32**, 614 (1946).

Underwood, A. J. V., "Fractional Distillation of Multicomponent Mixtures," *Chem. Eng. Prog.*, **44**, 603 (1948).

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Part II: Numerical Solution

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Two new algorithms for calculating minimum reflux conditions in multicomponent distillation columns are described. Both algorithms are based on the continuum model for an infinite stage column proposed by Nandakumar and Andres. Several example problems demonstrate the accuracy and computational efficiency of the new algorithms.

SCOPE

It has been shown (Nandakumar and Andres, 1981) that modeling the rectifying and stripping sections of a distillation column as continuous countercurrent exchangers leads to a particularly simple mathematical description of minimum reflux behavior. This approach not only guarantees the exact infinite plate limit but also substantially decreases the number of equations necessary to define a minimum reflux solution. Two calculation methods have been proposed based on this model. The first is a short-cut method which extends Underwood's classic minimum reflux treatment to variable molar overflow situations. The second is a rigorous method which incorporates nonideal equilibrium and enthalpy behavior.

The objective in this investigation is to apply these new equations in an algorithmic form to calculate minimum reflux conditions for adiabatic, multicomponent distillation columns. Two algorithms are described. The accuracy of the new algorithms is established by comparing their solution with Underwood solutions and with plate-by-plate simulations of large finite columns. The computational efficiency of the algorithms is also demonstrated by means of examples.

CONCLUSIONS AND SIGNIFICANCE

The first algorithm that is described parallels Underwood's classic minimum reflux algorithm and is similar in both speed and accuracy. This algorithm represents a short cut method for use when accurate thermodynamic data are not available or when a rigorous calculation is not warranted. It assumes that constant relative volatilities and constant molar heats of vaporization are known for all components. Although formally identical to the Underwood algorithm and as fast computationally, the new algorithm incorporates the important effects of variable molar overflows.

The second algorithm represents a rigorous minimum reflux method and can incorporate most non ideal equilibrium and enthalpy behavior. This algorithm is in the form of a double iteration. The inner iteration involves simultaneous solution of a set of algebraic equations whose dimension equals the number of chemical species in the feed plus twice the number of nondistributed species in the column plus five. These equations completely define minimum reflux conditions for the ideal solution case, and this portion of the algorithm can be used alone in such situations. The outer iteration accounts for the composition dependence of the temperature dependent equilibrium constants and partial molar enthalpies that are used in the inner iteration.

The numerical algorithm representing the inner iteration is shown to be rapidly convergent, and the outer iteration representing as it does a relatively small correction to the system equations also converges rapidly. This calculation is more analogous to a multicomponent flash calculation than a multistage, multicomponent distillation calculation. It requires much less computer time than does conventional plate-by-plate simulation of a large column.

Two calculation methods developed by Nandakumar and Andres (1981) are presented here in algorithmic form. The first is a short cut method for use when accurate thermodynamic information is not available. This method assumes ideal solution behavior, constant relative volatilities, and temperature independent partial molar enthalpies. This calculation is based on the constancy of the enthalpy flux in each section of an adiabatic column and incorporates the effects of variable molar overflows.

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