n = empirical exponent dependent on flow regimes in the two phases
N_{Nu} = hD/k_L, Nusselt number
N_{Pr} = $(\mu c/k)_L$, Prandtl number for liquid
N_{Re} = $(1 - x)G_T D/\mu_L$
N_1 = $G_T D/\mu_L \cdot \{1 - x + x(\rho_L/\rho_v)^{1/2}\}$
N_2 = $G_T D/\mu_L \cdot \{1 + (\rho_L - \rho_v)x/\rho_v\}^{5/8}$
p = pressure
q'' = heat flux rate based on inside tube area
T = temperature
$T^+(\delta^+)$ = dimensionless temperature
T_S = saturation temperature of vapor
T_W = inside wall temperature
v = local velocity in liquid film
v_* = shear velocity
v^+ = v/v_*
x = vapor quality, that is, local mass fraction of vapor to total flow
z = axial coordinate from tube inlet

Greek Letters

α = void fraction
δ = film thickness
δ^+ = dimensionless film thickness $\delta v_*/\nu_L$
ζ = dimensionless axial location z/L
μ_L = dynamic viscosity of liquid
ν_L = kinematic viscosity of liquid
ρ_L = density of liquid
ϕ = two-phase multiplier, ratio of two-phase frictional pressure gradient to single phase flowing only
$\underline{X}$ = two-phase multiplier, ratio of local frictional pressure gradients of the two phases

Subscripts

f = liquid phase flowing at mass velocity $(1 - x)G_T$
fr = frictional
g = vapor phase flowing at mass velocity $x\ G_T$
m = momentum
t = total static

LITERATURE CITED

1. Goodykoontz, J. H., and R. G. Dorsch, *NASA TN D-3953* (1967).
2. Bell, K. J., J. Taborek, and F. Fenoglio, *Chem. Eng. Progr. Supp. Ser. No. 102,* **66,** 150 (1970). Paper presented at AIChE 11th Natl. Heat Transfer Conf., Minneapolis (Aug. 1969).
3. Boyko, L. D., and G. N. Kruzhilin, *Intern. J. Heat Mass Transfer,* **10,** 361 (1967).
4. Ananiev, E. P., L. D. Boyko, and G. N. Kruzhilin, paper presented at Intern. Heat Transfer Conf., (Boulder, Colo., II, 290 (1961).
5. Akers, W. W., H. A. Deans, and O. K. Crosser, *Chem. Eng. Progr. Symp. Ser., No. 29,* **55,** 171 (1959).
6. Kutateladze, S. S., "Fundamentals of Heat Transfer," Chap. 15, Academic Press, New York (1963).
7. Rohsenow, W. M., J. H. Webber, and A. T. Ling, *Trans. ASME,* **78,** 1637 (1956).
8. Bae, S., J. S. Maulbetsch, and W. M. Rohsenow, *MIT Rept. DSR-72591* (Dec. 1970).
9. Kunz, H. R., and S. Yerazunis, *Trans. ASME, J. Heat Transfer,* **C91,** 413 (1969).
10. Altman, M., F. W. Staub, and R. H. Norris, *Chem. Eng. Progr. Symp. Series No. 30,* **56,** 151 (1960).
11. Martinelli, R. C., *Trans. ASME,* **69,** 947 (1947).
12. Lockhart, R. W., and R. C. Martinelli, *Chem. Eng. Progr. Symp. Ser. No. 1,* **45,** 39 (1949).
13. Martinelli, R. C., and D. B. Nelson, *Trans. ASME,* **70,** 695 (1948).
14. Wallis, G. B., "One Dimensional Two-Phase Flow," McGraw-Hill, New York (1969).
15. Boyko, L. D., *Teploenergetika,* **15** (12), 46 (1968).
16. Silver, R. S., and G. B. Wallis, *Proc. Inst. Mech. Eng. (London),* **180,** Pt. I, No. 1, 36 (1965-1966).
17. Linehan, J. H., M. Petrick, and M. M. El-Wakil, *Trans. ASME, J. Heat Transfer,* **C91,** 450 (1969).
18. Soliman, M., J. R. Schuster, and P. J. Berenson, *ibid.,* **C90,** 267 (1968).
19. Andeen, G. B., and P. Griffith, *ibid.,* **C90,** 211 (1968).
20. Zivi, S. M., *ibid.,* **C86,** 247 (1964).
21. Kosky, P. G., *Intern. J. Heat Mass Transfer,* to be published.
22. Dukler, A. E., M. Wicks III, and R. G. Cleveland, *AIChE J.,* **10,** 38 (1964).

Countercurrent Equilibrium Stage Separation with Reaction

PAUL A. NELSON

Shell Development Company, Emeryville, California 94608

SCOPE

A number of reactions of commercial interest are limited in their attainable extent of conversion by unfavorable reaction equilibrium. The most common schemes for overcoming this limitation are to feed one of the reactants, generally the cheapest one, in great excess or to separate and recycle the unconverted reactants in the reactor effluent or a combine of both methods. In some cases it is possible to remove continuously one or more of the products from the reaction zone and thereby drive the reaction

---

Paul A. Nelson is with Shell Oil Company, Technical Computing Center, P. O. Box 20127, Houston, Texas 77025.

toward completion. Cossider for example a reaction of the type

$$A + B \rightleftharpoons C + D$$

where B and D are more volatile than A and C. It has been suggested that a distillation column might be a very efficient reactor for this case (Figure 1). The liquid feed to the top stage of the column l_0 would be pure A, and the vapor feed to the bottom stage v_{N+1} would be pure B. Reactant B is absorbed into the liquid phase where the reaction takes place, and product D is stripped out of the liqiud phase and carried out the top of the column. In such a device, given enough stages and adequate residence time it should be possible to achieve any desired extent of conversion.

The proposal that a reaction may be profitable carried out in a fractionation column is nearly 50 years old (*2*). The equations which describe a reaction in any equilibrium stage device are not difficult to write down. At present, however, no generally applicable technique has appeared for obtaining the solution to these equations without making some rather severe restrictions. Invariably, these restrictions take the form of *a priori* specifications on the stage temperatures and the phase flow rates. Generally the form of the reaction rate expression is restricted as well.

The literature on computational methods for handling chemical reaction in an equilibrium stage device is relatively sparse. Leyes and Othmer (*12*) reported some calculations on the esterification of butanol with acetic acid. Hofmann (*10*) described a graphical technique which he applied to the production of furfural from xylose. Other examples appear in the literature (*5*, *7*, *9*, *15*). In all these, however, the calculation proceeds no further than the solution of material balance equations. The phase rates and stage temperatures are initially specified and are not modified by the ensuing computation.

Reported here is a technique for solving the equations which describe distillation with reaction without restricting the form of the reaction rate expression. Phase flow rates and stage temperatures are also determined. The formulation of a mathematical model of the process relies on the following assumptions:

1. Each stage is a perfectly mixed reactor, with the reaction taking place in the liquid bulk. The liquid composition in any stage is homogeneous and equal to the composition of the liquid leaving that stage. Realization of this assumption requires that the reaction rate be slow compared with the rate of mass transfer between phases.
2. The vapor leaving any stage is in physical equilibrium with the liquid in that stage.

The second assumption, while not necessary, considerably simplifies the problem. The first assumption also leads to simplification, since its violation implies the violation of the second. For any actual system, the first assumption should be carefully checked. When necessary, it can be removed by reformulating the reaction rate expression to include the effect of the rate of mass transfer.

SUMMARY

The solution of the complete problem is quite difficult. It was quickly found that the classical methods of solving the equations which describe distillation columns, for example, Thiele-Geddes, Lewis-Matheson, etc., do not converge when a nonlinear reaction rate expression is included. In order to solve the problem, a new approach was used which built heavily upon recent advances in the field of distillation calculations without reaction.

According to Friday and Smith (*6*) virtually all the modern published methods of solving equilibrium stage problems proceed as follows. [An exception is the method of Greenstadt, Bard, and Morse (*12*).] Initial estimates of the stage temperatures and phase flow rates are used to set up continuity equations, the solution of which gives the composition of each component on each stage. Since the initial estimates of temperature and flow rate are incorrect, the constraints of material balance (the component mole fractions must sum to unity) and heat balance (the enthalpy flows must sum to zero) at each stage will fail to be satisfied. The amount and direction of heat and material imbalance are used to adjust the initial estimates to a new set of estimated values. This procedure is iterated until successive changes in temperature and phase flow rates are negligible. The various techniques differ in the way in which they use heat and material imbalances to correct the temperature and phase flow rates.

This general scheme is followed in solving the problem with reaction. Initial estimates of temperature and phase flow rate are used to set up the continuity equations for component concentrations. Since the equations for composition are nonlinear, an iterative technique must be used to solve them. The particular one used is the Newton-Raphson method. At a given step, one looks ahead to see what composition the Newton-Raphson method will yield for each component on the next iteration provided that the temperatures and phase flow rates are left unchanged. This is done by actually solving the equations for the next iteration. From this calculation the expected heat and material imbalance on each tray can be determined. Analytical expressions are developed for the derivatives of these imbalances with respect to the current estimate of temperature and phase flow rate on each stage. These derivatives can be used to estimate the changes required in the current values of temperature and phase flow rate so that the predicted heat and material imbalances are zero for the next step. In effect, nonlinear iterative techniques are being applied on two levels: in an inner loop to calculate component concentrations; and in an outer loop to calculate the temperature and phase flow rates needed to satisfy the heat and material balances.

For the outer loop the Newton-Raphson method has not been found satisfactory. As the solution is approached, its use may lead to wild excursions in the estimates of temperatures and flow rates. This is a well-known shortcoming of the method. A slight modification, known as the method of damped least squares, can be used to damp out large excursions and to stabilize the approach to a solution. This technique has demonstrated rapid and reliable convergence for the limited number of cases on which it has been tested.

RECENT WORK ON DISTILLATION

The formulation and convergence of the equilibrium stage problem without reaction have been analyzed by Friday and Smith (*6*). They concluded that no single technique is uniformly applicable to all problems of this type. Methods designed for handling close-boiling distillation problems fail for absorption and extraction, and vice versa. They were able to achieve some understanding of why this is so, and found a class of problems intermediate to these two extremes which was incapable of solution by any technique known to them. They suggested that a Newton-Raphson technique might be developed which would solve this class of problems, although they assumed that numerical differentiation would be needed to establish the Jacobian matrix. Tierney and Bruno (*16*) have pursued this suggestion and have developed a Newton-Raphson procedure which gives a partial solution to the problem. Using the material balance constraint, the phase rate profile is calculated if the temperature profile is initially specified and held constant, or vice versa. They did not use the enthalpy balance to complete the solution. A major contribution of their paper was the demonstration that the necessary Jacobian matrices could be obtained by analytic differentiation. More recently, Tierney and Yanosik (*17*) have completed the analysis by generating the Jacobian matrices based on the enthalpy balance.

In this paper it is shown how the problem of countercurrent equilibrium stage separation with reaction may be solved using an algorithm which is a nontrivial extension of the work of Tierney and his collaborators. Consideration is also given to nonideal vapor-liquid equilibrium. The complication introduced by these additions is that the material balance equations are no longer linear in composition. This rather obvious fact has more subtle implications for the temperature and phase flow rate profile correction step. In the mathematical treatment which follows, analytic expressions are derived for the Jacobian matrices required for a Newton-Raphson technique. In practice it has been found preferable to use the method of damped least squares, but this involves only a slight modification of the algorithm. The latter method exhibits greater stability as the solution is approached.

MATHEMATICAL MODEL

A diagram of the general countercurrent equilibrium stage device is shown in Figure 1. For convenience the stages are arranged vertically and the streams leaving stage i are labeled l_i and v_i. As an example of a process of this type we will consider a tray column in which liquid and vapor flow countercurrently. The method is not restricted to this case, however, and can be applied equally well to any process of this type with two distinguishable streams. With appropriate modification in the flow connection matrices L and V, to be defined shortly, the restriction to countercurrent flow can be removed. The general equilibrium stage problem, in which N stages are connected in any desired fashion, can be attacked in this manner.

The assumptions used in the model have already been outlined. As a result of the second assumption, the concentration of component j in the vapor leaving stage i is given by

$$y_{ij} = K_{ij}(t_i; x_{i1}, x_{i2}, \ldots\ldots\ldots x_{iM})x_{ij} \tag{1}$$

The matrix formulation of the equilibrium stage problem first proposed by Amundson and Pontinen (*1*) has been generalized by Tierney and Bruno (*16*). The notation used here is based on that of the latter authors. We consider N stages with M components.

The material balance for component j around stage i may be written

$$-l_i x_{ij} - v_i y_{ij} + l_{i-1}x_{i-1,j} + v_{i+1}y_{i+1,j} + f_{ij} + r_{ij} = 0 \tag{2}$$

$$i = 1, 2, \ldots N$$

$$j = 1, 2, \ldots M$$

For the configuration shown in Figure 1, f_{ij} is nonzero only for $i = 1$ or N, where the external feeds streams are l_0 and v_{N+1}, respectively. All of the equations for component j can be grouped together and written in matrix notation:

$$LX^{(j)} + VY^{(j)} + F^{(j)} + R^{(j)} = 0, \quad j = 1, 2, \ldots\ldots M \tag{3}$$

The N-dimensional column vectors $X^{(j)}$, $Y^{(j)}$, $F^{(j)}$, and $R^{(j)}$ are composed of the elements x_{ij}, y_{ij}, f_{ij}, and r_{ij}, respectively. The $N \times N$ dimensional matrices L and V contain the following elements:

$$\begin{aligned} L_{ii} &= -l_i \\ L_{i+1,i} &= l_i \\ V_{ii} &= -v_i \\ V_{i-1,i} &= v_i \end{aligned} \tag{4}$$

with all others being zero. Tierney and Bruno show how the definition of L and V may be generalized such that Equation (3) describes the material balance for more general flow patterns than the countercurrent scheme considered here. It is convenient to define further a set of $N \times N$ dimensional matrices $K^{(j)}$ with diagonal elements $K_{ii}{}^{(j)} = K_{ij}$. Equation (3) can then be further simplified to

$$s^{(j)} = Z^{(j)}X^{(j)} + F^{(j)} + R^{(j)} = 0$$

$$j = 1, 2, \ldots.\ M \tag{5}$$

where

$$Z^{(j)} = L + VK^{(j)} \tag{6}$$

Equation (5) must be satisfied for each component j.

Another set of equations is obtained from the requirement that the mole fractions of all components for either phase in each stage must sum to unity;

$$\begin{aligned} \sum_{j=1}^{M} X^{(j)} - U = 0 \\ \sum_{j=1}^{M} Y^{(j)} - U = 0 \end{aligned} \tag{7}$$

where U is an N-dimensional vector in which each element is unity. The two Equations (7) are not independent. They are both implied by the single vector equation

$$D_m \equiv \sum_{j=1}^{M} (X^{(j)} - Y^{(j)}) = 0 \tag{8}$$

According to Amundson and Pontinen the form of the constraint in Equation (8) is preferable to either of Equations (7) for computation.

A final set of equations is obtained from an enthalpy balance around each stage:

$$-l_i h_i - v_i g_i + l_{i-1}h_{i-1} + v_{i+1}g_{i+1} = 0 \tag{9}$$

These terms are calculated as the sum of the partial molar enthalpies of the components, so that the heat of reaction is included implicitly in Equation (9). Defining H and G

to be N-dimensional vectors composed of the elements h_i and g_i, respectively, and Q_f to be the vector representing the total enthalpy of the external feed to each stage, we obtain

$$D_e \equiv LH + VG + Q_f = 0 \tag{10}$$

The variables in this problem are the $N \times M$ liquid mole fractions x_{ij}, the N temperatures t_i, and the N vapor rates v_i. Vapor-phase mole fractions are found through Equation (1), and liquid rates are obtained in terms of vapor rates through an overall material balance

$$l_i = v_{i+1} + l_0 - v_1 \tag{11}$$

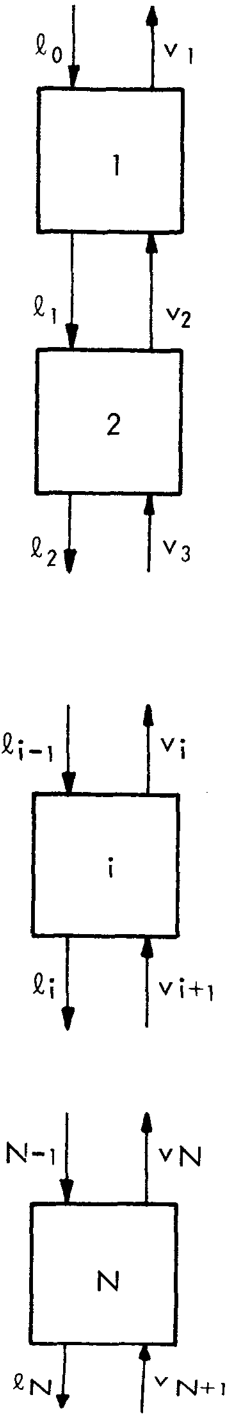

Fig. 1. Countercurrent equilibrium stage column.

This gives a total of $N(M + 2)$ variables, which are determined such that the $N(M + 2)$ equations contained in Equations (5), (8), and (10) are satisfied. The feed rates l_0 and v_{N+1} are considered to be specified, as well as the feed compositions and temperatures. Together with relations which determine K_{ij} and r_{ij} as functions of temperature and composition, this is sufficient to determine the problem.

METHOD OF SOLUTION

When there is no reaction and the dependence of K_{ij} on the liquid composition can be neglected, the exact solution of Equations (5) is particularly easy since they can be decoupled into M systems of linear equations of the form:

$$Z^{(j)}X^{(j)} = -F^{(j)} \tag{12}$$

in which the matrices $Z^{(j)}$ are tridiagonal. When a nonlinear reaction rate term is included in Equation (5), direct solution is not possible and an iterative scheme must be employed. The most obvious approach is to calculate $R^{(j)}$ on the basis of estimated values of the composition variables and rearrange Equation (5) to the following form, which can be solved for new estimates of the compositions:

$$X^{(j)}{}_{n+1} = Z^{(j)-1}\left[-F^{(j)} - R^{(j)}(X_n)\right] \tag{13}$$

It can be shown that when the reaction rate is of order greater than unity this approach will fail to converge in general (*3, 13*).

As an alternate to this first-order approach, it is possible to develop an approximate Newton-Raphson method. The approximation consists of neglecting the derivatives $(\partial r_{ij}/\partial x_{ik})$ and $(\partial K_{ij}/\partial x_{ik})$ for all $k \neq j$. This can only be justified a posteriori on the basis of the convergence or divergence of the iterative procedure. It appears to work quite well in the cases tried so far. The significance of this step is that it decouples the interaction between components, allowing one to solve an N-dimensional problem M times in going from one iteration to the next, rather than an $N \times M$ dimensional problem once. Having made this approximation, we find the formula for a Newton-Raphson iterative procedure to be (*14*)

$$X^{(j)}{}_{n+1} = X_n{}^{(j)} - \left[\frac{\partial s_n{}^{(j)}}{\partial X_n{}^{(j)}}\right]^{-1} s_n{}^{(j)} \tag{14}$$

In Equation (14) the defect vector $s_n{}^{(j)}$ and the Jacobian matrix $(\partial s_n{}^{(j)}/\partial X_n{}^{(j)})$ are evaluated using the composition from the $n + 1$th iteration for x_{ik}, $k < j$, and from the nth iteration for $k \geqq j$

$$s_n{}^{(j)} = s_n{}^{(j)}\left(X^{(1)}_{n+1}\ X^{(2)}_{n+1} \ldots X^{(j-1)}_{n+1}, X^{(j)}_{n} \ldots X^{(M)}_{n}\right) \tag{15}$$

Substituting the form of $s^{(j)}$ from Equation (5) into Equation (14)

$$X^{(j)}_{n+1} = X^{(j)}_{n} - \left[Z^{(j)} + V\frac{\partial K^{(j)}}{\partial X_n{}^{(j)}}X_n{}^{(j)} + \frac{\partial R_n{}^{(j)}}{\partial X_n{}^{(j)}}\right]^{-1}$$

$$\left[Z^{(j)}X_n{}^{(j)} + F^{(j)} + R_n{}^{(j)}\right]$$

$$= \left[Z^{(j)} + V\frac{\partial K^{(j)}}{\partial X_n{}^{(j)}}X_n{}^{(j)} + \frac{\partial R_n{}^{(j)}}{\partial X_n{}^{(j)}}\right]^{-1}$$

$$\left[V\frac{\partial K^{(j)}}{\partial X_n{}^{(j)}}X_n{}^{(j)}X_n{}^{(j)} + \frac{\partial R_n{}^{(j)}}{\partial X_n{}^{(j)}}X_n{}^{(j)} - F^{(j)} - R^{(j)}\right] \tag{16}$$

where $(\partial K^{(j)}/\partial X_n^{(j)})\ X_n^{(j)}$ and $(\partial R_n^{(j)}/\partial X_n^{(j)})$ are diagonal matrices composed of the elements $(\partial K_{ij}/\partial X_{ij})\ X_{ij}$ and $(\partial r_{ij}/\partial X_{ij})$, respectively, for $i = 1, 2, \ldots N$. The matrix $Z^{(j)} + (V\ \partial K^{(j)}/\partial X_n^{(j)})\ X_n^{(j)} + (\partial R_n^{(j)}/\partial X_n^{(j)})$ is tridiagonal, and Equation (16) is easily solved, for example, using Thomas' method (*11*). The application of Equation (16) successively to all components $j = 1, 2, \ldots M$ results in a closer approximation to the solution of Equation (5) at the given values of t_i and v_i.

The temperature and vapor rate profiles are the independent variables, on which the compositions are dependent through the material balances. The size of the problem is reduced from $N(M + 2)$ to $2N$ variables in this way. In order to use a Newton-Raphson method for correcting the temperature and vapor rate, it is necessary to obtain the Jacobian matrices indicating the variation in composition with changes in the independent variables. The method used by Tierney and Bruno is to differentiate Equation (5) with respect to any one variable, say t_i, and rearrange to obtain the column vector $(\partial X^{(j)}/\partial t_i)$. If this is done for all $i = 1, 2, \ldots N$ the series of column vectors generated can be arranged into the Jacobian matrix $(\partial X^{(j)}/\partial t)$. When $R^{(j)}$ is included as a nonlinear function of $X^{(j)}$, the situation is slightly more complex. This is because the differentiation must take into account the fact that at any iteration Equation (5) is only approximately satisfied, and $s^{(j)} \neq 0$. In this case the correct procedure is as follows. First the material balance correction equation, Equation (16), is used to determine a set of compositions X'. This is the $N \times M$ matrix of compositions which we will have after the next iteration if the temperature and vapor rate profiles are left unchanged. On the basis of this set of compositions, the definitions in Equations (8) and (10) can be used to determine the defect vector D_m' and D_e' which will be obtained after the next iteration, again provided that t and v are left unchanged. The object now is to estimate the changes in t and v which must be made, so that after the next iteration, Equations (8) and (10) will be satisfied, that is, $D_m = 0$ and $D_e = 0$. In order to estimate the required changes, Equation (16) is differentiated with respect to each of the independent variables t_i and v_i.

Differentiation of Equation (16) with respect to t yields

$$\frac{\partial X'^{(j)}}{\partial t} = -\left(Z^{(j)} + V\frac{\partial K^{(j)}}{\partial X_n^{(j)}} X_n^{(j)} + \frac{\partial R_n^{(j)}}{\partial X_n^{(j)}} \right)^{-1} \left(V\frac{\partial K^{(j)}}{\partial t} X'^{(j)} + \frac{\partial R_n^{(j)}}{\partial t} + \alpha_j \sum_{k=1}^{j-1} \frac{\partial R}{\partial X'^{(k)}} \frac{\partial X'^{(k)}}{\partial t} \right) \tag{17}$$

The final term in Equation (17) is necessary because of the sequential solution of the mass balance equations by components. By the time the equation for component j is solved, the composition will have been updated for all components numbered less than j. This results in a change in the reaction rate which is accounted for by the final term. It is convenient in this term to replace $R^{(j)}$ by $\alpha_j R$ where R is the reaction rate on each tray, and α_j is the stoichiometric coefficient of component j according to the usual convention—positive for products, negative for reactants. The matrix represented by this term is simply carried along as an accumulated sum. If there is more than one reaction, an additional term is needed for each reaction. The matrix $(\partial K^{(j)}/\partial t)\ X'^{(j)}$ is diagonal, with elements $(\partial K_{ij}/\partial t_i)\ X'_{ij}$ for $i = 1, 2, \ldots N$.

Differentiation of Equation (16) with respect to v yields

$$\frac{\partial X'^{(j)}}{\partial v} = -\left(Z^{(j)} + V\frac{\partial K^{(j)}}{\partial X_n^{(j)}} X_n^{(j)} + \frac{\partial R_n^{(j)}}{\partial X_n^{(j)}} \right)^{-1} \left(\frac{\partial Z^{(j)}}{\partial v} X'^{(j)} + \alpha_j \sum_{k=1}^{j-1} \frac{\partial R}{\partial X'^{(k)}} \frac{\partial X'^{(k)}}{\partial v} \right) \tag{18}$$

It can be shown that the matrix $(\partial Z^{(j)}/\partial v)\ X'^{(j)}$ has the following structure:

$$\frac{\partial Z^{(j)}}{\partial v} X'^{(j)} = \begin{bmatrix} (1 - K_{1j})X_{1j} & K_{2j}X_{2j} - X_{1j} & & \\ X_{2j} - X_{1j} & X_{1j} - K_{2j}X_{2j} & K_{3j}X_{3j} - X_{2i} & \\ X_{3j} - X_{2j} & & X_{2j} - K_{3j}X_{3j} & \ddots \\ \vdots & & & \ddots \\ X_{Nj} - X_{N-1,j} & & & \end{bmatrix} \tag{19}$$

having elements only in the first column, along the diagonal, and along the superdiagonal.

We now have a measure of the variation in X' caused by variations in t and v. This information is used in taking the derivatives of Equation (8) and Equation (10). These derivatives are

$$\frac{\partial D_m'}{\partial v} = \sum_{j=1}^{M} (I - K^{(j)}) \frac{\partial X'^{(j)}}{\partial v} \tag{20}$$

$$\frac{\partial D_m'}{\partial t} = \sum_{j=1}^{M} \left[(I - K^{(j)}) \frac{\partial X'^{(j)}}{\partial t} - \frac{\partial K^{(j)}}{\partial t} X'^{(j)} \right] \tag{21}$$

$$\frac{\partial D_e'}{\partial v} = \sum_{j=1}^{M} [L\hat{H}^{(j)} + VK^{(j)}\hat{G}^{(j)}] \frac{\partial X'^{(j)}}{\partial v} + \xi \tag{22}$$

$$\frac{\partial D_e'}{\partial t} = \sum_{j=1}^{M} \left[(L\hat{H}^{(j)} + VK^{(j)}\hat{G}^{(j)}) \frac{\partial X'^{(j)}}{\partial t} + V\hat{G}^{(j)} \frac{\partial K^{(j)}}{\partial t} X'^{(j)} \right] + L\Gamma_{(\mathrm{liq})} + V\Gamma_{(\mathrm{vap})} \tag{23}$$

The previously undefined matrices ξ, $\Gamma_{(\mathrm{liq})}$, and $\Gamma_{(\mathrm{vap})}$ have the following meaning. ξ has the structure

$$\xi = \begin{bmatrix} h_1 - g_1 & g_2 - h_1 & & \\ h_2 - g_1 & h_1 - g_2 & g_3 - h_2 & \\ h_3 - h_2 & & h_2 - g_3 & \\ \vdots & & & g_n - h_{n-1} \\ h_n - h_{n-1} & & & h_{n-1} - g_n \end{bmatrix} \tag{24}$$

$\Gamma_{(\mathrm{liq})}$ is a diagonal matrix, the elements of which are the heat capacities of the liquid streams leaving each tray. $\Gamma_{(\mathrm{vap})}$ is similarly defined for the vapor phase.

In Equations (20) through (23) the quantities D_m' and D_e' are primed to remind us that these are not the current values of the mass and energy defect vectors, but the values which will be obtained on the next iteration of Equation (16) if no change is made in the vectors v and t. We would like to change v and t in such a way that these defect vectors become zero. Were we to do this using the linearized equations, the next estimate of t and v would be given, according to the Newton-Raphson method, by

$$\left[\begin{array}{c} v \\ \hline t \end{array}\right]_{n+1} = \left[\begin{array}{c} v \\ \hline t \end{array}\right]_{n} - \left[\begin{array}{cc} \dfrac{\partial D_m'}{\partial v} & \dfrac{\partial D_m'}{\partial vt} \\ \hline \dfrac{\partial D_e'}{\partial v} & \dfrac{\partial D_e'}{\partial t} \end{array}\right]^{-1} \left[\begin{array}{c} D_m' \\ \hline D_e' \end{array}\right] \qquad (25)$$

The notation in Equation (25) may be simplified by writing it as

$$\Delta w = -J^{-1}D. \qquad (26)$$

As a solution is approached, the Newton-Raphson method has been found to be unreliable, often yielding large excursions in the estimations of t and v. No satisfactory explanation for this is available in the present circumstance, but it is known to be a not uncommon shortcoming of the method. The Newton-Raphson method is equivalent to choosing from the linearized equations, that set of values of t and v which minimizes D^TD. A more stable procedure results when t and v are chosen to minimize the quantity $D^TD + \alpha(\Delta w)^T(\Delta w)$, making the excursion in t and v part of the minimization problem. This is known as the method of damped least squares (*4*), and has the effect of preventing wild variations in the values of t and v. The solution to this new minimization problem is given by

$$\Delta w = -(J^TJ + \alpha I)^{-1}J^TD \qquad (27)$$

which replaces Equation (26), where α is the damping factor. When $\alpha = 0$, Equation (27) reduces to Equation (26). As α is increased, the step size decreases, and for α suitably large, convergence can be achieved. A convenient value which combines relatively rapid convergence with stability has been found to be 0.003 times the average value of a diagonal element in the J^TJ matrix.

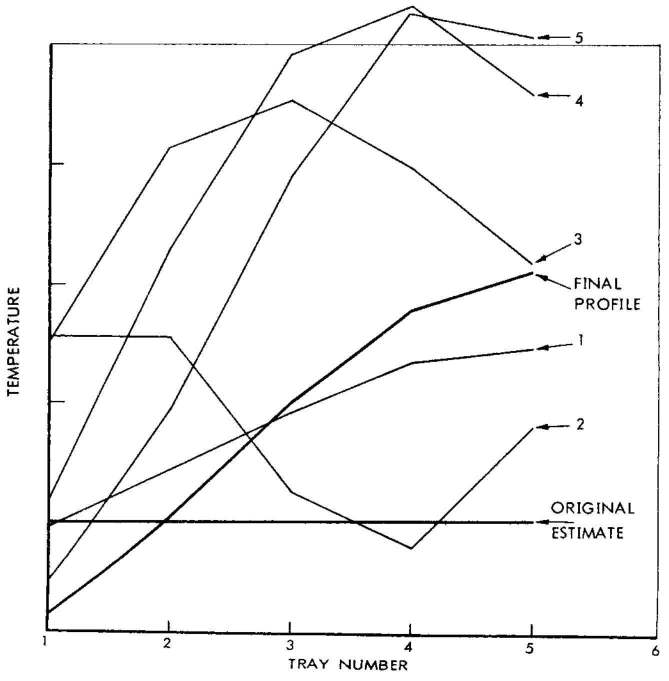

Fig. 2. Temperature profile convergence.

EXAMPLE

As an example, we return to the reaction type with which this discussion was begun

$$A + B \rightleftharpoons C + D$$

with B and D more volatile than A and C. For the rate of reaction we take the nonlinear, and autocatalytic, expression

$$R = K_1[C]\{[A][B] - K_2[C][D]\}$$

The chemical process for which the foregoing technique was developed includes a reaction of this type. The process is of potential commercial interest, and details of the chemistry cannot be disclosed. A qualitative discussion should serve to illustrate the general findings.

A column with five equilibrium stages was simulated, with the temperature and vapor rate profiles initially assumed flat. The subsequent excursions of these profiles are indicated in Figures 2 and 3. Following the fifth iteration, the final profiles were approached systematically, and convergence was declared after 23 iterations. Execution time on a UNIVAC 1108 was 5 sec. The approach to convergence is shown also in Figure 4, where the norm of the defect vector $\sqrt{||D_m||^2 + ||D_e||^2}$ is plotted versus iteration number. This figure is interesting since it shows convergence

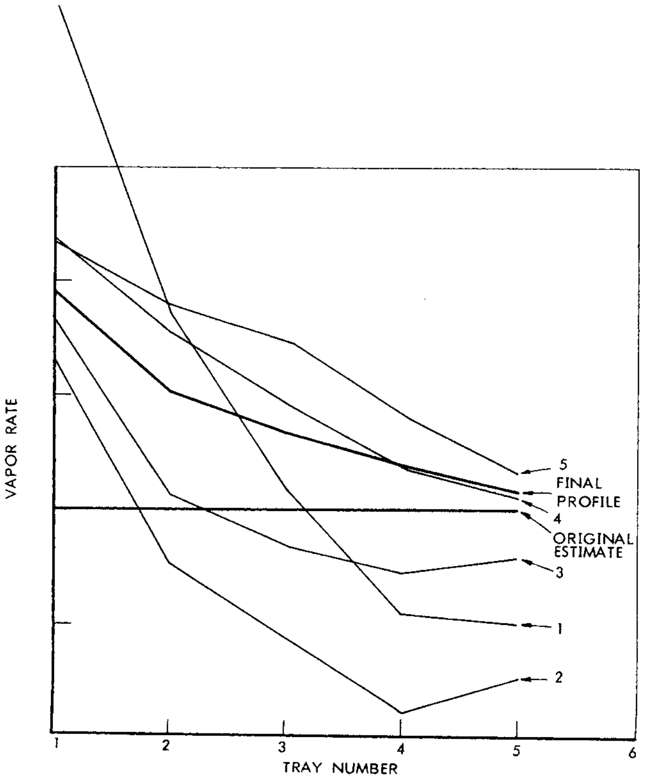

Fig. 3. Vapor rate profile convergence.

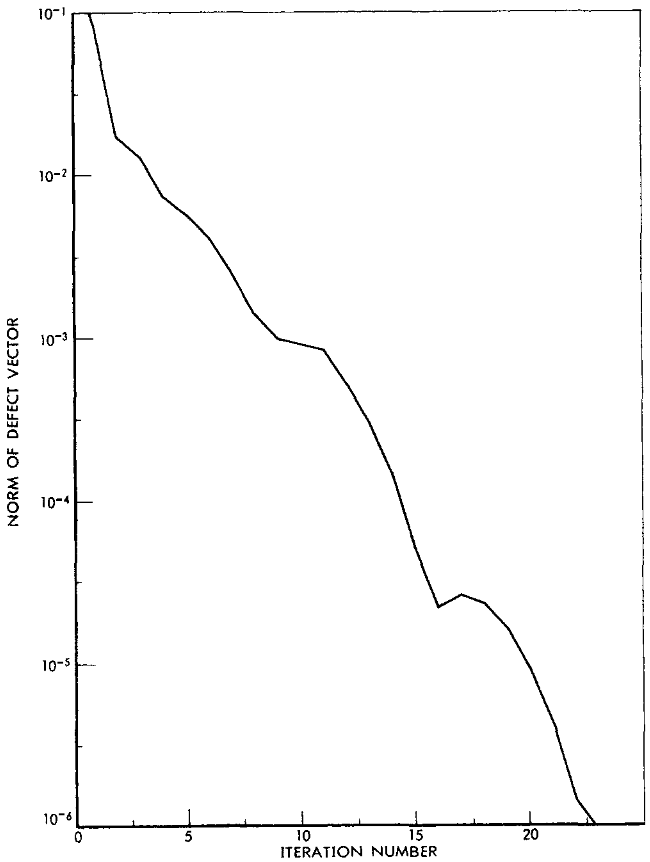

Fig. 4. Convergence of iterative process.

not to be monotonic. No good explanation for this phenomenon is available. The most likely answer is to be found in the interaction between the nonlinear solution techniques being applied at two levels. This is still an open question, however.

NOTATION

D_e = enthalpy defect vector, defined in Equation (10)
D_m = defect vector in mole fraction summation constraint, Equation (8)
D = vector consisting of D_e and D_m together
$F^{(j)}$ = vector composed of elements f_{ij}, $i = 1, 2, \ldots N$
f_{ij} = external feed rate of component j to tray i
G = vapor stream enthalpy vector
$\hat{G}^{(j)}$ = vapor stream partial enthalpy for component j
g_i = enthalpy of vapor stream leaving stage i
H = liquid stream enthalpy vector
$\hat{H}^{(j)}$ = liquid stream partial enthalpy for component j
h_i = enthalpy of liquid stream leaving stage i
I = identity matrix
J = Jacobian matrix, defined by comparison of Equations (25) and (26)
$K^{(j)}$ = diagonal matrix with elements K_{ij}, $i = 1, 2, \ldots N$
K_{ij} = vapor-liquid equilibrium constant for component j on tray i
L = liquid flow connection matrix, defined in Equation (4)
l = vector of liquid flow rates
M = number of components
N = number of stages
R = vector representing the rate of reaction in each stage
$R^{(j)}$ = vector composed of elements r_{ij}; $i = 1, 2, \ldots N$
r_{ij} = rate of creation of component j on stage i by reaction
$s^{(j)}$ = material balance defect, defined by Equation (5)
t = temperature profile vector
U = column vector with each element equal to unity
V = vapor flow connection matrix, defined in Equation (4)
v = vapor rate profile vector
w = $2N$ dimensional vector of variables, composed of v and t
$X^{(j)}$ = vector composed of elements x_{ij}; $i = 1, 2, \ldots N$
x_{ij} = liquid mole fraction of component j in stage i
$Y^{(j)}$ = vector composed of elements y_{ij}; $i = 1, 2, \ldots N$
y_{ij} = vapor mole fraction of component j in stage i
$Z^{(j)}$ = tridiagonal matrix defined in Equation (6)
α = damping factor, defined in Equation (18)
α_j = stoichiometric coefficient for component j in reaction
Γ = diagonal matrix of molar heat capacities for liquid or vapor streams
ξ = matrix defined in Equation (24)

Subscripts

i = generally used in reference to tray number
j = generally used in reference to component number
n = generally used to number iterations

Superscripts

T = transpose of a matrix
(j) = refers to component j
$'$ = value to be calculated on the next iteration of the material balance equations, provided v and t are unchanged

LITERATURE CITED

1. Amundson, N. R., and A. J. Pontinen, *Ind. Eng. Chem.*, **50**, 730 (1958).
2. Backhaus, A. A., U.S. Pat. 1,400,849-51 (1921); 1,403,-224-5 (1922); 1,425,624-5, 1,454,462 (1923).
3. Collatz, Lothar, "Functional Analysis and Numerical Mathematics," p. 200, Academic Press, New York (1966).
4. Feder, D. P., *Appl. Optics*, **2**, 1209 (1963).
5. Frank, Andrew, *Chem. Eng. Progr. Symp. Ser. No. 72*, **63**, 54 (1967).
6. Friday, J. R., and B. D. Smith, *AIChE J.*, **10**, 698 (1964).
7. Geelen, H., and J. B. Wijffels, in "Proc. 3rd European Symp. Chemical Reaction Engineering, Amsterdam, Sept. 1964," Pergamon Press, New York (1965).
8. Greenstadt, J. L., Yonathan Bard, and Burt Morse, *Ind. Eng. Chem.*, **50**, 1644 (1958).
9. Hofmann, H., *Chem. Eng. Sci.*, **8**, 113 (1958).
10. *Ibid.*, **14**, 56 (1961).
11. Lapidus, Leon, "Digital Computation for Chemical Engineers," McGraw-Hill, New York (1964).
12. Leyes, C. E., and D. F. Othmer, *Trans. Am. Inst. Chem. Eng.*, **41**, 157 (1945).
13. Ostrowski, A. M., "Solution of Equations and Systems of Equations," p. 27, Academic Press, New York (1966).
14. Saaty, T. L., and Joseph Bram, "Nonlinear Mathematics," McGraw-Hill, New York (1964).
15. Schoenemann, K., *Chem. Eng. Sci.*, **8**, 161 (1958).
16. Tierney, J. W., and J. A. Bruno, *AIChE J.*, **13**, 556 (1967).
17. Tierney, J. W., and J. L. Yanosik, *ibid.*, **15**, 897 (1969).