

MODELING OF MULTICOMPONENT MULTISTAGE  
SEPARATION PROCESSES

By

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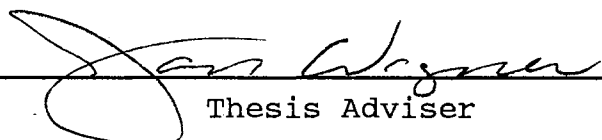
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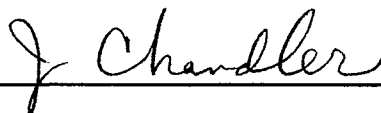
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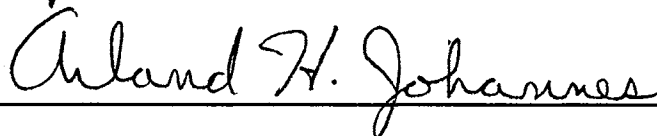
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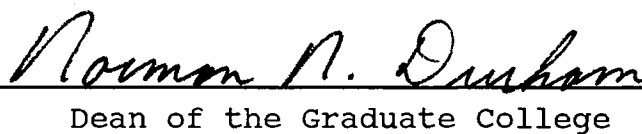
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C O P Y R I G H T

by

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## PREFACE

The number of equations to be solved in modeling a multicomponent multistage separation process could be in the thousands. These equations are complex and nonlinear. A robust, and computationally efficient method to solve these equations is presented in this study. Conventionally, matrix solving algorithms are written in row-major order. Whereas A.N.S.I standard Fortran stores arrays in column-major order. This aspect is considered in this study and algorithms are developed in column-major order. An equation of state is used to estimate the thermodynamic properties. The thermodynamic property derivatives are derived analytically. Homotopy, or path following method is used to solve difficult problems. An algorithm, based on the above model, has been developed and tested on a number of problems.

The study shows that, in a virtual storage machine, column oriented algorithms are computationally efficient and produce a reduction in the number of page faults. Column oriented algorithms are recommended for all matrix operations; including multiplication, addition, and subtraction. Homotopy, or path following methods are effective in solving problems which are otherwise

difficult to converge. This difficulty may be due to the specifications being a very nonlinear function of the independent variables and/or the phase behavior of the mixture being highly nonideal. The algorithms developed in this study are computationally efficient and robust.

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## CHAPTER I

### INTRODUCTION

#### Scope and Objectives

The objective of this work was to develop a computationally efficient and robust numerical model to simulate multistage, multicomponent separation processes. Four basic sets of equations are used to describe these processes. They are Material balance equations, Equilibrium relationships, Summation equations for mole fractions, and Heat balance equations. These equations are often referred to as the MESH equations after Wang and Henke (1966). In addition to these equations, correlations are needed to estimate thermodynamic equilibrium constants and liquid and vapor enthalpies. Since these correlations are complex and nonlinear, it is not possible to solve the MESH equations analytically or directly. Iterative, numerical methods are used and convergence of such methods is not always guaranteed.

The literature survey is presented in Chapter II, and the mathematical model is discussed in Chapter III. As discussed in Chapter II, so that a wide range of problems, distillation, absorption, etc., can be solved by the same

model, the MESH equations are solved simultaneously. To account for nonideality in phase equilibria, composition is included as an independent variable in the model. The model is formulated in  $N_s(N_c+2)$  independent variables. The  $N_c$  component mole fractions in liquid,  $N_s$  total vapor flow rates, and  $N_s$  stage temperatures are used as the independent variables. The equations are linearized and solved by the Newton's method. The approach of Ishii and Otto (1973) is used to manipulate the matrices.

A cubic equation of state is used to estimate thermodynamic properties. The equation is solved for liquid and vapor compressibility factors, which in turn are used to calculate the fugacity coefficients and enthalpy departure functions. The equilibrium constants are obtained as the ratio of the fugacity coefficients. The equations for the derivative properties for both the phases are derived analytically. These are discussed in Chapter IV. In solving the cubic equation of state, convergence to trivial roots and spurious derivatives must be avoided. The procedures outlined by Poling et al. (1980), Gundersen (1982), and Aftab (1987) are used to avoid convergence to 'wrong' roots.

Depending on the number of stages and/or components, the number of equations to be solved could be in the thousands. These equations are solved iteratively, until a convergence is obtained. The computational efficiency

of such large problems, when programmed in A.N.S.I. standard Fortran in a virtual storage machine, is improved by using what are known as column oriented algorithms. In these methods the matrix equations are solved column-by-column instead of the more conventional row-by-row approach. These modifications result in a savings in computation time and also a reduction in the number of page faults. This is because, as discussed in Chapter V, Fortran stores arrays in column-major order.

The Newton's method needs initial estimates for the independent variables. The convergence characteristics of the problem depend on these initial estimates. A "good" initial estimate is required for the success of this method. Otherwise, there could be difficulties in obtaining a converged solution. These difficulties may be due to the specifications being a very nonlinear function of the independent variables and/or the phase behavior of the mixture being highly non-ideal.

For "difficult" to solve problems, a path, or homotopy, is defined from ideal to non-ideal thermodynamic properties. Such methods have been successfully used in other fields (Garcia and Zangwill, 1981) and recently in chemical engineering by Salgovic et al. (1981), Bhargava et al. (1984), Seader et al. (1984), and Vickery et al. (1986).

### Significance

The numerical model developed in this work can be used to solve a wide range of separation problems, including distillation, absorption, and reboiled absorption. The matrix equations are solved using computationally efficient column oriented algorithms. This approach has produced a modest to significant savings in computation time. In estimating the thermodynamic properties from a cubic equation of state, convergence to trivial roots and spurious derivatives has been avoided. For difficult to solve problems, a homotopy, or path has been defined for thermodynamic properties. Using this method, convergence has been obtained to problems which were otherwise difficult to converge, and also convergence has been accelerated for some problems.

## CHAPTER II

### LITERATURE SURVEY

Multistage, multicomponent separation processes such as distillation and absorption are among the most important unit operations in the chemical and petrochemical industries. Until the 1950's, distillation calculations were mostly done by short-cut approximate methods. In the 1930's, Lewis and Matheson (1932) and Thiele and Geddes (1933) proposed a rigorous method but it was too tedious for hand calculations. A rigorous simulation of separation processes could be done only after digital computers became readily available.

In general, a separation process is formulated as an equilibrium stage model in  $N_s(2N_c+3)$  equations in as many independent variables, where  $N_s$  is the number of stages, and  $N_c$  is the number of components. The equations are Material balance equations, Equilibrium relationships, Summation equations for mole fractions, and Heat balance equations. These equations are often referred to as the MESH equations after Wang and Henke (1966). Rigorous simulation of multistage multicomponent separation processes involves solving these equations. A number of



solution methods have been proposed in the literature to solve them. These can be classified into relaxation, equation-decoupling, and simultaneous-solution methods.

#### Relaxation Methods

In these methods, the MESH equations are solved in unsteady state form. The material balance equations are written in unsteady state form as the rate of change of component  $i$  on stage  $j$  (King, 1981). A set of compositions, temperatures, and liquid and vapor flow rates are assumed at time  $t$ . The material balance equations are then solved for compositions at time  $t+\Delta t$ . New temperatures and flow rates are calculated from summation and heat balance equations. This procedure is repeated until changes in compositions do not exceed a preset tolerance.

The convergence is usually much slower, of the order of one, with this method. However there are procedures available to accelerate this class of methods (Chandler, 1988). Recently this method is gaining some attention for generating initial estimates for highly nonideal mixtures (King, 1981).

#### Equation Decoupling Methods

If the equilibrium constants are not composition dependent, then the model is formulated in terms of  $2N_s$

independent variables. This is the basis of equation-decoupling methods, and the equations are grouped either by stages or by types of equations. Initial estimates are needed for the independent variables and these are updated later. The groups of equations are solved in a prescribed order, one group at a time, for certain sets of variables while holding the other variables fixed.

Lewis and Matheson (1932) and Thiele-Geddes (1933) grouped the equations by stage and solved them stage-by-stage from both ends of the column. These methods are prone to a buildup of truncation errors and are seldom used.

Amundson and Pontinen (1958) were the first to group the equations by their type instead of stages. They chose stage temperatures and total vapor flow rates as the independent variables. They proposed to solve the summation equations for temperatures and the heat balance equations for flow rates. This is commonly known as the bubble point (BP) method.

The BP method is better suited to distillation of close boiling mixtures that are not far removed from ideal behavior. Then the latent heat differences determine the total vapor and liquid flow rates through heat balances, and the compositions determine the stage temperatures through summation equations. If the feed contains components of widely different volatility then the BP

method fails. This is because the sensible heat effects dominate the heat balances, and the temperatures are determined more by heat balances than by compositions. The total flow rates are determined more by compositions than by heat balances. Gas absorbers and strippers exhibit such characteristics. For such problems Sujata (1961) proposed to solve the heat balance equations for temperatures and the summation equations for flow rates. He used the Newton's method to solve the heat balance equations. This is commonly known as the sum-of-rates (SR) method.

Friday and Smith (1964) analyzed different solution methods for convergence characteristics. They discussed the capabilities and limitations of the BP and SR methods. Wang and Henke (1966) used the efficient Thomas algorithm to solve the material balance equations in tridiagonal form and developed the BP method in detail.

Tierney and Janosik (1969), and Tomich (1970) proposed to solve the heat balance and summation equations simultaneously for temperatures and vapor flow rates. Hence their methods were not as restricted as BP and SR methods. Tomich also recommended the use of Broyden procedure (1956) for matrix solution as this was helpful in accelerating the convergence.

For problems where the equilibrium constants are composition dependent, the equation decoupling method

will fail to converge or converge slowly. Compositions must be included as independent variables for such problems, and the common practice is to solve the MESH equations simultaneously.

#### Simultaneous-Solution Methods

Naphthali and Sandholm (1971) proposed a simultaneous-solution procedure employing  $N_s(2N_c+1)$  independent variables. They used  $N_c$  component vapor flow rates,  $N_c$  component liquid flow rates and  $N_s$  stage temperatures as the independent variables. Their method involves a large number of calculations and is computationally expensive to use, particularly when composition dependent enthalpies and equilibrium constants are used.

Goldstein and Stanfield (1970) proposed a sectioning technique in which the equations were written for sections instead of stages. Each section could contain one or more stages. So long as average values of flow rates, etc. can be used, the section concept gives a good approximation of the stages in the section.

Bruno et al. (1972) proposed a method in  $N_s(N_c+1)$  independent variables. They used  $N_c-1$  component mole fractions in liquid,  $N_s$  total vapor flow rates, and  $N_s$  stage temperatures as the independent variables. Their matrix solution technique proved to be inefficient, as

they did not order the functions and variables effectively.

Ishii and Otto (1973) proposed a method employing  $N_s(N_c+2)$  independent variables. They used  $N_c$  component mole fractions in liquid,  $N_s$  total vapor flow rates, and  $N_s$  stage temperatures as the independent variables. They used Chao and Seader (1961) correlation to estimate the thermodynamic properties. In calculating the Jacobian matrix, they assumed that the thermodynamic equilibrium constants were independent of the vapor phase compositions. They proposed an efficient matrix manipulation technique to solve the MESH equations.

Gallun (1975) modified the method of Bruno et al. (1972) by rearranging the functions and variables. But still, a large number of calculations need to be done in Gallun's method. He recommends the method for problems involving only a few components when complex thermodynamic functions are to be used.

Naphthali and Sandholm (1971) and Gallun (1975) consider all the thermodynamic derivative properties in their formulation. Still, for "difficult" to solve problems, convergence could not be obtained without a forcing technique (Gallun, 1979). To obtain convergence on a difficult problem, Gallun (1979) solved a series of easier problems until the original system was solved. The method is suited to the particular problem solved by

Gallun, and can not be generalized.

### Initial Estimates

The Newton's method, or one of its relatives, is commonly used to solve the linearized set of MESH equations. The method requires initial estimates for the independent variables, and the convergence characteristics of the problem depend on these initial estimates. For the success of this method, "good" initial estimates are required. In the past, different techniques have been used to improve the domain of convergence (Powell, 1970; Ketchum, 1979). The domain of convergence is defined as the set of initial estimates from which a solution is achieved.

The techniques most recently used to solve "difficult" problems are the homotopy, or path following, methods. This method has been popular in other fields for some time (Garcia and Zangwill, 1981). In the field of chemical engineering there have been but a few applications of this method by Salgovic et al. (1981), Bhargava et al. (1984), Seader et al. (1984), and Vickery et al. (1986).

### Summary

The number of equations required to simulate multicomponent multistage separation processes could be in

the thousands. Generally, these equations are nonlinear and complex. So that a wide range of separation problems can be solved by the same method, these equations are solved simultaneously.

Computationally efficient iterative algorithms must be developed to solve these equations. In addition, the model must be robust so that a converged solution is obtained to 'difficult' problems.

The methods to improve computational efficiency and robustness are the main features of this work.

## CHAPTER III

### MATHEMATICAL MODEL

A generalized countercurrent, multistage, multicomponent separation process with  $N_s$  number of stages is shown in Figure 1. The stages are numbered down from the top. A condenser, if any, is the stage 1 and reboiler, if any, is the stage  $N_s$ . Heat can be transferred to or from each stage, and also side streams can be withdrawn from each stage. The nomenclature is defined in Figure 1. The subscript  $i$  refers to component number and subscript  $j$  refers to stage number. It is assumed that phase equilibrium is achieved at each stage and that no chemical reactions occur.

#### Number of Variables

The total number of variables in the process is  $N_s(3N_c+9)+1$ ; where  $N_s$  is the number of stages, and  $N_c$  is the number of components. These variables are listed in Table I. The first nine, for a total of  $N_s(N_c+6)+1$  variables, can be conveniently specified. This leaves  $N_s(2N_c+3)$  variables to be determined. These are the component mole fractions in the liquid and vapor phases,



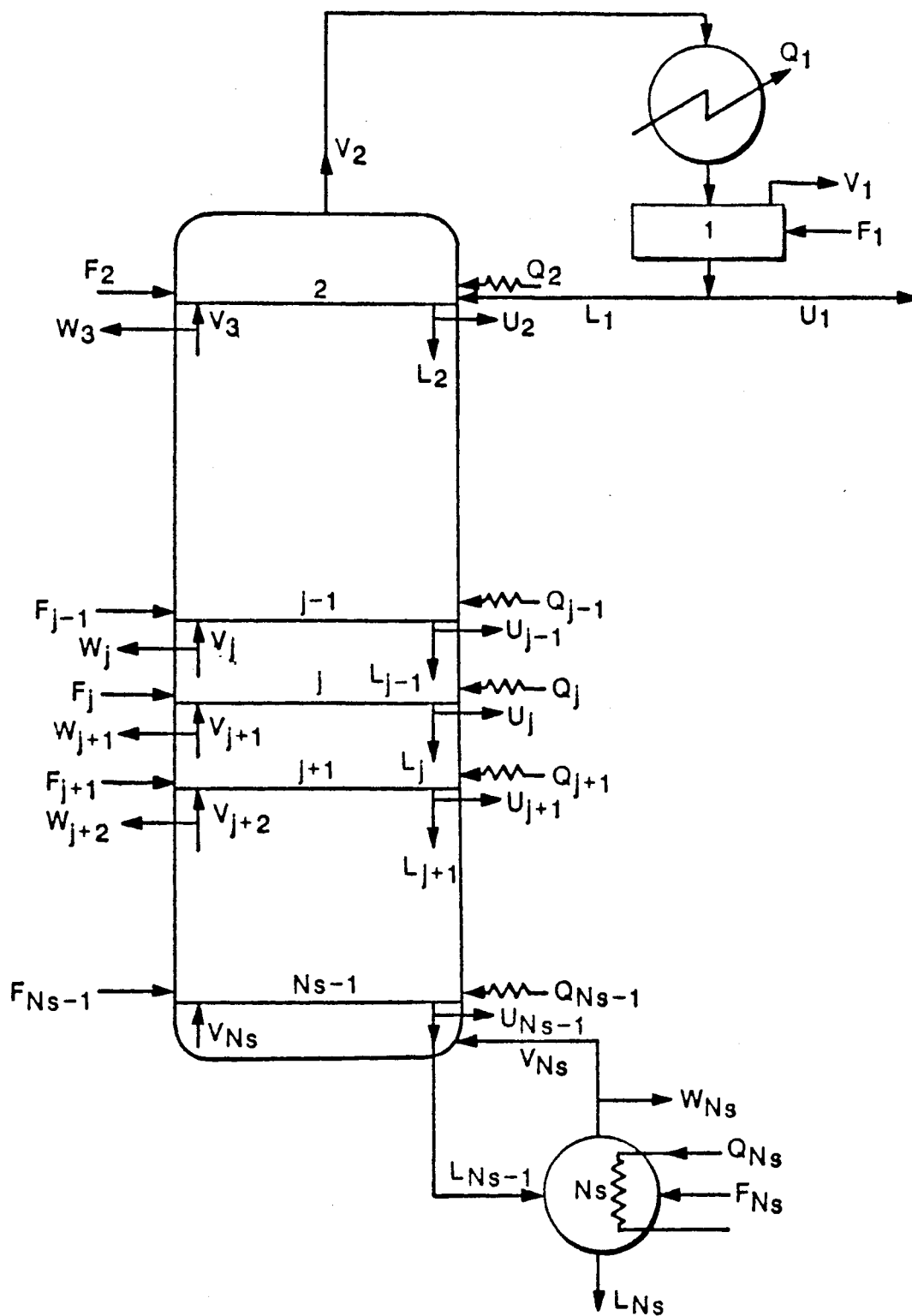


Figure 1. A Schematic Representation of Multistage Multicomponent Separation Process

TABLE I  
 NUMBER OF VARIABLES IN A MULTICOMPONENT  
 MULTISTAGE SEPARATION PROCESS

| S.N. | Type of variable                                | Number of variables |
|------|---|---------------------|
| 1    | Number of stages, $N_s$                         | 1                   |
| 2    | Feed flow rate, $F_j$                           | $N_s$               |
| 3    | Feed composition, $z_{i,j}$                     | $N_s(N_c-1)$        |
| 4    | Feed pressure, $P_{F,j}$                        | $N_s$               |
| 5    | Feed temperature, $T_{F,j}$                     | $N_s$               |
| 6    | Stage pressure, $P_j$                           | $N_s$               |
| 7    | Liquid side stream, $U_j$                       | $N_s$               |
| 8    | Vapor side stream, $W_j$                        | $N_s$               |
| 9    | Heat in each stage, $Q_j$                       | $N_s$               |
| 10   | Component mole fraction<br>in liquid, $x_{i,j}$ | $N_s(N_c)$          |
| 11   | Component mole fraction<br>in vapor, $y_{i,j}$  | $N_s(N_c)$          |
| 12   | Liquid flow rate, $L_j$                         | $N_s$               |
| 13   | Vapor flow rate, $V_j$                          | $N_s$               |
| 14   | Stage Temperature, $T_j$                        | $N_s$               |

$$\text{Total} = N_s(3N_c+9)+1$$

total liquid and vapor flow rates, and stage temperatures.

### MESH Equations

The  $N_s(2N_c+3)$  equations used to describe the process are  $N_s(N_c)$  Material balance equations,  $N_s(N_c)$  Equilibrium relationships,  $2N_s$  Summation equations for mole fractions, and  $N_s$  Heat balance equations. These equations are the MESH equations (Wang and Henke, 1966), which can be written as follows.

#### Material Balance Equations

$$F_j z_{i,j} + L_{j-1} x_{i,j-1} + V_{j+1} y_{i,j+1} - (L_j + U_j) x_{i,j} - (V_j + W_j) y_{i,j} = 0 = M_{i,j} \quad 1 \leq i \leq N_c, 1 \leq j \leq N_s \quad (3.1)$$

#### Equilibrium Relationships

$$y_{i,j} = K_{i,j} x_{i,j} \quad 1 \leq i \leq N_c, 1 \leq j \leq N_s \quad (3.2)$$

#### Summation Equations

$$\sum_i x_{i,j} - 1 = 0 = S_{x,j} \quad 1 \leq j \leq N_s \quad (3.3a)$$

$$\sum_i y_{i,j} - 1 = 0 = S_{y,j} \quad 1 \leq j \leq N_s \quad (3.3b)$$

### Heat Balance Equations

$$F_j H_{F,j} + Q_j + L_{j-1} h_{j-1} + V_{j+1} H_{j+1} - (L_j + U_j) h_j - (V_j + W_j) H_j = 0 \quad 1 \leq j \leq N_s \quad (3.4)$$

Where  $h$  and  $H$  are liquid and vapor enthalpies, and  $K$  is the thermodynamic equilibrium constant. A solution to the MESH equations is obtained by determining the compositions, temperatures and flow rates so that the error terms are all forced to zero.

### Independent Variables

The unknowns in Equations 3.1 through 3.4 are component mole fractions in liquid and vapor,  $x_{i,j}$  and  $y_{i,j}$ ; total liquid and vapor flow rates,  $L_j$  and  $V_j$ ; and stage temperatures,  $T_j$ . After a set of manipulations, discussed below, the mathematical model is formulated in  $N_s(N_c+2)$  independent variables. The independent variables used are  $N_s(N_c)$  component mole fractions in liquid,  $N_s$  stage temperatures, and  $N_s$  vapor flow rates.

The component mole fractions in vapor,  $y_{i,j}$ , are eliminated from Equations 3.1 and 3.3b by combination with Equation 3.2. A total material balance equation is derived and used in place of Equation 3.3b. The equation is derived by summing Equation 3.1 over the  $N_c$  components and stages 1 to  $j$ , with Equations 3.3a, 3.3b, and

$\sum_i z_{i,j} = 1.0$ , where  $z_{i,j}$  is the component mole fraction in feed. This yields the following expression.

$$L_j - V_{j+1} - \sum_{k=1}^j (F_k - U_k - W_k) + V_1 = 0 = \sum_{k=1}^j M_k \quad 1 \leq j \leq N_s \quad (3.5)$$

For the selected independent variables, Equation 3.5 is explicit in total liquid flow rates,  $L_j$ . Hence from Equations 3.1 and 3.4, the total liquid flow rates,  $L_j$ , are eliminated by combination with Equation 3.5. This yields  $N_s(N_c+2)$  equations to be solved in as many independent variables. The equations are written as follows:

#### Material Balance Equations

$$F_j z_{i,j} + L_{j-1} x_{i,j-1} + V_{j+1} K_{i,j+1} x_{i,j+1} - (L_j + U_j) x_{i,j} - (V_j + W_j) K_{i,j} x_{i,j} = 0 = M_{i,j} \quad 1 \leq i \leq N_c, 1 \leq j \leq N_s \quad (3.6)$$

#### Summation Equations

$$\sum_i x_{i,j} - 1 = 0 = S_{x,j} \quad 1 \leq j \leq N_s \quad (3.7)$$

### Heat Balance Equations

$$F_j H_{F,j} + Q_j + L_{j-1} h_{j-1} + V_{j+1} H_{j+1} - (L_j + U_j) h_j - (V_j + W_j) H_j = 0 \quad 1 \leq j \leq N_s \quad (3.8)$$

where the liquid flow rates,  $L_j$ , are given by Equation 3.5. Equations 3.6 through 3.8 are linearized and solved by a Newton's method. When specifications other than reboiler and condenser duties are made, these can be handled by a slight modification of the equations for these stages. A brief description of the Newton's method is given below.

#### Newton's Method

If  $\bar{w}$  is a vector of independent variables, then Equations 3.6 through 3.8 can be expressed in a matrix form as,

$$\bar{f}(\bar{w}) = 0 \quad (3.9)$$

Using a first order Taylor series expansion, Equation 3.9 is written as

$$\frac{\partial \bar{f}}{\partial \bar{w}} (\Delta \bar{w}) = - \bar{f}(\bar{w}) \quad (3.10)$$

From an initial estimate for  $\bar{w}$ , Equation 3.10 is solved for the vector increments  $\overline{\Delta w}$ . New values for  $\bar{w}$  are then obtained from

$$\bar{w}^{k+1} = \bar{w}^k + \lambda \overline{\Delta w}^k \quad (3.11)$$

where  $k$  is the iteration number, and  $\lambda$  is the relaxation factor. This procedure is repeated until convergence is obtained.

#### Linearization

The equilibrium constants,  $K$ , and enthalpies,  $h$  and  $H$ , in Equations 3.6 through 3.8 are estimated from the Soave-Redlich-Kwong (Soave, 1972) equation of state. These properties are a function of pressure, temperature, and phase compositions and are calculated at each iteration. The details of these calculations are given in Chapter IV. For the purpose of linearization only, the following relations are assumed.

$$K = K(P, T, x, y) \quad (3.12)$$

$$H = H(P, T) \quad (3.13)$$

$$h = h(P, T) \quad (3.14)$$

Equation 3.5 is linearized by setting the error term from the material balance equation,  $M_j$ , to zero. This yields the following expression.

$$\Delta L_j = \Delta V_{j+1} - \Delta V_1 \quad 1 \leq j \leq N_s \quad (3.15)$$

Using Equation 3.15, Equations 3.6 through 3.8 are linearized as follows:

#### Material Balance Equations

$$\Delta x_{i,j-1} L_{j-1} +$$

$$\Delta x_{i,j} \left[ - \left\{ (L_j + U_j) + (V_j + W_j) \left( K_{i,j} + x_{i,j} \frac{\partial K_{i,j}}{\partial x_{i,j}} \right) \right\} \right] +$$

$$\Delta x_{i,j+1} \left[ V_{j+1} \left( K_{i,j+1} + x_{i,j+1} \frac{\partial K_{i,j+1}}{\partial x_{i,j+1}} \right) \right] +$$

$$\Delta T_j \left[ - \left( (V_j + W_j) x_{i,j} \frac{\partial K_{i,j}}{\partial T_j} \right) \right] + \Delta T_{j+1} \left[ \left( V_{j+1} x_{i,j+1} \frac{\partial K_{i,j+1}}{\partial T_{j+1}} \right) \right] +$$

$$\Delta V_1 [ (-x_{i,j-1} + x_{i,j}) ] + \Delta V_j [ (x_{i,j-1} - K_{i,j} x_{i,j}) ] +$$

$$\Delta V_{j+1} [ (K_{i,j+1} x_{i,j+1} - x_{i,j}) ] = - M_{i,j}$$

$$1 \leq i \leq N_c, \quad 1 \leq j \leq N_s \quad (3.16)$$



Heat Balance Equations

$$\begin{aligned} & \Delta T_{j-1} \left[ \left( L_{j-1} \frac{\partial h_{j-1}}{\partial T_{j-1}} \right) \right] + \Delta T_j \left[ - \left\{ (L_j + U_j) \frac{\partial h_j}{\partial T_j} + (V_j + W_j) \frac{\partial H_j}{\partial T_j} \right\} \right] + \\ & \Delta T_{j+1} \left[ \left( V_{j+1} \frac{\partial H_{j+1}}{\partial T_{j+1}} \right) \right] + \Delta V_1 [(-h_{j-1} + h_j)] + \Delta V_j [(h_{j-1} - H_j)] + \\ & \Delta V_{j+1} [(H_{j+1} - h_j)] = - E_j \quad 1 \leq j \leq N_s \end{aligned} \quad (3.17)$$

Summation Equations

$$i \sum \Delta x_{i,j} = S_{x,j} \quad 1 \leq j \leq N_s \quad (3.18)$$

The details of the calculation of the thermodynamic derivative properties,  $\partial K_i / \partial x_i$ ,  $\partial K_i / \partial T$ ,  $\partial h / \partial T$ , and  $\partial H / \partial T$ , in Equations 3.16 and 3.17, are given in Chapter IV.

Matrix Form of Linearized Equations

The linearized material balance equation, Equation 3.16, is rearranged in a matrix form. This is shown in Equation 3.19 for the  $i^{\text{th}}$  component over the  $N_s$  stages. In this, and all the other equations, subscript  $j$  refers to stage number and subscript  $i$  refers to component number.

Material Balance Equations

$$\begin{bmatrix} a_{2i,1} & a_{3i,1} & & & \\ a_{1i,2} & a_{2i,2} & a_{3i,2} & & \\ & a_{1i,j} & a_{2i,j} & a_{3i,j} & \\ & & a_{1i,Ns-1} & a_{2i,Ns-1} & a_{3i,Ns-1} \\ & & & a_{1i,Ns} & a_{2i,Ns} \end{bmatrix} \begin{bmatrix} \Delta x_{i,1} \\ \Delta x_{i,2} \\ \Delta x_{i,j} \\ \Delta x_{i,Ns-1} \\ \Delta x_{i,Ns} \end{bmatrix} +$$

$$\begin{bmatrix} b_{1i,1} & b_{2i,1} & & & \\ & b_{1i,2} & b_{2i,2} & & \\ & & b_{1i,j} & b_{2i,j} & \\ & & & b_{1i,Ns-1} & b_{2i,Ns-1} \\ & & & & b_{1i,Ns} \end{bmatrix} \begin{bmatrix} \Delta T_1 \\ \Delta T_2 \\ \Delta T_j \\ \Delta T_{Ns-1} \\ \Delta T_{Ns} \end{bmatrix} +$$

$$\begin{bmatrix} c_{3i,1} + c_{1i,1} & c_{2i,1} & & & \\ c_{3i,2} & c_{1i,2} & c_{2i,2} & & \\ c_{3i,j} & & c_{1i,j} & c_{2i,j} & \\ c_{3i,Ns-1} & & c_{1i,Ns-1} & c_{2i,Ns-1} & \\ c_{3i,Ns} & & & c_{1i,Ns} & \end{bmatrix} \begin{bmatrix} \Delta V_1 \\ \Delta V_2 \\ \Delta V_j \\ \Delta V_{Ns-1} \\ \Delta V_{Ns} \end{bmatrix} = \begin{bmatrix} d_{i,1} \\ d_{i,2} \\ d_{i,j} \\ d_{i,Ns-1} \\ d_{i,Ns} \end{bmatrix}$$

$1 \leq i \leq N_c \qquad (3.19)$

where,

$$a_{1i,j} = L_{j-1} \quad (3.20)$$

$$a_{2i,j} = - \left\{ (L_j + U_j) + (V_j + W_j) \left( K_{i,j} + x_{i,j} \frac{\partial K_{i,j}}{\partial x_{i,j}} \right) \right\} \quad (3.21)$$

$$a_{3i,j} = V_{j+1} \left( K_{i,j+1} + x_{i,j+1} \frac{\partial K_{i,j+1}}{\partial x_{i,j+1}} \right) \quad (3.22)$$

$$b_{1i,j} = - \left( (V_j + W_j) x_{i,j} \frac{\partial K_{i,j}}{\partial T_j} \right) \quad (3.23)$$

$$b_{2i,j} = \left( V_{j+1} x_{i,j+1} \frac{\partial K_{i,j+1}}{\partial T_{j+1}} \right) \quad (3.24)$$

$$c_{1i,j} = (x_{i,j-1} - K_{i,j} x_{i,j}) \quad (3.25)$$

$$c_{2i,j} = (K_{i,j+1} x_{i,j+1} - x_{i,j}) \quad (3.26)$$

$$c_{3i,j} = (-x_{i,j-1} + x_{i,j}) \quad (3.27)$$

$$d_{i,j} = - M_{i,j} \quad (3.28)$$

In a similar manner, the linearized heat balance equation, Equation 3.17, is rearranged in a matrix form as



$$e_{2j} = - \left( (L_j + U_j) \frac{\partial h_j}{\partial T_j} + (V_j + W_j) \frac{\partial H_j}{\partial T_j} \right) \quad (3.31)$$

$$e_{3j} = \left( V_{j+1} \frac{\partial H_{j+1}}{\partial T_{j+1}} \right) \quad (3.32)$$

$$f_{1j} = (h_{j-1} - H_j) \quad (3.33)$$

$$f_{2j} = (H_{j+1} - h_j) \quad (3.34)$$

$$f_{3j} = (-h_{j-1} + h_j) \quad (3.35)$$

$$g_j = - E_j \quad (3.36)$$

### Solution to Matrix Equations

Using a generalized matrix notation, Equations 3.19 and 3.29 are written as

$$\bar{A}_i \bar{\Delta X}_i + \bar{B}_i \bar{\Delta T} + \bar{C}_i \bar{\Delta V} = \bar{D}_i \quad 1 \leq i \leq N_c \quad (3.37)$$

and

$$\bar{E} \bar{\Delta T} + \bar{F} \bar{\Delta V} = \bar{G} \quad (3.38)$$

where  $\bar{A}_i$ ,  $\bar{B}_i$ ,  $\bar{C}_i$ ,  $\bar{D}_i$ ,  $\bar{E}$ ,  $\bar{F}$ , and  $\bar{G}$  are the corresponding

sub-matrices; and  $\overline{\Delta x}_i$ ,  $\overline{\Delta T}$ , and  $\overline{\Delta V}$  are the corresponding vectors. Equations 3.18, 3.37, and 3.38 are the  $N_s(N_c+2)$  equations in the  $N_s(N_c+2)$  unknowns;  $\overline{\Delta x}_i$ ,  $\overline{\Delta T}$ , and  $\overline{\Delta V}$ . The matrix manipulation technique by Ishii and Otto (1973) is used to solve the Equations 3.37 and 3.38.

The sub-matrices in Equation 3.37 are pre-multiplied by the inverse of  $\overline{A}_i$ , yielding,

$$\overline{I} \overline{\Delta x}_i + \overline{A}_i^{-1} \overline{B}_i \overline{\Delta T} + \overline{A}_i^{-1} \overline{C}_i \overline{\Delta V} = \overline{A}_i^{-1} \overline{D}_i \quad 1 \leq i \leq N_c \quad (3.39)$$

The sub-matrix  $\overline{A}_i$  is a tridiagonal matrix. The details of the inversion are given in Chapter V. Equation 3.39 is summed over all the  $N_c$  components to yield,

$$\overline{I} \sum_i \overline{\Delta x}_i + \sum_i \overline{A}_i^{-1} \overline{B}_i \overline{\Delta T} + \sum_i \overline{A}_i^{-1} \overline{C}_i \overline{\Delta V} = \sum_i \overline{A}_i^{-1} \overline{D}_i \quad (3.40)$$

In Equation 3.18, the error term  $S_{x,j}$  is set to zero. This yields,  $\sum_i \overline{\Delta x}_{i,j} = 0$  or  $\sum_i \overline{\Delta x}_i = 0$ . Hence, Equation 3.40 reduces to,

$$\overline{P} \overline{\Delta T} + \overline{Q} \overline{\Delta V} = \overline{R} \quad (3.41)$$

where

$$\begin{aligned}\bar{P} &= {}_i \Sigma \bar{A}_i^{-1} \bar{B}_i \\ \bar{Q} &= {}_i \Sigma \bar{A}_i^{-1} \bar{C}_i\end{aligned}\tag{3.42}$$

and

$$\bar{R} = {}_i \Sigma \bar{A}_i^{-1} \bar{D}_i$$

The actual inversion of matrices is usually considered inefficient, but in this model the actual inversion is efficient in avoiding the block band matrices.

Equations 3.38 and 3.41 constitute  $2Ns$  equations in unknowns  $\bar{\Delta T}$  and  $\bar{\Delta V}$ . These two equations are combined to yield a square matrix, as shown below.

$$\begin{bmatrix} E & F \\ P & Q \end{bmatrix} \begin{bmatrix} \Delta T \\ \Delta V \end{bmatrix} = \begin{bmatrix} G \\ R \end{bmatrix}\tag{3.43}$$

This equation is solved for  $\bar{\Delta T}$  and  $\bar{\Delta V}$ . Equation 3.39 is then solved for  $\bar{\Delta x}_i$ . The details of the solution of these matrices are given in Chapter V.

New values for  $x_{i,j}$ ,  $V_j$ , and  $T_j$  are then calculated from

$$x_{i,j}^{k+1} = x_{i,j}^k + \lambda \Delta x_{i,j}^k\tag{3.44}$$

$$V_j^{k+1} = V_j^k + \lambda \Delta V_j^k \quad (3.45)$$

and

$$T_j^{k+1} = T_j^k + \lambda \Delta T_j^k \quad (3.46)$$

where  $k$  is the iteration number, and  $\lambda$  is the relaxation factor. The component mole fractions in vapor,  $y_{i,j}$ , and the liquid flow rates,  $L_j$ , are then updated from Equations 3.2 and 3.15. In Equations 3.44-3.46, the relaxation factor,  $\lambda$ , varies from 0 to 1. The original Newton's method is obtained for  $\lambda$  equal to one.

A line search is made for a local minimum, and the relaxation factor,  $\lambda$ , in Equations 3.44-3.46 is chosen so that the error is reduced from iteration to iteration. The error to be reduced, ERROR, is computed as follows.

$$\text{ERROR} = \sum_j \left\{ (i^{\Sigma} y_{i,j} - 1)^2 + \left( \frac{H_j}{F_j H_{F,j} + Q_j + L_{j-1} h_{j-1} + V_{j+1} H_{j+1}} \right)^2 \right\} \quad (3.47)$$

This equation is a measure of the sum-of-errors from Equations 3.1-3.4. In the vicinity of the solution, after a few iterations, Newton's method has a order of



convergence of two.

The error term  $M_j$  is set to zero when the liquid flow rates,  $L_j$ , are updated from Equation 3.15. The error term,  $H_j$ , is normalized in Equation 3.47 by dividing by the heat input to the stage. This makes each error term in Equation 3.47 the same order of magnitude. The calculation procedure is repeated until a specified convergence criterion is satisfied. The criterion used is

$$\left| \frac{\text{ERROR}}{N_s} \right| < \epsilon \quad (3.48)$$

where  $\epsilon$  is a convergence tolerance. A value of  $10^{-6}$  was used for  $\epsilon$  in this work.

## CHAPTER IV

### THERMODYNAMIC PROPERTIES

#### AND ITS DERIVATIVES

An estimate of thermodynamic equilibrium constants, liquid and vapor enthalpies, and derivative properties are needed to solve the MESH equations discussed in Chapter III. These are obtained from the Soave-Redlich-Kwong (Soave, 1972) equation of state. This equation is often referred to as the SRK equation of state and is

$$P = \frac{RT}{v-b} - \frac{a(T)}{v(v+b)} \quad (4.1)$$

where  $v$  is the molar volume,  $P$  is the pressure,  $T$  is the temperature, and  $R$  is the universal gas constant. The parameter  $a$  and constant  $b$  are defined by Soave. Equation 4.1 is cubic in volume and can be written in terms of compressibility factor,  $Z$ , as

$$Z^3 - Z^2 + Z(A-B-B^2) - AB = 0 \quad (4.2)$$

where,

$$Z = \frac{Pv}{RT} \quad (4.3)$$

$$A = \frac{aP}{R^2T^2} \quad (4.4)$$

$$B = \frac{bp}{RT} \quad (4.5)$$

The procedure to estimate the thermodynamic equilibrium constants, enthalpies, and the derivative properties are discussed in this chapter.

#### Equilibrium Constants

The cubic equation of state, Equation 4.2, is solved for liquid and vapor roots. Convergence to "wrong" roots (liquid or vapor) is avoided by using the procedures outlined by Poling et al. (1980), Gundersen (1982), and Aftab (1987). The corresponding roots are then used to calculate the fugacity coefficients,  $\phi_i$ , defined as

$$\ln\phi_i = \frac{1}{RT} \int_{\infty}^V \left[ \frac{RT}{V} - \left( \frac{\partial P}{\partial n_i} \right)_{T,V,n_j} \right] dV - \ln Z \quad (4.6)$$

where  $V$  is the total volume, and  $n_i$  is the number of moles of component  $i$ . Using Equations 4.1 and 4.6, an

expression is derived for  $\ln\phi_i$  from the SRK equation of state. This is given in the Appendix.

The thermodynamic equilibrium constants,  $K_i$ , are then calculated from

$$K_i = \frac{\phi_i^L}{\phi_i^V} \quad (4.7)$$

where the superscripts L and V refer to the liquid and vapor phases, respectively.

#### Enthalpies

The liquid and vapor enthalpies,  $h$  and  $H$ , per mole of mixture are calculated from

$$h = \sum_i x_i H_i^{\circ} + \Omega^L \quad (4.8)$$

$$H = \sum_i y_i H_i^{\circ} + \Omega^V \quad (4.9)$$

In Equations 4.8 and 4.9,  $H_i^{\circ}$  is the molar enthalpy of component  $i$  in the ideal gas state at the temperature  $T$  and a pressure of one atm. The function  $\Omega$  is the isothermal enthalpy departure per mole of mixture for the corresponding phases. The ideal gas state enthalpies,  $H_i^{\circ}$ ,

are obtained from

$$H_i^O = \int_{T_0}^T C_{p,i} dT \quad (4.10)$$

In Equation 4.10,  $C_{p,i}$  is the molal specific heat of component  $i$  in the ideal gas state, and  $T_0$  is the reference temperature. The molal specific heat,  $C_{p,i}$ , is evaluated from a polynomial

$$C_{p,i} = a_i + b_i T + c_i T^2 + d_i T^3 \quad (4.11)$$

where  $a_i$ ,  $b_i$ ,  $c_i$ , and  $d_i$  are empirical constants and are obtained from Reid et al. (1977).

The isothermal enthalpy departure,  $\Omega$ , for both the liquid and vapor phases is calculated from

$$\Omega = \int_{\infty}^v T \left[ \left( \frac{\partial P}{\partial T} \right)_v - P \right] dv + RT(Z-1) \quad (4.12)$$

The corresponding  $Z$  and  $v$  for the liquid and vapor phases are used in this equation. Using Equations 4.1 and 4.12, an expression is derived for  $\Omega$ , from the SRK equation of state. This is given in the Appendix.

### Derivative Properties

The derivative properties;  $\partial K_i/\partial T$ ,  $\partial K_i/\partial x_i$ ,  $\partial h/\partial T$ , and  $\partial H/\partial T$ , are evaluated analytically in this work. There are other techniques available to evaluate the derivatives: finite difference, quasi-newton, symbolic differentiation etc., but analytical procedure is the most efficient of all these techniques (Macchietto et al., 1988).

The analytical expressions are obtained by differentiating Equations 4.7, 4.8, and 4.9 with respect to the independent variables. This yields,

$$\frac{\partial K_i}{\partial T} = K_i \left[ \frac{\partial \ln \phi_i^L}{\partial T} - \frac{\partial \ln \phi_i^V}{\partial T} \right] \quad (4.13)$$

$$\frac{\partial K_i}{\partial x_i} = K_i \frac{\left[ \frac{\partial \ln \phi_i^L}{\partial x_i} - K_i \frac{\partial \ln \phi_i^V}{\partial y_i} \right]}{\left[ 1 + Y_i \frac{\partial \ln \phi_i^V}{\partial y_i} \right]} \quad (4.14)$$

$$\frac{\partial h}{\partial T} = \sum_i x_i \frac{\partial H_i^O}{\partial T} + \frac{\partial \Omega^L}{\partial T} \quad (4.15)$$

$$\frac{\partial H}{\partial T} = \sum_i y_i \frac{\partial H_i^O}{\partial T} + \frac{\partial \Omega^V}{\partial T} \quad (4.16)$$

These derivative properties for the SRK equation of state are given in the Appendix. As discussed in the Appendix, the number of mathematical operations to calculate these properties are minimized by efficient algebraic manipulations.

## CHAPTER V

### MATRIX SOLVING ALGORITHMS

Simulating multistage multicomponent separation processes is translated to solving the large number of simultaneous equations discussed in Chapter III. Due to the large size of problems encountered and iterative calculations involved, the efficiency of matrix solving algorithms becomes a major factor. The algorithms used to solve the matrices are discussed in this chapter.

#### Column and Row Oriented Algorithms

Fortran stores an array in a linear string, even when it has several dimensions. Given an array  $\bar{A}$  of dimension  $n \times n$ , Fortran stores the elements in column-major order so that the left-most dimension varies most rapidly and the right-most dimension varies least rapidly. This is illustrated by an example.

Let the dimension of array  $\bar{A}$  be  $4 \times 4$ . Denoting the elements by  $a$ , the array is shown below.



$$\bar{A} = \begin{bmatrix} a_{1,1} & a_{1,2} & a_{1,3} & a_{1,4} \\ a_{2,1} & a_{2,2} & a_{2,3} & a_{2,4} \\ a_{3,1} & a_{3,2} & a_{3,3} & a_{3,4} \\ a_{4,1} & a_{4,2} & a_{4,3} & a_{4,4} \end{bmatrix} \quad (5.1)$$

Fortran uses 16 positions to store this array in a linear string. Table II illustrates how array elements correspond to storage positions. The elements in the first column of array  $\bar{A}$  are stored in the first four positions. The elements in the second column of array  $\bar{A}$  are stored in the second four positions, and so on. This is what is referred to as storage in column-major order.

Conventionally, matrix solving algorithms are written in row-major order. That is, the right-most variable is varied most rapidly and the left-most variable is varied least rapidly in these algorithms. The successive array elements referenced by these algorithms are separated by a large increment, which depends upon the declared dimension of the array.

Modern operating systems, in virtual storage machines, partition and store the arrays in a number of separate pages. The user has no control over this operation. When row-major order matrix solving algorithms are used for large problems, the number of page faults may be very large. This considerably decreases the efficiency

TABLE II  
STORAGE OF ARRAY ELEMENTS BY FORTRAN

---

| Position | Array Element Name |
|----------|--------------------|
| 1        | $a_{1,1}$          |
| 2        | $a_{2,1}$          |
| 3        | $a_{3,1}$          |
| 4        | $a_{4,1}$          |
| 5        | $a_{1,2}$          |
| 6        | $a_{2,2}$          |
| 7        | $a_{3,2}$          |
| 8        | $a_{4,2}$          |
| 9        | $a_{1,3}$          |
| 10       | $a_{2,3}$          |
| 11       | $a_{3,3}$          |
| 12       | $a_{4,3}$          |
| 13       | $a_{1,4}$          |
| 14       | $a_{2,4}$          |
| 15       | $a_{3,4}$          |
| 16       | $a_{4,4}$          |

---

of computation (Moler, 1972, Digital, 1984).

The large number of page faults is avoided by re-writing the matrix solving algorithms in column-major order. Successive array elements accessed by these algorithms are along a column, and this is the order in which Fortran stores arrays. Both the row oriented and column oriented algorithms are illustrated below.

Let  $\bar{A}$  be a matrix of dimension  $n \times n$  and  $\bar{b}$  be a vector of dimension  $n$ . An algorithm for matrix-vector multiplication,  $\bar{A} \bar{b} = \bar{c}$ , using conventional row-major order is written as follows.

Algorithm 5.1    Row Oriented Algorithm for  
Matrix-Vector Multiplication

```

For i = 1,n
  ci = 0.
  For j = 1,n
    ci = ci + ai,jbj
  end j
end i

```

It is the inner loop which varies most rapidly in such algorithms. Hence, the order in which array elements are successively accessed by the algorithm depends on how

the inner loop is varied. In Algorithm 5.1, the inner loop is on  $j$  and is varied so that the array elements are successively accessed in row order. As discussed earlier, this is not the way Fortran stores array elements and such algorithms are computationally inefficient.

The matrix-vector multiplication is re-written in column-major order as shown below.

Algorithm 5.2    Column Oriented Algorithm for  
Matrix-Vector Multiplication

```

For k = 1,n
  ck = 0.
end k
For j = 1,n
  t = bj
  For i = 1,n
    ci = ci + ai,jt
  end i
end j

```

In this algorithm the inner loop is on  $i$  instead of  $j$ , and is varied so that the array elements are successively accessed in column order. As discussed earlier, this is the way Fortran stores array elements and such algorithms are computationally efficient.

Column oriented algorithms are used in this work for all matrix operations; including multiplication, addition, and subtraction. When compared to row oriented algorithms, these algorithms produce a savings in computation time and a reduction in the number of page faults. A comparison of the two approaches is presented in Chapter VII.

### Matrix Inversion

In Chapter III, Equation 3.39 is pre-multiplied by the inverse of  $\bar{A}_i$ , summed over all the components, and reduced to Equation 3.41. Sub-matrix  $\bar{A}_i$  is a tri-diagonal matrix, and advantage of this structure is taken in calculating the inverse.

Let  $\bar{E}$  be a tri-diagonal matrix, of dimension  $N_s \times N_s$ , with  $e_1$ ,  $e_2$ , and  $e_3$  as the elements. The matrix is shown below.

$$\bar{E} = \begin{bmatrix} e_{21} & e_{31} & & & \\ e_{12} & e_{22} & e_{32} & & \\ & e_{1j} & e_{2j} & e_{3j} & \\ & & & e_{1_{N_s-1}} & e_{2_{N_s-1}} & e_{3_{N_s-1}} \\ & & & & e_{1_{N_s}} & e_{2_{N_s}} \end{bmatrix}$$

(5.2)

This is inverted using Gaussian elimination, with partial pivoting and scaling. The elements of  $\bar{E}$  are stored in  $3Ns$  storage spaces and the algorithm needs only  $2Ns$  additional storage spaces to invert the matrix.

The algorithm, scaling excluded, is given below. In this algorithm;  $d1$  and  $d2$ , each of size  $Ns$ , refer to the additional vectors needed to invert the matrix, and 'einv' refers to the elements in the inverted matrix .

Algorithm 5.3    Algorithm for Inverting a  
Tridiagonal Matrix

*Find the Lower and Upper factors*

*Set  $d1_i = 0.$ , (for  $i=1,Ns$ )*

*Set  $p_k = k$  (for  $k = 1,Ns$ )*

*$nm = Ns-1$*

*For  $k = 1,nm$*

*Set  $p_k = k+1$ , If  $|a1_{k+1}| > |a2_k|$*

*If  $p_k \neq k$ , Then (swap the elements)*

*$t = a1_{k+1}$*

*$a1_{k+1} = a2_k$*

*$a2_k = t$*

*$t = a2_{k+1}$*

*$a2_{k+1} = a3_k$*

*$a3_k = t$*

$$t = a3_{k+1}$$

$$a3_{k+1} = d1_k$$

$$d1_k = t$$

*EndIf*

$$a1_{k+1} = -a1_{k+1}/a2_k$$

$$a2_{k+1} = a2_{k+1} + a1_{k+1}a3_k$$

$$a3_{k+1} = a3_{k+1} + a1_{k+1}d1_k$$

*end k*

*Solve for the Inverse*

*For jc = 1, Ns*

*Set d2<sub>i</sub> = 0. (for i = 1, Ns)*

*d2<sub>jc</sub> = 1.*

*For k = 1, nm (forward elimination)*

*kp = k+1*

*m = p<sub>k</sub>*

*t = d2<sub>m</sub>*

*d2<sub>m</sub> = d2<sub>k</sub>*

*d2<sub>k</sub> = t*

*d2<sub>kp</sub> = d2<sub>kp</sub> + a1<sub>kp</sub>t*

*end k*

*For kb = 1, nm-1 (backward substitution)*

*km = ns-kb*

*k = km + 1*

*d2<sub>k</sub> = d2<sub>k</sub>/a2<sub>k</sub>*

*t = -d2<sub>k</sub>*

```

d2km = d2km + a3kmt
d2km-1 = d2km-1 + d1km-1t
end kb

d22 = d22/a22
d21 = d21 - a31d22
d21 = d21/a21

For i = 1,Ns
einvi,jc = d2i
end i

end jc

```

Solve For  $\overline{\Delta T}$  And  $\overline{\Delta V}$

In Chapter III, Equation 3.43 is to be solved for the vectors  $\overline{\Delta T}$  and  $\overline{\Delta V}$ . The equation is

$$\begin{bmatrix} \overline{E} & \overline{F} \\ \overline{P} & \overline{Q} \end{bmatrix} \begin{bmatrix} \overline{\Delta T} \\ \overline{\Delta V} \end{bmatrix} = \begin{bmatrix} \overline{G} \\ \overline{R} \end{bmatrix} \quad (3.43)$$

As discussed in Chapter III, sub-matrices  $\overline{P}$  and  $\overline{Q}$  result after a set of operations on the linearized material balance equations, Equation 3.16. Sub-matrices  $\overline{E}$  and  $\overline{F}$  are obtained directly from linearized heat balance equations, Equation 3.17.

In Equation 3.43, sub-matrices  $\overline{E}$  and  $\overline{F}$  are sparse



whereas  $\bar{P}$  and  $\bar{Q}$  are not sparse. Hence, instead of solving this equation, a modified form of the equation is solved.

Equation 3.43 is pre-multiplied by the inverse of  $\bar{E}$ . This yields,

$$\bar{I} \bar{\Delta T} + \bar{E}^{-1} \bar{F} \bar{\Delta V} = \bar{E}^{-1} \bar{G} \quad (5.3)$$

Setting  $\bar{H} = \bar{E}^{-1} \bar{F}$ , and  $\bar{S} = \bar{E}^{-1} \bar{G}$ , this is written as,

$$\bar{I} \bar{\Delta T} + \bar{H} \bar{\Delta V} = \bar{S} \quad (5.4)$$

Sub-matrix  $\bar{E}$  is a tri-diagonal matrix and as discussed in section 5.2, advantage of this structure is taken in calculating the inverse. In Equation 5.3,  $\bar{I}$  is an identity matrix and matrices  $\bar{H}$  and  $\bar{S}$  are not sparse.

Equations 5.3 and 3.41 are combined to yield,

$$\begin{bmatrix} \bar{I} & \bar{H} \\ \bar{P} & \bar{Q} \end{bmatrix} \begin{bmatrix} \bar{\Delta T} \\ \bar{\Delta V} \end{bmatrix} = \begin{bmatrix} \bar{S} \\ \bar{R} \end{bmatrix} \quad (5.5)$$

This equation is solved by Gaussian elimination, with scaling and partial pivoting. The top left quadrant of this matrix is an identity sub-matrix and this structure is considered in the solution. The algorithm, scaling

excluded, is given below.

Let  $\bar{A}$  be a square matrix of dimension  $2Ns \times 2Ns$  with an identity sub-matrix in the top left quadrant, and let  $\bar{b}$  be a vector of dimension  $2Ns$ . The algorithm solves for vector  $\bar{x}$  which satisfies  $\bar{A} \bar{x} = \bar{b}$ .

Algorithm 5.4    Column Oriented Algorithm for Solving A Square Matrix Having an Identity Sub-matrix in the Top Left Quadrant

*Find the Lower and Upper Factors*

$nn = 2Ns$

Set  $p_k = k$  (for  $k = 1, nn$ )

*Take Advantage of the Identity Matrix*

$kp = Ns + 1$

For  $k = 1, Ns$

Set  $a_{i,k} = -a_{i,k}$  (for  $i=1, nn$ )

For  $j = kp, nn$

$t = a_{k,j}$

If  $t \neq 0$  then

quit

else

For  $i = kp, nn$

$a_{i,j} = a_{i,j} + a_{i,k}t$

end i

```

                                Endif
                                end j
                                end k

Find the Pivot and perform elimination

nm = nn - 1
For k = kp, nm
kp1 = k + 1
    Find m so  $|a_{m,k}| = \max |a_{i,k}|$ 
                                (for i=kp1,nn)

pk = m
t =  $a_{m,k}$ 
 $a_{m,k} = a_{k,k}$ 
 $a_{k,k} = t$ 
    For i = kp1,nn
         $a_{i,k} = -a_{i,k}/t$ 
    end i

    For j = kp1,nn
        t =  $a_{m,j}$ 
         $a_{m,j} = a_{k,j}$ 
         $a_{k,j} = t$ 
        If t .EQ. 0 then
            quit
        else
            For i = kp1,nn
                 $a_{i,j} = a_{i,j} + a_{i,k}t$ 
            end i
        end if
    end j
end For

```

```

                end i
            Endif
        end j
    end k

```

*Solve for the Vectors*

*For*  $k = 1, nm$  (forward elimination)

$kp = k+1$

$m = P_k$

$t = b_m$

$b_m = b_k$

$b_k = t$

*For*  $i = kp, nn$

$b_i = b_i + a_{i,k}t$

*end*  $i$

*end*  $k$

*For*  $kb = 1, nm$  (backward substitution)

$km = nn - kb$

$k = km + 1$

$b_k = b_k / a_{k,k}$

$t = -b_k$

*For*  $i = 1, km$

$b_i = b_i + a_{i,k}t$

*end*  $i$

*end*  $kb$

$b_1 = b_1 / a_{1,1}$

The solution vector  $\bar{x}$  is stored in the vector  $b$ , and no additional storage space is used.

Once  $\bar{\Delta T}$  and  $\bar{\Delta V}$  are known, Equation 3.39 is solved for  $\bar{\Delta x}_i$ . As outlined in Chapter 3, the procedure is repeated until convergence is obtained. Other major mathematical operations involving matrices are Equations 3.39, 3.40, and 5.5. Column oriented algorithms are used to solve these equations.

## CHAPTER VI

### INITIAL ESTIMATES AND HOMOTOPIES

In Chapter III, a mathematical model is formulated in  $N_s(N_c+2)$  independent variables to simulate multicomponent, multistage separation processes. The independent variables are  $N_s(N_c)$  component mole fractions in liquid,  $x_{i,j}$ ,  $N_s$  total vapor flow rates,  $V_j$ , and  $N_s$  stage temperatures,  $T_j$ . Initial estimates of these variables are needed to initiate the calculation procedure discussed in Chapter III. The procedure to obtain these initial estimates is discussed in this chapter. For 'difficult' to solve problems a homotopy, or path is defined from ideal to nonideal thermodynamic properties.

#### Initial Estimates

##### Temperatures and Flow Rates

Initial estimates for top and bottom stage temperatures,  $T_1$  and  $T_{N_s}$ , are obtained by calculating the bubble, or dew, point temperatures of estimated top and bottom product composition. The temperatures of intermediate stages are assumed to vary linearly as follows.

$$T_j = T_1 + \left( \frac{T_{Ns} - T_1}{Ns - 1} \right) * (j-1) \quad 2 \leq j \leq Ns-1 \quad (6.1)$$

The liquid and vapor flow rates,  $L_j$  and  $V_j$ , are estimated by assuming constant molal overflow (King, 1981).

### Thermodynamic Equilibrium Constants and Compositions

Initial estimates for thermodynamic equilibrium constants are obtained by assuming ideal liquid and vapor phases. Raoult's law is used to calculate these values as

$$K_i^{id} = \frac{P_i^S}{P} \quad (6.2)$$

where  $P_i^S$  is the saturation, or vapor, pressure. In Equation 6.2, the superscript id refers to ideal conditions. The thermodynamic equilibrium constants from Equation 6.2 are independent of phase composition, vary inversely with pressure, and exponentially with temperature.

The estimated flow rates, and composition-independent thermodynamic equilibrium constants are substituted into the material balance equation, Equation 3.7. These set of algebraic equations are then solved for component mole

fractions in liquid,  $x_{i,j}$ , by Thomas algorithm (Wang and Henke, 1966).

The computed  $x_{i,j}$  values are normalized by the relation

$$(x_{i,j})_{\text{norm.}} = \frac{x_{i,j}}{\sum_i x_{i,j}} \quad (6.3)$$

A new set of stage temperatures,  $T_j$ , are calculated by computing bubble point temperatures from the normalized  $x_{i,j}$  values.

### Enthalpies

The liquid and vapor enthalpies,  $h$  and  $H$ , are estimated by assuming the liquid and vapor phases to behave ideally. The relations used are

$$h^{\text{id}} = \sum_i x_i (H_i^{\text{O}} - \Delta H_i^{\text{V}}) \quad (6.4)$$

$$H^{\text{id}} = \sum_i y_i H_i^{\text{O}} \quad (6.5)$$

where  $H_i^{\text{O}}$  is the molar enthalpy of component  $i$  at the ideal gas state at temperature  $T$  and pressure of one atm. The procedure to calculate this term is discussed in Chapter IV, Equation 4.10.



The term  $\Delta H_i^V$  is the molar heat of vaporization of component  $i$  at one atm. This is calculated from

$$\Delta H_i^V = RT^2 \frac{d \ln P_i^S}{dT} \quad (6.6)$$

The vapor pressure,  $P_i^S$ , is obtained from the Antoine equation

$$\ln P_i^S = A_1 - \frac{A_2}{T + A_3} \quad (6.7)$$

where  $A_1$ ,  $A_2$ , and  $A_3$  are Antoine coefficients and are obtained from Reid et al. (1977).

Equation 6.7 is differentiated with respect to temperature and substituted into Equation 6.6. This yields

$$\Delta H_i^V = \frac{A_2 RT^2}{(T + A_3)^2} \quad (6.8)$$

These estimates, based on the assumption of ideal behavior of liquid and vapor phases, are used to initiate the iteration procedure discussed in Chapter III. The nonideal thermodynamic properties from the Soave-Redlich-Kwong (Soave, 1972) equation of state, discussed in

Chapter IV, are then used in subsequent iterations. The iterative procedure is carried out until a specified convergence is obtained.

Using this procedure, for some problems it becomes difficult or impossible to obtain convergence from certain initial estimates. That is, the domain of convergence becomes limited, where the domain of convergence is defined as the set of initial values from which convergence is obtained. The iteration procedure is modified for such problems by defining a homotopy, or path, from ideal to nonideal thermodynamic properties.

#### Homotopies

Given a system of  $n$  nonlinear equations in  $n$  variables, the goal is to find the  $n$  points that satisfy the system. Using a homotopy approach, the solution is found by following a path from a simple, obvious point to the desired point. The concept is described below.

Let  $F(x)$  represent a system of  $n$  nonlinear equations in  $n$  variables. The goal is to solve

$$\begin{aligned}
 F_1(x_1, x_2, \dots, x_n) &= 0 \\
 F_2(x_1, x_2, \dots, x_n) &= 0 \\
 \dots\dots\dots & \\
 F_n(x_1, x_2, \dots, x_n) &= 0
 \end{aligned}
 \tag{6.9}$$

for  $x^* = (x_1^*, x_2^*, \dots, x_n^*)$ . This is the desired solution.

First set up a simple, obvious, system  $E(x) = 0$ . Let  $x^0$  be a solution which solves

$$\begin{aligned} E_1(x_1, x_2, \dots, x_n) &= 0 \\ E_2(x_1, x_2, \dots, x_n) &= 0 \\ \dots\dots\dots & \\ E_n(x_1, x_2, \dots, x_n) &= 0 \end{aligned} \tag{6.10}$$

The system  $E(x)$  is set up in such a way that the points  $x^0 = (x_1^0, x_2^0, \dots, x_n^0)$  are already known, or they are easy to find. This is the starting point.

A special function  $H(x, t)$ , which has the original  $n$  variables plus an extra one,  $t$ , is defined as

$$H(x, t) = (1-t)E(x) + tF(x) \tag{6.11}$$

This is referred to as an homotopy function, and from Equation 6.11,

$$H(x, 0) = E(x)$$

$$\text{and} \tag{6.12}$$

$$H(x, 1) = F(x)$$

It follows that at  $t = 0$ ,

$$H(x,0) = E(x) = 0 \quad (6.13)$$

has a solution  $x^0$  which is already known, or is easy to find. At  $t = 1$ ,

$$H(x,1) = F(x) = 0 \quad (6.14)$$

and this has to be solved for  $x^*$ .

The parameter  $t$  is known as an homotopy parameter. This serves to 'bend' a simple system,  $E(x)$ , to the original system,  $F(x)$ . In this process a simple solution,  $x^0$ , is 'bent' to the desired solution,  $x^*$ , and the original system is solved. For an arbitrary  $t$ ,  $x(t)$  is a solution of

$$H(x(t),t) = 0 \quad (6.15)$$

The idea is to start at  $x(0) = x^0$  and then increase  $t$  until  $x(1) = x^*$  is reached. Generally,  $x(t)$  generates a path that can be followed from  $t = 0$  to  $t = 1$ , thereby solving the original system. A path must exist from  $t = 0$  to  $t = 1$  for the success of this method. The existence of a path is assured if  $H(x,t)$  is continuously differentiable

and the function  $H'_x(x,t)$  is invertible (Garcia and Zangwill, 1981, Bhargava et al., 1984).

In Equation 6.11, if  $E(x) = (F(X)-F(x^0))$  then it is referred to as Newton homotopy, and if  $E(X) = (x-x^0)$  then it is referred to as fixed point homotopy. Bhargava et al. (1984) and Wayburn et al. (1984) used Newton homotopy to solve difficult problems. Recently Kuno et al. (1988) have used fixed point homotopy to find all real roots of nonlinear equations. In this work, Equation 6.11 is used to define a path from ideal to nonideal thermodynamic properties by a linear combination of functions  $E(x)$  and  $F(x)$  (Garcia and Zangwill, 1981). The nonidealities are now imposed step-by-step as  $t$  varies from zero to one, and this is the advantage of such methods over the other homotopies (Vickery et al., 1986).

#### Application to Separation Problems

As discussed in Section 6.1, initial estimates for independent variables are obtained by assuming the liquid and vapor phases to be ideal. This is the starting point. The desired point is a solution for independent variables which accounts for nonidealities in the liquid and vapor phases. In this work, the nonidealities are accounted for by the SRK equation of state.

The common approach is to impose nonideal conditions into Equations 3.6 through 3.8, right after the initial

estimates are obtained. Using this approach, it may be difficult or impossible to obtain convergence for some problems. To overcome this difficulty a homotopy, or path, is defined from ideal to nonideal conditions.

Homotopies for equilibrium constants and enthalpies are defined as follows.

$$\ln K_i = (1-t) \ln \frac{P_i^S}{P} + t \ln \frac{\phi_i^L}{\phi_i^V} \quad (6.16)$$

$$h = (1-t) \sum x_i (H_i^O - \Delta H_i^V) + t (\sum x_i H_i^O + \Omega^L) \quad (6.17)$$

$$H = (1-t) \sum y_i H_i^O + t (\sum y_i H_i^O + \Omega^V) \quad (6.18)$$

The homotopy parameter,  $t$ , varies from 0 to 1. At  $t = 0$ , Equations 6.16 through 6.18 reduce to

$$\ln K_i = \ln \frac{P_i^S}{P} \quad \text{or} \quad K_i = \frac{P_i^S}{P} \quad (6.19)$$

$$h = \sum x_i (H_i^O - \Delta H_i^V) \quad (6.20)$$

$$H = \sum y_i H_i^O \quad (6.21)$$

As discussed in Section 6.1, initial estimates for the independent variables are obtained by substituting these expressions into Equations 3.6 through 3.8. This is the starting point.

At  $t = 1$ , Equations 6.16 through 6.18 reduce to

$$\ln K_i = \ln \frac{\phi_i^L}{\frac{\phi_i}{V}} \quad \text{or} \quad K_i = \frac{\phi_i^L}{\frac{\phi_i}{V}} \quad (6.22)$$

$$h = \sum_i x_i H_i^O + \Omega^L \quad (6.23)$$

$$H = \sum_i y_i H_i^O + \Omega^V \quad (6.24)$$

As discussed in Chapter IV, these expressions are to be substituted into Equations 3.6 through 3.8 to solve for the independent variables. This is the desired point.

Equations 6.16 through 6.18 define a path from ideal to nonideal conditions as  $t$  varies from 0 to 1. The thermodynamic equilibrium constants and enthalpies range from ideal values, at  $t = 0$ , to nonideal values, at  $t = 1$ . The solutions for independent variables obtained also follow the path and vary from initial estimates, at  $t = 0$ , to the desired solution, at  $t = 1$ .

Following Equations 6.16 through 6.18, thermodynamic

derivative properties,  $\partial K_i/\partial x_i$ ,  $\partial K_i/\partial T$ ,  $\partial h/\partial T$ , and  $\partial H/\partial T$ , are modified as follows.

$$\frac{\partial K_i}{\partial x_i} = t K_i \left( \frac{\phi_i^L}{\phi_i^V} \right)^{-1} \frac{\partial}{\partial x_i} \left( \frac{\phi_i^L}{\phi_i^V} \right) \quad (6.25)$$

$$\frac{\partial K_i}{\partial T} = t K_i \left( \frac{\phi_i^L}{\phi_i^V} \right)^{-1} \frac{\partial}{\partial T} \left( \frac{\phi_i^L}{\phi_i^V} \right) + (1-t) K_i \frac{d \ln P_i^S}{dT} \quad (6.26)$$

where  $\ln P_i^S$  is given by Equation 6.7 and

$$\frac{d \ln P_i^S}{dT} = \frac{A_2}{(T + A_3)^2} \quad (6.27)$$

$$\frac{\partial h}{\partial T} = (1-t) \sum_i x_i \left( \frac{\partial H_i^O}{\partial T} - \frac{\partial \Delta H_i^V}{\partial T} \right) + t \left( \sum_i x_i \frac{\partial H_i^O}{\partial T} + \frac{\partial \Omega^L}{\partial T} \right) \quad (6.28)$$

$$\frac{\partial H}{\partial T} = (1-t) \sum_i y_i \frac{\partial H_i^O}{\partial T} + t \left( \sum_i y_i \frac{\partial H_i^O}{\partial T} + \frac{\partial \Omega^V}{\partial T} \right) \quad (6.29)$$

At  $t=1$ , the desired point, Equations 6.25 through 6.29 reduce to the expressions derived in Chapter IV.

The homotopy parameter,  $t$ , ranges from 0 to 1.



Increment by which  $t$  is increased depends on the difficulty of the problem. Convergence criteria are relaxed at intermediate iterations. One iteration was performed at  $t = 0$ , and at other values of  $t$  the convergence tolerance  $\epsilon$ , in Equation 3.48, was set to  $\epsilon_0/t^7$ .

The method used in this work to define a path is referred to as continuation by iteration. A path can also be generated by a method described below.

Differentiating Equation 6.15 with respect to  $t$  yields

$$\frac{dx}{dt} = - H'_x H'_t \quad (6.30)$$

From  $x(0) = x^0$ , Equation 6.30 can be integrated to obtain  $x(1) = x^*$  (Bhargava et al., 1984; Vickery et al., 1986). This method is referred to as continuation by integration. Using the matrix manipulation technique presented in this work, it is difficult to use continuation by integration.

## CHAPTER VII

### RESULTS AND DISCUSSION

Column oriented algorithms have been developed to simulate multistage multicomponent separation processes. The homotopy, or path following, method has been used to solve difficult problems. Using this procedure, convergence has been obtained to problems which were otherwise difficult to converge, and in some cases the convergence has been accelerated. A number of test problems have been solved, and the results to a few of these problems are discussed in this chapter.

#### Column Oriented Algorithms

The storage structure of Fortran, and the advantages of column oriented algorithms over row oriented algorithms are discussed in Chapter V. These two algorithms are compared on a VAX 11/780 computer, at Oklahoma State University, to solve a 40x40 linear system.

Table III shows the computation times (CPU times), and page faults to solve a 40x40 linear system by Gaussian elimination method (Golub and Van Loan, 1985). The results show that the column oriented algorithms run

TABLE III  
 A COMPARISON OF CPU TIMES (SEC.), AND  
 PAGE FAULTS TO SOLVE A 40x40 LINEAR  
 SYSTEM BY GAUSSIAN ELIMINATION,  
 ON A VAX 11/780

| Run no. | Row Oriented Algorithm |             | Run no. | Column Oriented Algorithm |             |
|---------|------------------------|-------------|---------|---------------------------|-------------|
|         | Time                   | Page Faults |         | Time                      | Page Faults |
| 1       | 4.17                   | 492         | 2       | 4.09                      | 474         |
| 3       | 4.18                   | 496         | 4       | 4.08                      | 472         |
| 5       | 4.12                   | 492         | 6       | 4.08                      | 472         |
| 7       | 4.12                   | 494         | 8       | 4.05                      | 472         |
| 9       | 4.17                   | 497         | 10      | 4.07                      | 475         |
| Average | 4.15                   | 495         | Average | 4.07                      | 473         |

faster than the row oriented algorithms, and produce a reduction in the number of page faults. These results support the discussion in Chapter V.

The savings in computation time is about 2 percent, and the reduction in page faults is about 5 percent, for solving a 40x40 linear system by Gaussian elimination. Moler (1972) has reported a savings in computation time of about 7 percent, and a reduction in elapsed time, primarily due to decrease in page faults, of about 32 percent for solving a 200x200 linear system, by Gaussian elimination, on a IBM 360/67. These savings will increase as the number of matrix operations increases, and in particular the savings in page faults will increase rapidly.

Moler (1972) has reported that William Jones at NASA Ames Laboratory has obtained a higher savings in computation time by using column oriented algorithms, but has not reported how much higher. Dongarra (1986) has reported that at Argonne National Laboratory they have increased the efficiency of their programs by using column oriented algorithms. He has not quantified their results.

Given a matrix of size  $N_s \times N_s$ , the number of flops needed to perform Gaussian elimination is approximately  $N_s^3/3$ . A flop is defined as the effort of doing a floating point add, a floating point multiply, and a little subscripting (Golub and Van Loan, 1985).

A large number of matrix equations are to be solved in simulating a multistage multicomponent separation process, and the procedure to solve these equations are discussed in Chapters 3 and 5. The major calculation steps, involving matrices, are Equations 3.39, 3.40, 5.3, and 5.5. In these equations, there are  $N_s \times N_s$  matrix elements in the inverse matrices  $\bar{A}_i$  and  $\bar{E}_i$ , and about  $2N_s$  matrix elements in the matrices  $\bar{B}_i$ ,  $\bar{C}_i$ , and  $\bar{F}$ . In Equation 5.5, the matrix to be solved is of size  $2N_s \times 2N_s$ .

The number of flops needed to solve these equations are:  $(5N_s^2)N_c$  for Equation 3.39,  $(2N_s^2 + N_s)N_c$  for Equation 3.40,  $3N_s^2$  for Equation 5.3, about  $3N_s^3$  for Equation 5.5, and  $(3N_s^2)N_c$  to calculate  $\Delta x_i$  from Equation 3.39. In these equations  $N_s$  is the number of stages, and  $N_c$  is the number of components. The total number of flops needed are about  $(10N_s^2N_c + 3N_s^3 + N_s(N_c) + 3N_s^2)$ . It is important to note that these many flops are needed for each iteration.

A computer program has been developed to simulate multicomponent multistage separation processes, using the procedure discussed in Chapters 3-6. The program is written so that there are no limitations on the number of stages, and the number of components that can be handled. The program has been tested on a VAX 11/780 computer, at Oklahoma State University, on a number of problems. Out of these, a few of them are discussed in this chapter. As

discussed in Chapter 4, the SRK equation of state is used to estimate the thermodynamic properties. However, the program is not tied to this equation of state and another thermodynamic solving routine can be easily substituted.

The computation times from this work are compared to that of Shah and Bishnoi (1978). They took the program developed by Ishii and Otto (1973) and modified it to be able to use an equation of state to estimate the thermodynamic properties. The matrix manipulation technique suggested by Ishii and Otto (1973) is efficient, and the technique is applied in this work.

#### Test Problem 1

The feed component flow rates for Test Problem 1 is given in Table IV. This is an absorption problem from Shah et al. (1978). The column consists of 20 stages; there are a total of 14 components, and the operating pressure is 55.16 atm. Feed and lean oil are supplied at 55.16 atm., and at a temperature of 255.2 K and 256.8 K, respectively. Initial estimates for the independent variables that were used in this work are given in Table V.

The computation times (CPU times) to obtain a converged solution to this problem are shown in Figure 2. The homotopy method, discussed in Chapter VI, was not used for Test Problem 1. Using the present procedure, a

TABLE IV  
 FEED COMPONENT FLOW RATES FOR  
 TEST PROBLEM 1 (MOLES/HR.)

| Components      | Feed    | Lean Oil |
|-----------------|---------|----------|
| CO <sub>2</sub> | 0.4703  | 0.0000   |
| N <sub>2</sub>  | 0.1822  | 0.0000   |
| C <sub>1</sub>  | 88.7000 | 0.0000   |
| C <sub>2</sub>  | 6.6747  | 0.0000   |
| C <sub>3</sub>  | 2.7786  | 0.0015   |
| iC <sub>4</sub> | 0.6375  | 0.0006   |
| nC <sub>4</sub> | 0.3655  | 0.0013   |
| iC <sub>5</sub> | 0.1158  | 0.0067   |
| nC <sub>5</sub> | 0.0505  | 0.0061   |
| C <sub>6</sub>  | 0.0146  | 0.1495   |
| C <sub>7</sub>  | 0.0081  | 0.5736   |
| C <sub>8</sub>  | 0.0020  | 1.8214   |
| C <sub>9</sub>  | 0.0000  | 1.6866   |
| C <sub>10</sub> | 0.0000  | 2.0619   |

Feed flow rate = 100 moles/hr.

Lean oil flow rate = 6.3092 moles/hr.

TABLE V  
INITIAL ESTIMATES OF INDEPENDENT  
VARIABLES FOR TEST PROBLEM 1

| Stage<br>Number | Temperature<br>(K) | Liquid<br>Flow Rate | Vapor<br>Flow Rate |
|-----------------|--------------------|---------------------|--------------------|
| 1               | 256.8              | 6.3092              | 100                |
| 2               | 256.9              | 6.3092              | 100                |
| 3               | 257.0              | 6.3092              | 100                |
| 4               | 257.1              | 6.3092              | 100                |
| 5               | 257.2              | 6.3092              | 100                |
| 6               | 257.3              | 6.3092              | 100                |
| 7               | 257.4              | 6.3092              | 100                |
| 8               | 257.5              | 6.3092              | 100                |
| 9               | 257.6              | 6.3092              | 100                |
| 10              | 257.7              | 6.3092              | 100                |
| 11              | 257.8              | 6.3092              | 100                |
| 12              | 257.9              | 6.3092              | 100                |
| 13              | 258.0              | 6.3092              | 100                |
| 14              | 258.1              | 6.3092              | 100                |
| 15              | 258.2              | 6.3092              | 100                |
| 16              | 258.3              | 6.3092              | 100                |
| 17              | 258.4              | 6.3092              | 100                |
| 18              | 258.5              | 6.3092              | 100                |
| 19              | 258.6              | 6.3092              | 100                |
| 20              | 258.7              | 6.3092              | 100                |



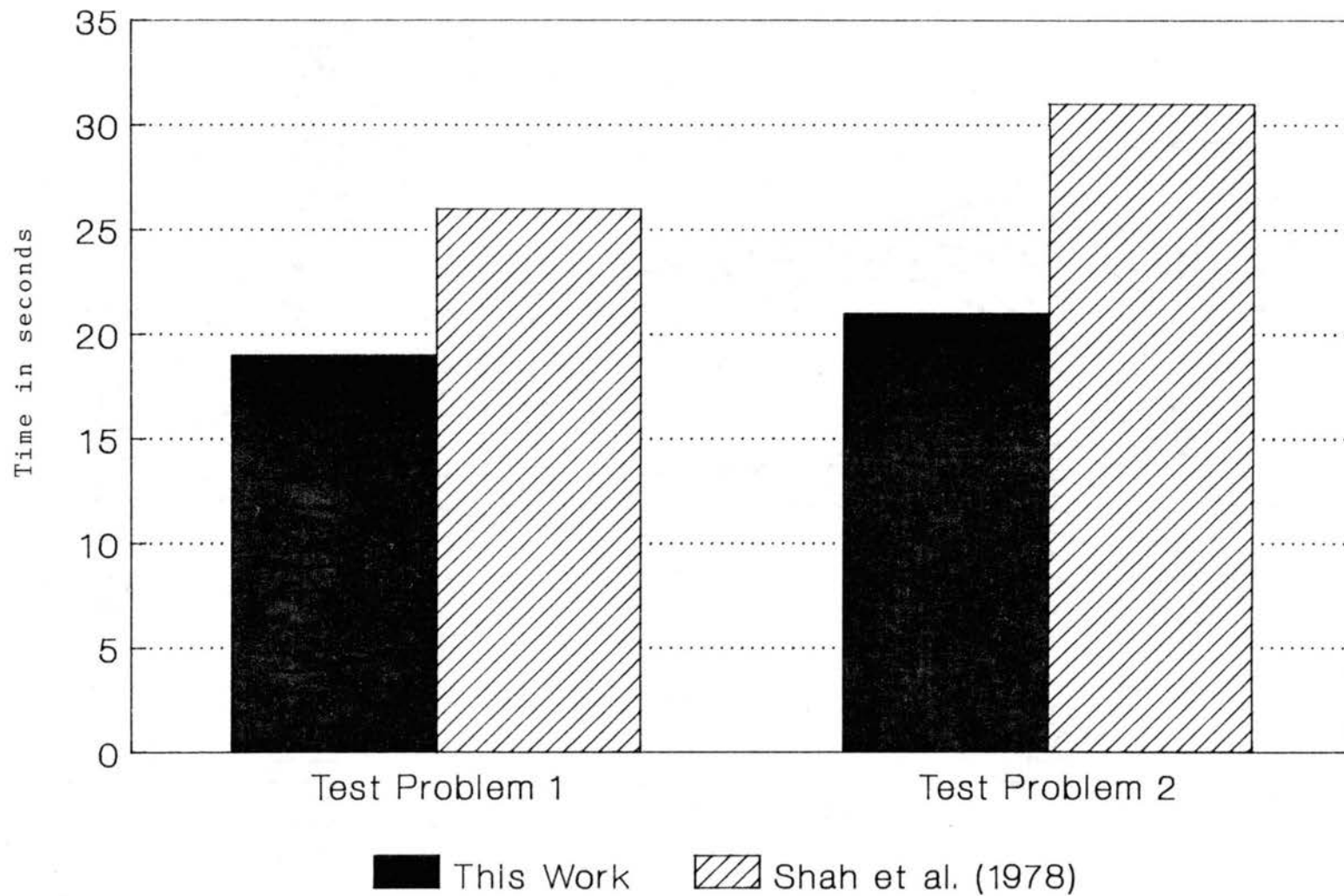


Figure 2: A Comparison of CPU Times

computation time of about 19 sec is needed to obtain a converged solution to this problem, in 6 iterations.

Shah et al. (1978) have reported a computation time of 26 sec (VAX 11/780 equivalent) (Dongarra, 1987; Nelson, 1987) to solve this problem, in 6 iterations.

The converged top and bottom product compositions are given in Table VI, along with those of Shah et al. The  $N_2$  composition reported by Shah et al., in the bottom product, is in error. Most likely this is a typographical error. Otherwise the results are in good agreement, and the present model is computationally efficient.

#### Temperature Profile

In absorbers, the temperature increases downward in the column due to the release of heat of absorption by the phase change of components in passing from gas to liquid. The heat release increases the sensible heat of the liquid stream. If there is a competing cooling effect by the transfer of components from liquid to gas, then the temperature decreases downward in the column after producing a maximum.

The converged temperature profile for Test Problem 1 is shown in Figure 3. Proceeding from top to bottom, the profile shows an increase in temperature and then a decrease. The decrease is sharpest in the middle of the column. The temperature profile is in accordance with the

TABLE VI  
 TOP AND BOTTOM PRODUCT FLOW RATES  
 FOR TEST PROBLEM 1 (MOLES/HR.)

| Component       | Top Product |             | Bottom Product |             |
|-----------------|-------------|-------------|----------------|-------------|
|                 | This Work   | Shah et al. | This Work      | Shah et al. |
| CO <sub>2</sub> | 0.4039      | 0.3981      | 0.0664         | 0.0722      |
| N <sub>2</sub>  | 0.1786      | 0.1784      | 0.0036         | 0.0638      |
| C <sub>1</sub>  | 83.0400     | 82.8760     | 5.6600         | 5.8240      |
| C <sub>2</sub>  | 4.5210      | 4.4802      | 2.1535         | 2.1945      |
| C <sub>3</sub>  | 0.3861      | 0.3361      | 2.3939         | 2.4140      |
| iC <sub>4</sub> | 0.0004      | 0.0004      | 0.6376         | 0.6377      |
| nC <sub>4</sub> | 0.0006      | 0.0006      | 0.3661         | 0.3662      |
| iC <sub>5</sub> | 0.0014      | 0.0015      | 0.1210         | 0.1210      |
| nC <sub>5</sub> | 0.0010      | 0.0010      | 0.0556         | 0.0556      |
| C <sub>6</sub>  | 0.0078      | 0.0083      | 0.1562         | 0.1558      |
| C <sub>7</sub>  | 0.0094      | 0.0111      | 0.5722         | 0.5706      |
| C <sub>8</sub>  | 0.0100      | 0.0122      | 1.8128         | 1.8113      |
| C <sub>9</sub>  | 0.0030      | 0.0041      | 1.6836         | 1.6825      |
| C <sub>10</sub> | 0.0012      | 0.0018      | 2.0607         | 2.0601      |

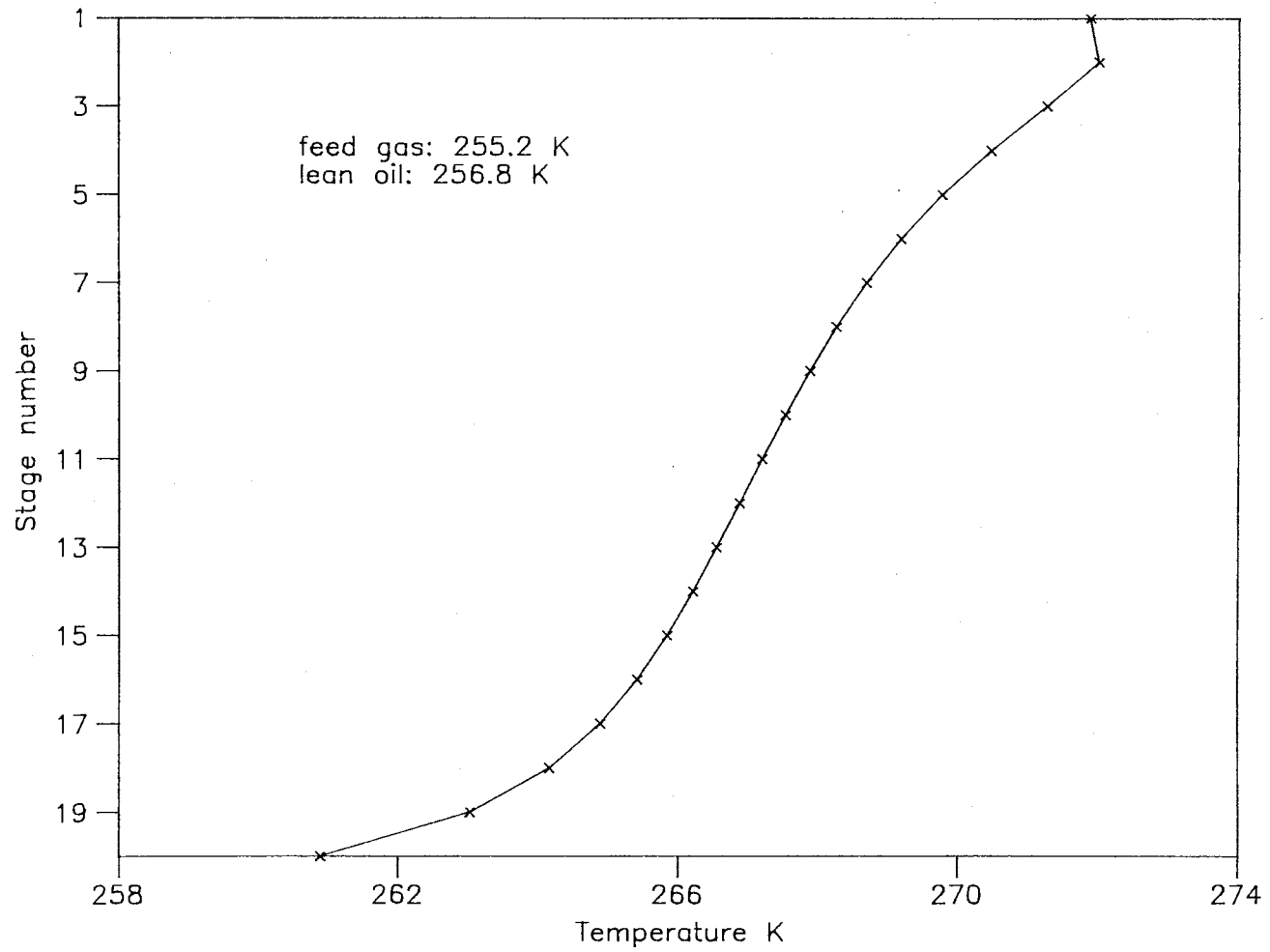


FIGURE 3: Converged Temperature Profile for Test Problem 1

converged composition profiles shown in Figures 4-8.

### Composition Profiles

Figures 4-6 show converged  $C_1$ ,  $C_2$ , and  $C_3$  flow rate profiles in vapor. These are the three components whose mass transfer takes place only from gas to liquid. Whereas the mass transfer of  $C_8$ ,  $C_9$ , and  $C_{10}$  takes place only from liquid to gas. Figures 4-5 show that the absorption of  $C_1$  and  $C_2$  takes place exclusively at the top stage. This is where the lean oil comes in contact with the feed for the first time. Figure 6 shows that  $C_3$  is absorbed throughout the column, but mainly at the two terminal stages.

The mass transfer of  $iC_4$ ,  $nC_4$ ,  $iC_5$ ,  $nC_5$ ,  $C_6$ , and  $C_7$  takes place in both directions, gas to liquid and liquid to gas. Figure 7 shows converged  $iC_5$  and  $nC_5$  flow rate profiles in liquid. These components are absorbed from gas to liquid in the bottom three stages, when the feed first comes in contact with the lean oil. In stages sixteen and above, a small percentage of these components are transferred from liquid to gas. This is due to the changes in temperature and compositions in the column.

The equilibrium concentration of a component in liquid is given by  $x_i = y_i/K_i$ . Going up in the column, the temperature is increasing which tends to make  $K_i$  higher. When the feed first comes in contact with the

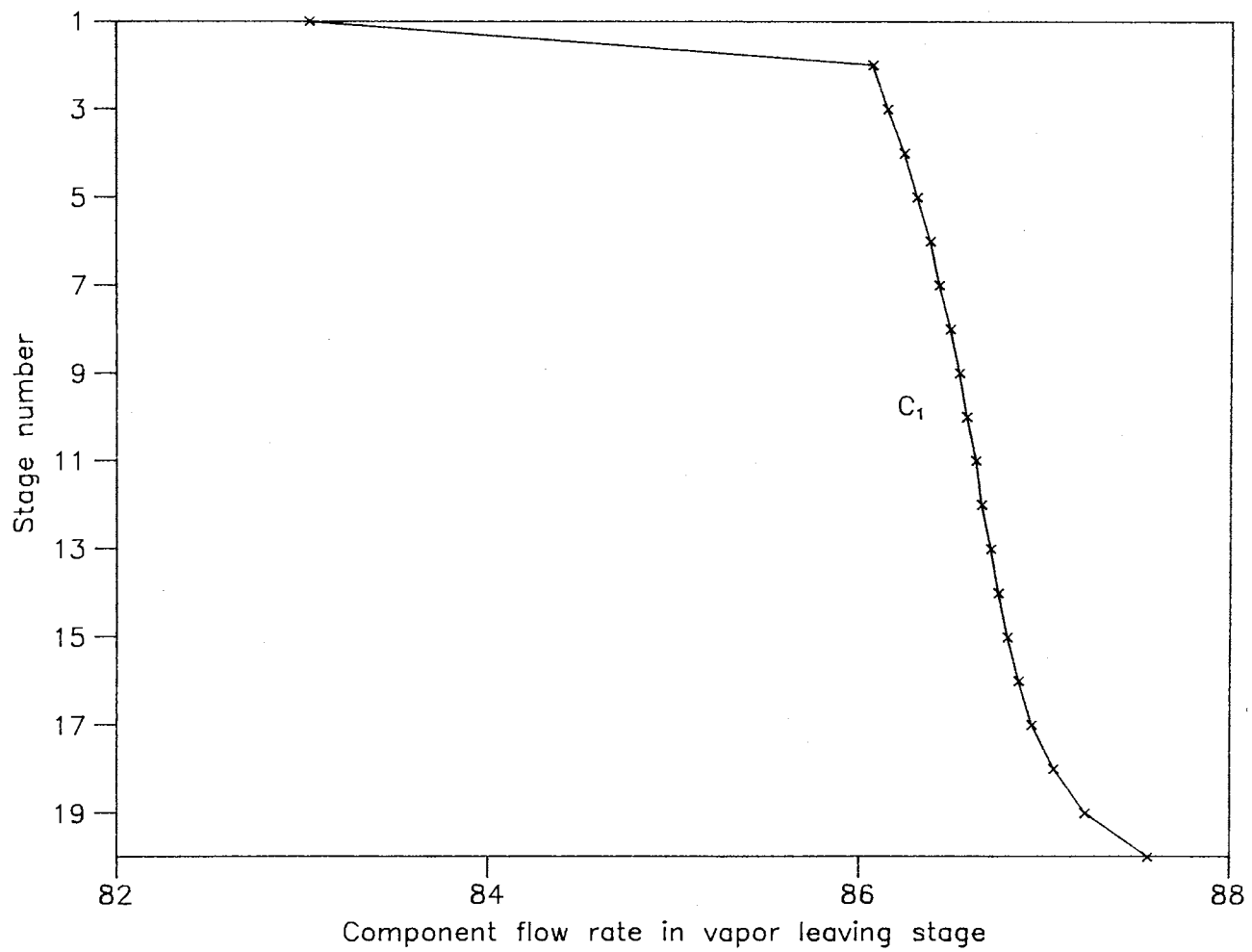


Figure 4: Converged  $C_1$  Profile in Vapor for Test Problem 1

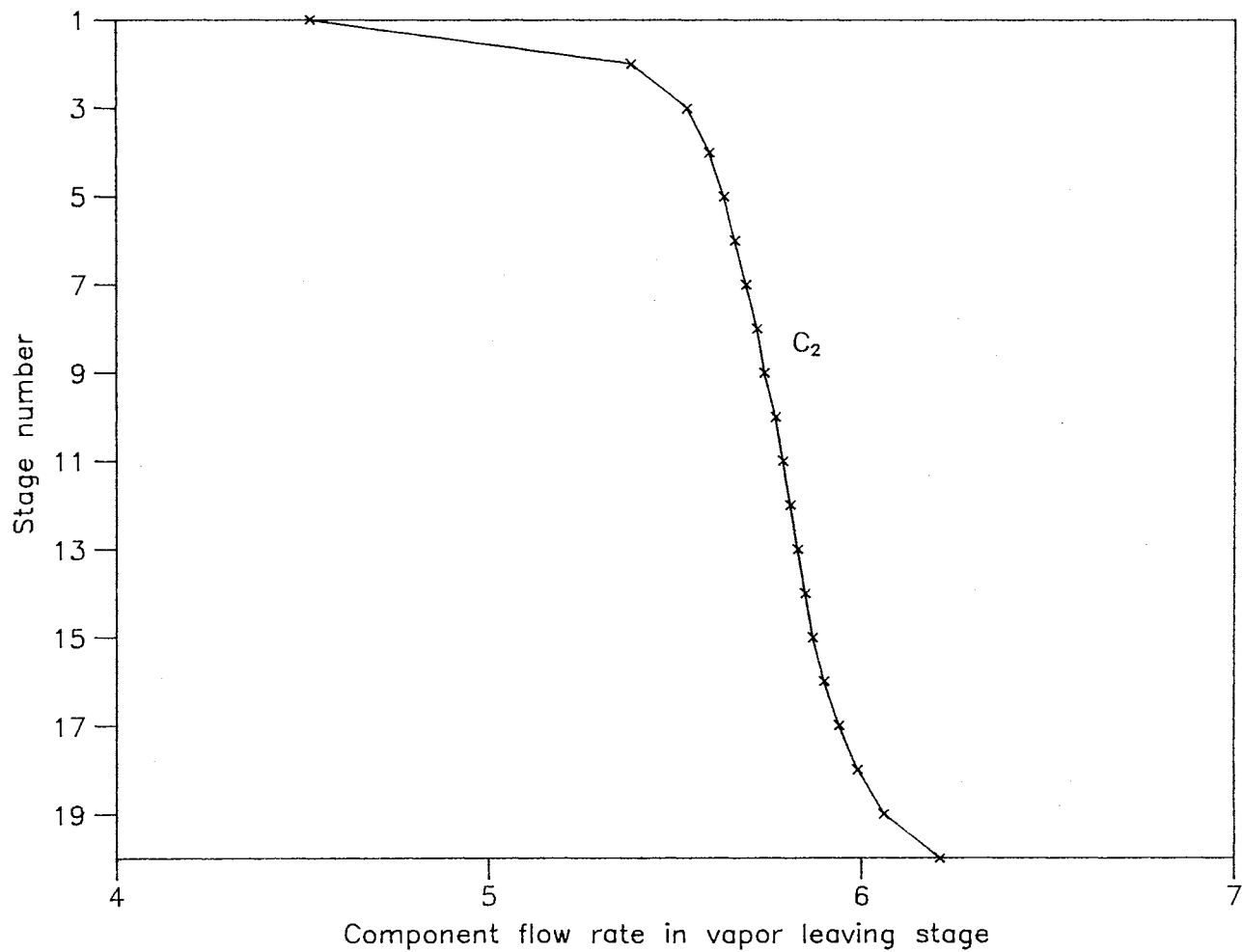


Figure 5: Converged  $C_2$  Profile in Vapor for Test Problem 1

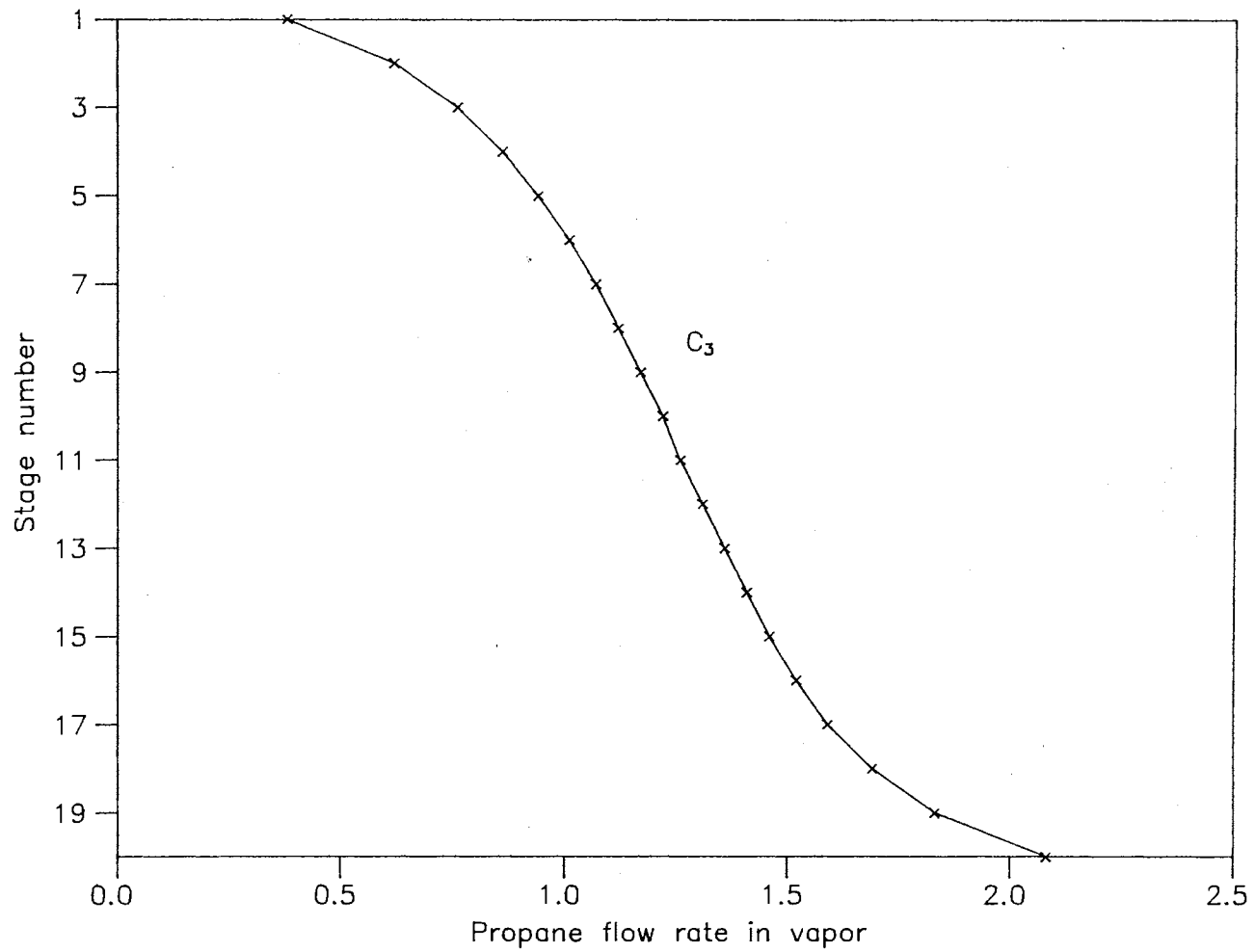


Figure 6: Converged C<sub>3</sub> Profile in Vapor for Test Problem 1



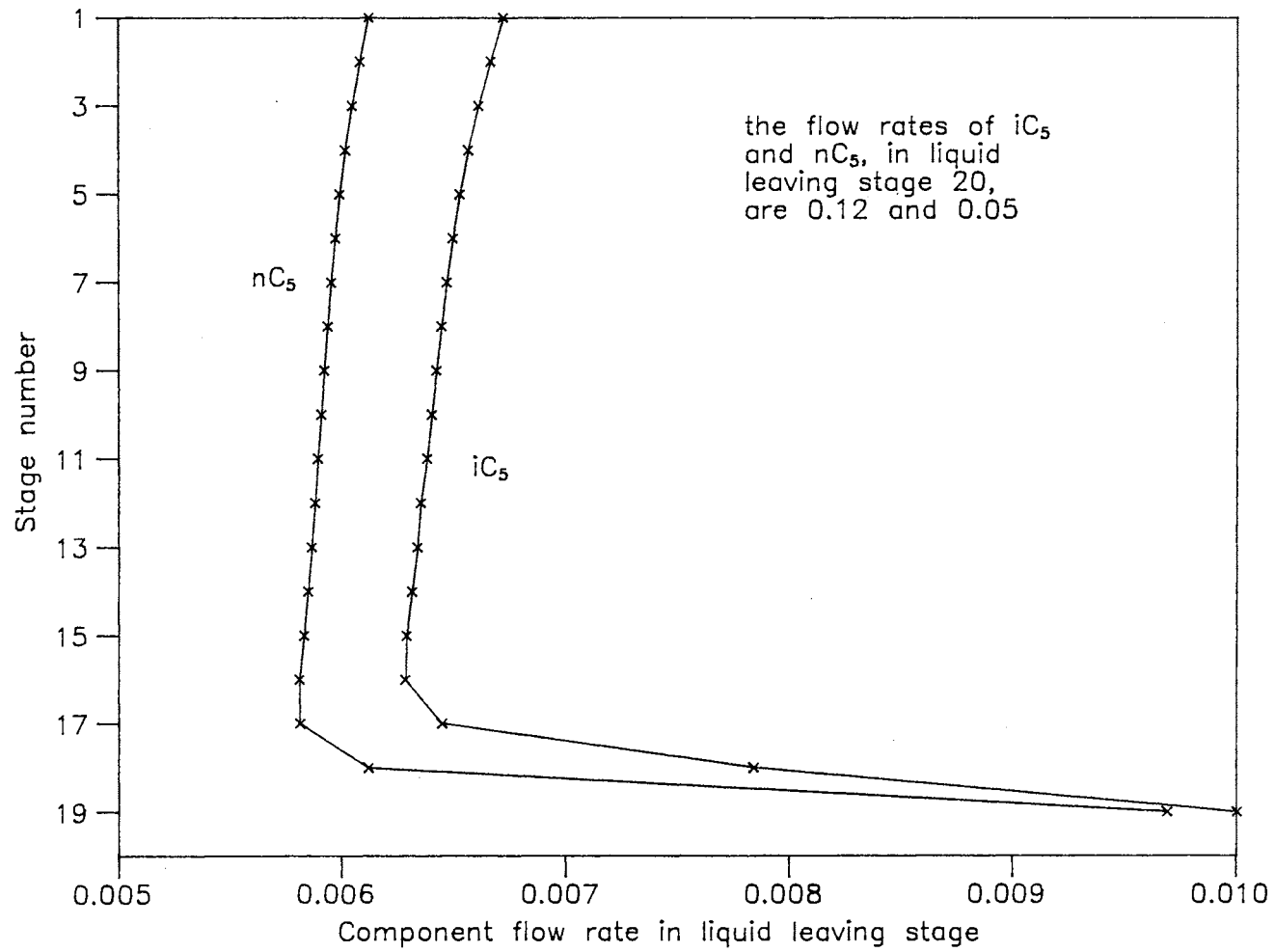


Figure 7: Converged  $C_5$  Profiles in Liquid for Test Problem 1

lean oil, the concentration of  $iC_5$  and  $nC_5$  are high in vapor to favor the mass transfer from gas to liquid. As the gas flows upward, the concentration of  $iC_5$  and  $nC_5$  in vapor are decreasing and coupled with the increasing  $K_i$ , the mass transfer is favored from liquid to gas after 3 stages from the bottom.

The mass transfer of  $iC_4$  takes place from gas to liquid on stages five through twenty, and from liquid to gas on stages one through four. The mass transfer of  $nC_4$  takes place from gas to liquid on stages eleven through twenty, and from liquid to gas on stages one through ten.

The mass transfer of  $C_6$  and  $C_7$  takes place from gas to liquid on the bottom stage. This is when the feed first comes in contact with the lean oil. In the rest of the stages, the mass transfer takes place from liquid to gas.

The  $C_8$  flow rate profile in liquid is shown in Figure 8. The feed has negligible amount of  $C_8$ , and none of  $C_9$  and  $C_{10}$ . Hence the mass transfer of these components takes place in only one direction, liquid to gas. The mass transfer of  $C_9$  and  $C_{10}$  takes place exclusively on the bottom stage.

From the results it is evident that Test Problem 1 is not a simple absorber problem. Due to the presence of close boiling components, the column combines the characteristics of both distillation and simple

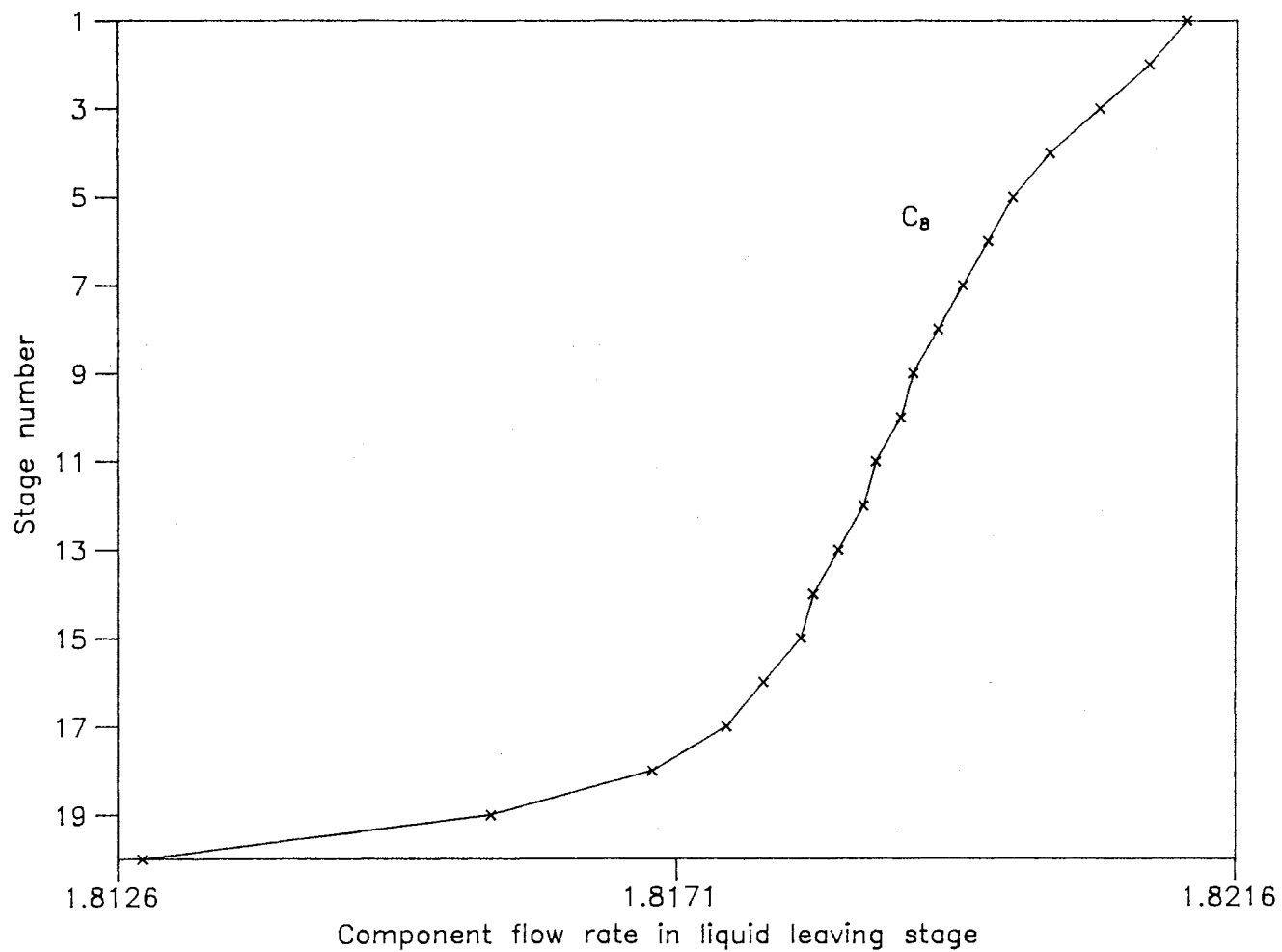


Figure 8: Converged  $C_B$  Profile in Liquid for Test Problem 1

absorption.

### Test Problem 2

The feed component flow rates for Test Problem 2 are given in Table VII. This is a distillation problem from Shah et al. (1978). The column is used as a deethaniser in an ethane recovery plant. The column consists of 18 stages, operates at 31.72 atm., and there are a total of 10 components. A bubble point feed at 31.72 atm. is fed to the 7th stage. Almost 95% of the feed is composed of ethane and propane. The column operates at a reflux ratio of 1.6 and the top product contains about 1.0% vapor. The initial temperatures are assumed to be linear between 283 K and 368 K. This is same as that of Shah et al. The initial estimates for the independent variables that were used in this work is given in Table VIII.

The computation times to obtain a converged solution to this problem are shown in Figure 2. The homotopy method, discussed in Chapter VI, was not used for Test Problem 2. Using the present procedure, a computation time of about 21 sec is needed to obtain a converged solution to this problem, in 10 iterations. Shah et al. have reported a computation time of 31 sec (VAX 11/780 equivalent) (Dongarra, 1987; Nelson, 1987) to solve this problem, in 9 iterations.

The converged top and bottom product compositions and

TABLE VII  
FEED COMPONENT FLOW RATES FOR TEST  
PROBLEMS 2 AND 2A (MOLES/HR.)

---

| Components      | Flow Rate |
|-----------------|-----------|
| CO <sub>2</sub> | 1.759     |
| N <sub>2</sub>  | 6.74E-06  |
| C <sub>1</sub>  | 1.266     |
| C <sub>2</sub>  | 80.350    |
| C <sub>3</sub>  | 13.580    |
| iC <sub>4</sub> | 0.719     |
| nC <sub>4</sub> | 1.168     |
| iC <sub>5</sub> | 0.290     |
| nC <sub>5</sub> | 0.310     |
| C <sub>7</sub>  | 0.539     |

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Feed flow rate: 100 moles/hr.

TABLE VIII  
INITIAL ESTIMATES OF INDEPENDENT  
VARIABLES FOR TEST PROBLEMS  
2 AND 2A

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| Stage<br>Number | Temperature<br>(K) | Liquid<br>Flow Rate | Vapor<br>Flow Rate |
|-----------------|--------------------|---------------------|--------------------|
| 1               | 283                | 140                 | 0.082              |
| 2               | 288                | 140                 | 222.082            |
| 3               | 293                | 140                 | 222.082            |
| 4               | 298                | 140                 | 222.082            |
| 5               | 303                | 140                 | 222.082            |
| 6               | 308                | 140                 | 222.082            |
| 7               | 313                | 240                 | 222.082            |
| 8               | 318                | 240                 | 222.082            |
| 9               | 323                | 240                 | 222.082            |
| 10              | 328                | 240                 | 222.082            |
| 11              | 333                | 240                 | 222.082            |
| 12              | 338                | 240                 | 222.082            |
| 13              | 343                | 240                 | 222.082            |
| 14              | 348                | 240                 | 222.082            |
| 15              | 353                | 240                 | 222.082            |
| 16              | 358                | 240                 | 222.082            |
| 17              | 363                | 240                 | 222.082            |
| 18              | 368                | 17.918              | 22.082             |

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heat loads from this work are given in Table IX, along with those of Shah et al (1978). The results from this work are in good agreement, and the present model is computationally efficient.

### Composition Profiles

The converged composition profiles in liquid and vapor are shown in Figures 9 and 10. The separation is being achieved primarily between ethane and propane, as shown in Table IX. These are the light and heavy keys respectively. Components heavier than propane, butane through heptane, are heavy nonkeys. Components lighter than ethane, nitrogen, carbondioxide, and methane, are light nonkeys.

The mole fraction of ethane increases upward and the mole fraction of propane increases downward. This reflects the separation between the two keys. In addition separation is also taking place between keys and nonkeys.

Heavy nonkeys,  $iC_4$  etc., have relatively constant mole fractions in the liquid and vapor below the feed stage until three or four stages from the bottom of the column. This is because the separation takes place between the heavy nonkeys and the two keys on the bottom few stages.

The heavy nonkeys increase on the bottom few stages at the expense of the light and heavy keys,  $C_2$  and  $C_3$ , and

TABLE IX  
TOP AND BOTTOM PRODUCT FLOW RATES  
FOR TEST PROBLEM 2

| Components      | Top Product |             | Bottom Product |             |
|-----------------|-------------|-------------|----------------|-------------|
|                 | This Work   | Shah et al. | This Work      | Shah et al. |
| CO <sub>2</sub> | 1.7590      | 1.7590      |                |             |
| N <sub>2</sub>  | 6.74E-06    | 6.70E-06    |                |             |
| C <sub>1</sub>  | 1.2660      | 1.2660      |                |             |
| C <sub>2</sub>  | 79.8380     | 78.9380     | 0.5167         | 1.4146      |
| C <sub>3</sub>  | 0.6497      | 0.5298      | 12.9370        | 13.0580     |
| iC <sub>4</sub> | 8.530E-04   | 6.740E-04   | 0.7181         | 0.7183      |
| nC <sub>4</sub> | 3.911E-04   | 4.493E-04   | 1.1676         | 1.1679      |
| iC <sub>5</sub> |             |             | 0.2920         | 0.2920      |
| nC <sub>5</sub> |             |             | 0.3140         | 0.3140      |
| C <sub>7</sub>  |             |             | 0.5392         | 0.5392      |

|                               | This Work | Shah et al. |
|-------------------------------|-----------|-------------|
| Condenser Load:<br>(Kcal/hr.) | 4.05E+05  | 3.94E+05    |
| Reboiler Duty:<br>(Kcal/hr.)  | 4.50E+05  | 4.23E+05    |



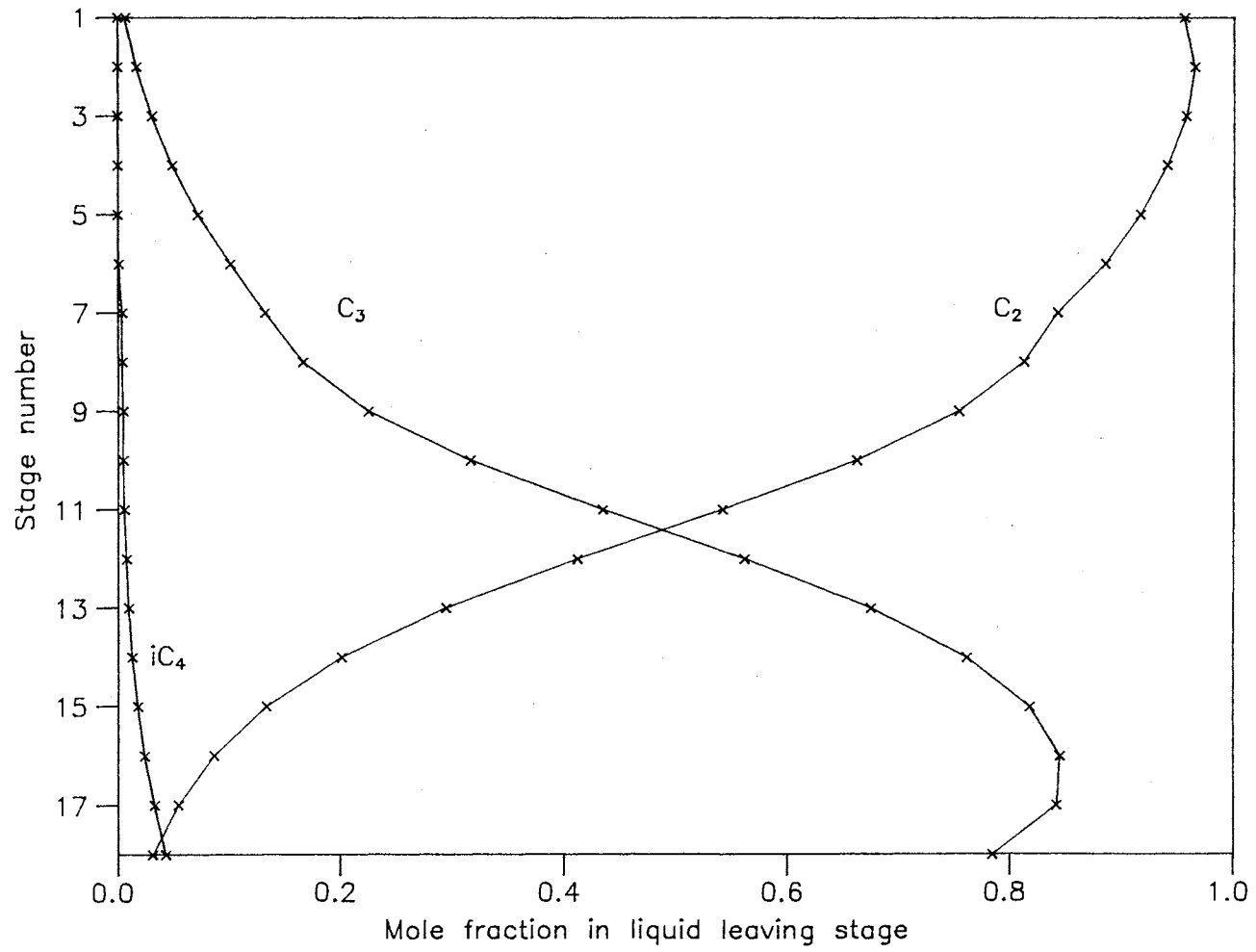


Figure 9: Converged Liquid Profile for Test Problem 2

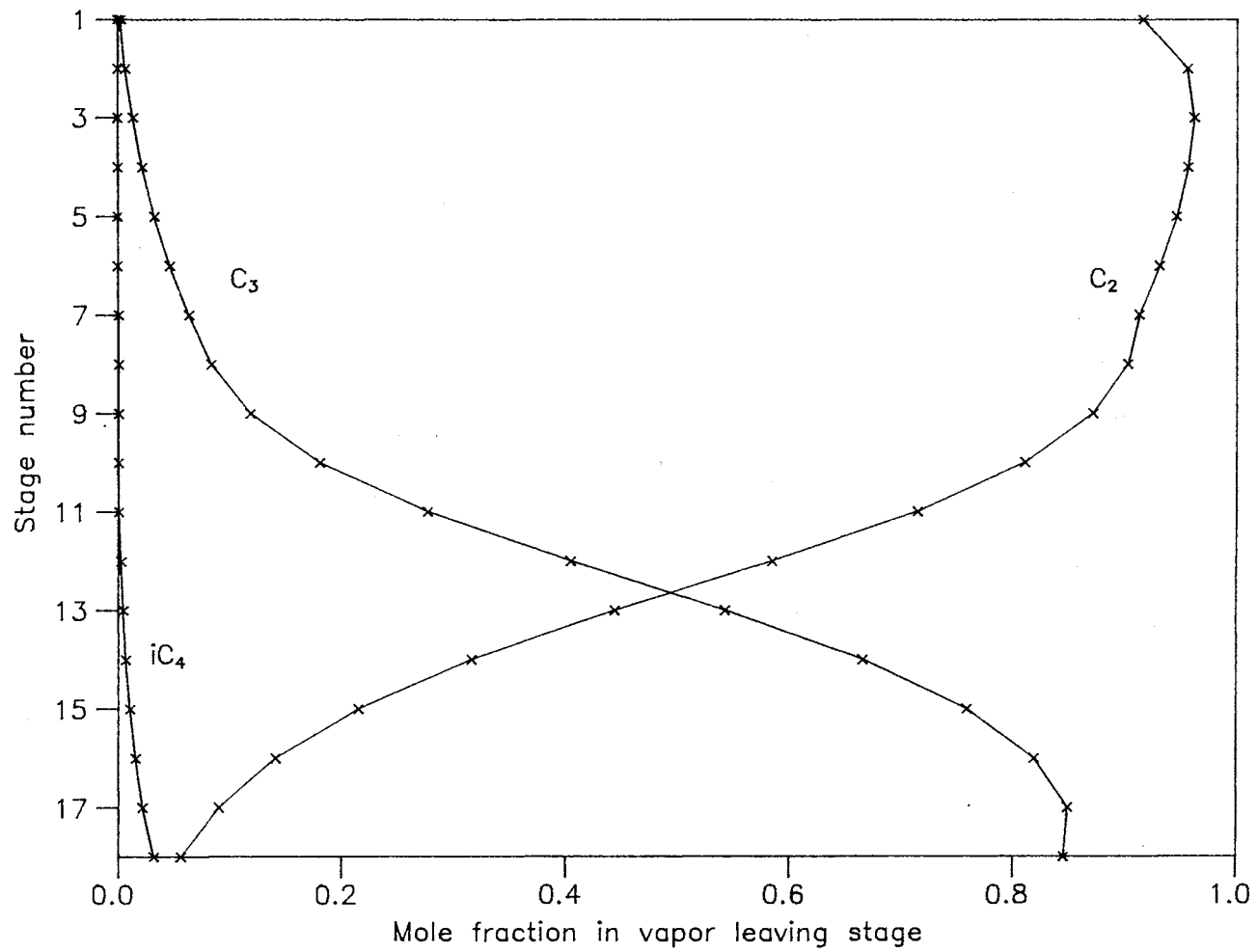


Figure 10: Converged Vapor Profile for Test Problem 2

especially the plentiful heavy key. This is the cause of maximum in propane mole fraction towards the bottom of the column.

At the very top of the column separation takes place between light nonkeys and keys. The light nonkeys increase on the top few stages at the expense of the light and heavy keys,  $C_2$  and  $C_3$ , and especially the plentiful light key. This is the cause of maximum in ethane concentration towards the top of the column.

#### Temperature Profile

The converged temperature profile is shown in Figure 11. This shows that the temperature change is rapid at the very bottom of the column, and in the vicinity of the feed stage. These are the regions where the compositions are changing rapidly, for nonkeys in particular.

At the top, and below the feed in particular the light nonkeys are reduced rapidly in liquid. At the bottom, in particular, and also above the feed, the heavy nonkeys are reduced rapidly in vapor. Due to a very high concentration of ethane in the stages above the feed, there is only a 10 K change in temperature between the top and feed stage.

#### Sensitivity to Temperature Profile

Shah et al. (1978) have reported that the convergence

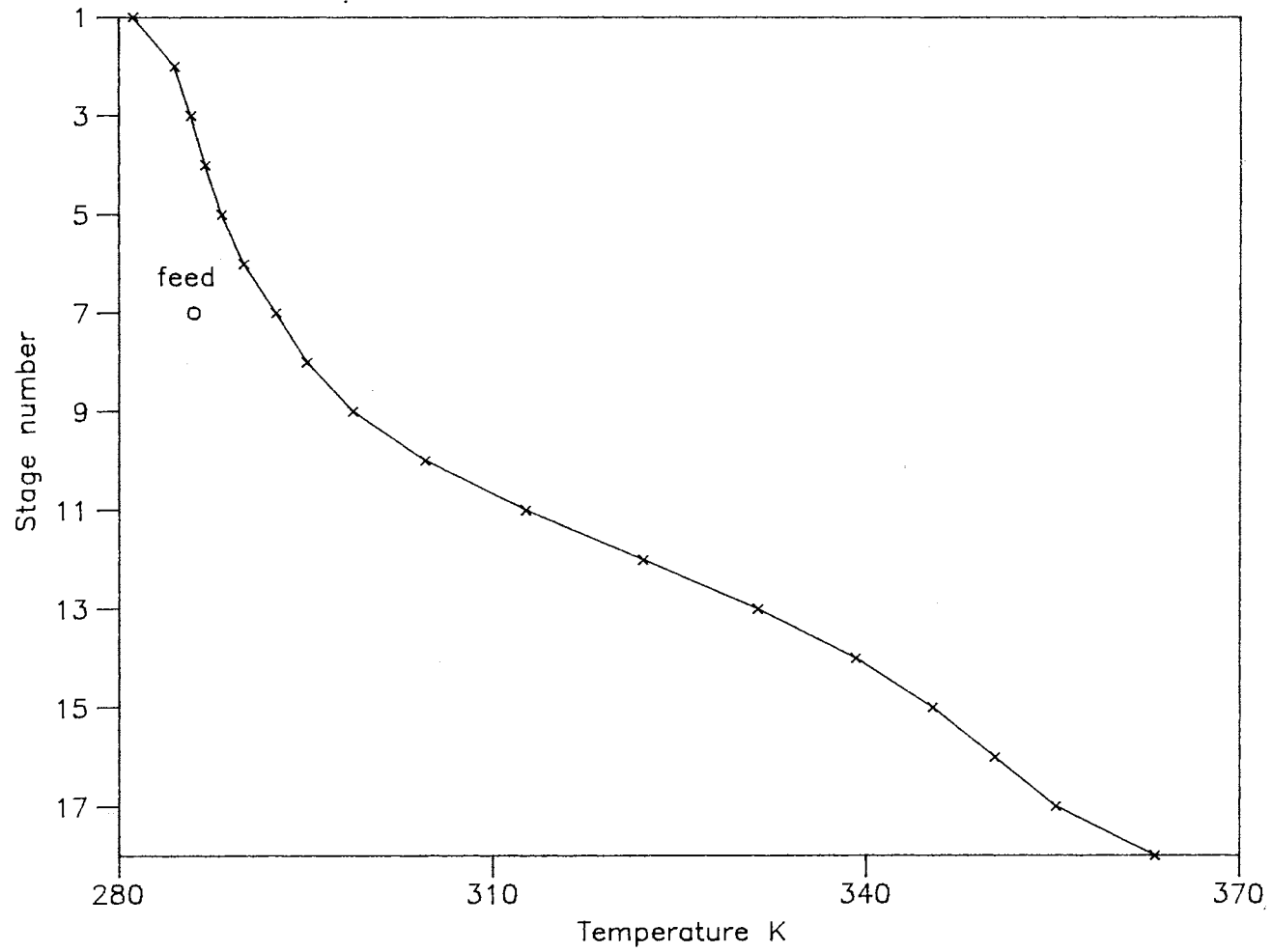


Figure 11: Converged Temperature Profile for Test Problem 2

of this problem is sensitive to temperature profiles. In the present study, the operating conditions of Problem 2 were perturbed by changing only the condenser load. This is referred to as Test Problem 2A. When the condenser load was reduced to  $4.0E+05$  Kcal/hr., convergence characteristics of the problem changed and divergence was observed. Henley and Seader (1981) have reported such sensitivity to distillate temperatures in some of their test problems.

#### Homotopy Method

The homotopy method, discussed in Chapter VI, has a stabilizing effect on Test Problem 2A, and it suppresses the divergent behavior. The function  $H(x,t)$  is used on this problem, with an increment  $\Delta t = 0.5$ . Such stabilizing effects have been reported by Bhargava et al. (1984) on some of their test problems. They also report that an increment of  $\Delta t = 0.5$  is satisfactory in producing stabilizing effects. If a  $\Delta t$  of 0.5 does not produce stabilizing effects, then smaller increments must be tried. The computation time could increase in such cases, but obtaining a converged solution becomes the major concern at this point.

It is seen from this example that the incorporation of homotopy, or path following method, makes the algorithm robust. As discussed in Chapter VI, there will be no path

and this method will fail if the Jacobian matrix becomes singular (Garcia and Zangwill, 1981; Bhargava et al., 1984, Wayburn and Seader, 1984). These are the turning points and can be overcome by perturbing the Jacobian matrix (Bhargava et al., 1984).

The converged temperature profile for Test Problem 2A is shown in Figure 12. The temperatures along the column are much higher and are reflected in the composition profiles shown in Figures 13-14. When compared with Figures 9-10, these show higher concentrations of propane, and heavier components in the vapor and liquid.

### Test Problem 3

Feed component flow rates for Test Problem 3 are shown in Table X. This is a distillation problem from Poling et al. (1981). The column consists of 16 stages and operates at 30 atm. The feed enters as 30% vapor on the 5th stage. The column has a partial condenser and the top product rate is 37.5 moles/hr.

This problem is an example of the separation of narrow boiling mixtures. It is for this problem that Poling et al. (1981) have reported a number of mixture adjustments, to avoid trivial roots in evaluating the thermodynamic properties. They have reported that this problem proved their most severe test for convergence. The initial estimates for the independent variables that

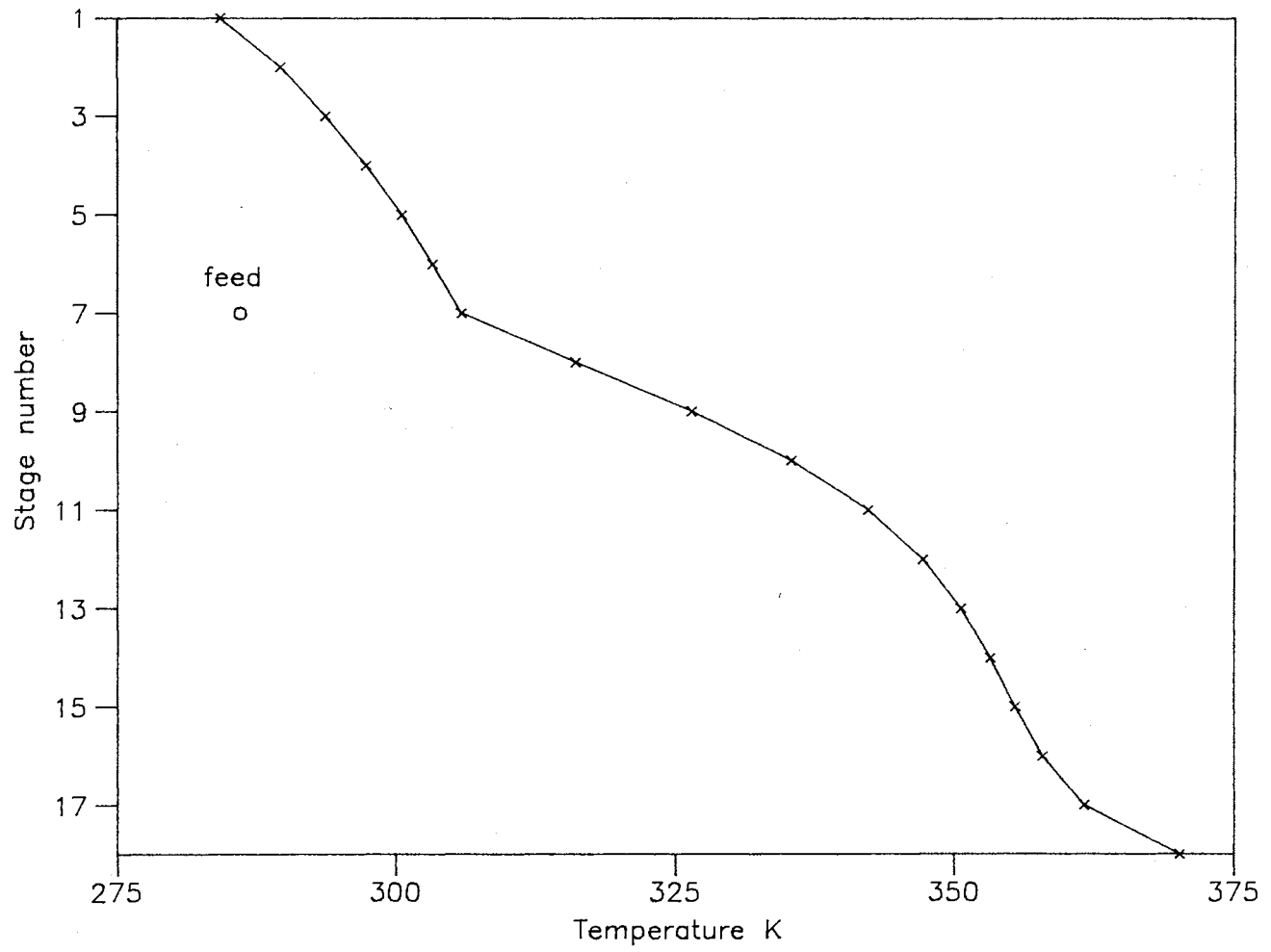


Figure 12: Converged Temperature Profile for Test Problem 2A

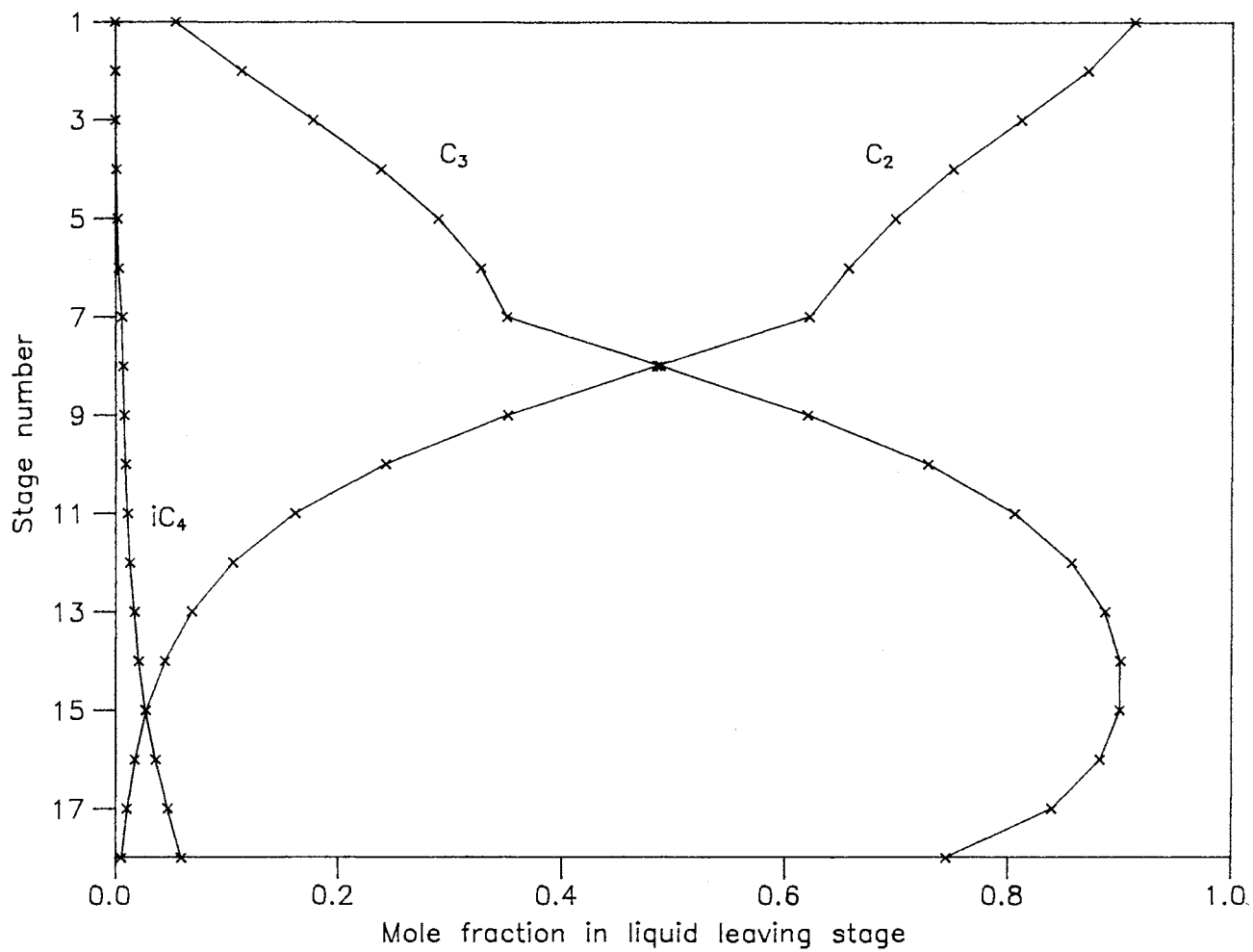


Figure 13: Converged Liquid Profile for Test Problem 2A



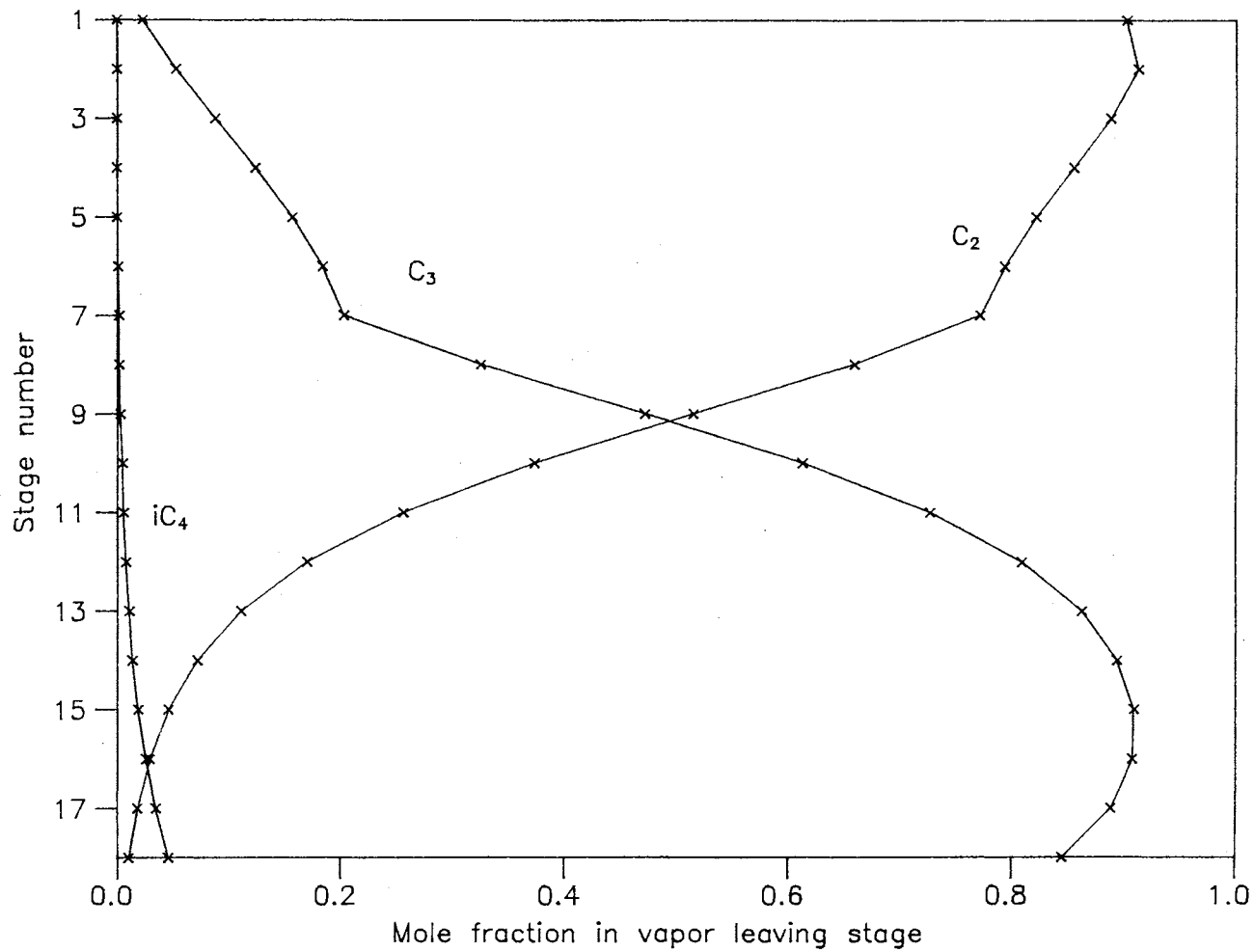


Figure 14: Converged Vapor Profile for Test Problem 2A

TABLE X  
FEED COMPONENT FLOW RATES FOR  
TEST PROBLEM 3 (MOLES/HR.)

| Component              | Flow Rate |
|------------------------|-----------|
| $\text{CH}_4$          | 36.2      |
| $\text{C}_2\text{H}_4$ | 37.4      |
| $\text{C}_2\text{H}_6$ | 9.0       |
| $\text{C}_3\text{H}_6$ | 15.7      |
| $\text{C}_3\text{H}_8$ | 1.7       |

were used in this work are given in Table XI.

### Temperature and Composition

#### Profiles

The converged temperature profile is shown in Figure 15. There are three stages below the feed stage over which the temperature change is minimal. The converged composition profiles are shown in Figures 16 and 17. The change in composition over these three stages is minimal. This is due to the presence of narrow boiling components, and the location of feed stage has no effect on the nature of the profiles.

The converged top and bottom product compositions are shown in Table XII. As can be seen from the table, all the components are present to some extent in both the top and bottom products. Poling et al. have not reported the product compositions for their computations.

#### Homotopy Method

A converged solution is obtained to this problem in about 20.7 sec, when the homotopy method is not used. Using the homotopy method, convergence is obtained in about 16.3 sec of computation time. The function  $H(x,t)$  is used, with an increment  $\Delta t$  of 0.5. The reduction in computation time is because there is no need to make the large number of mixture adjustments to avoid trivial roots

TABLE XI  
INITIAL ESTIMATES OF INDEPENDENT  
VARIABLES FOR TEST PROBLEM 3

---

| Stage<br>Number | Temperature<br>(K) | Liquid<br>Flow Rate | Vapor<br>Flow Rate |
|-----------------|--------------------|---------------------|--------------------|
| 1               | 200                | 33                  | 7.5                |
| 2               | 210                | 33                  | 70.5               |
| 3               | 215                | 33                  | 70.5               |
| 4               | 220                | 33                  | 70.5               |
| 5               | 230                | 103                 | 70.5               |
| 6               | 240                | 103                 | 40.5               |
| 7               | 250                | 103                 | 40.5               |
| 8               | 255                | 103                 | 40.5               |
| 9               | 260                | 103                 | 40.5               |
| 10              | 265                | 103                 | 40.5               |
| 11              | 270                | 103                 | 40.5               |
| 12              | 280                | 103                 | 40.5               |
| 13              | 285                | 103                 | 40.5               |
| 14              | 290                | 103                 | 40.5               |
| 15              | 295                | 103                 | 40.5               |
| 16              | 300                | 62.5                | 40.5               |

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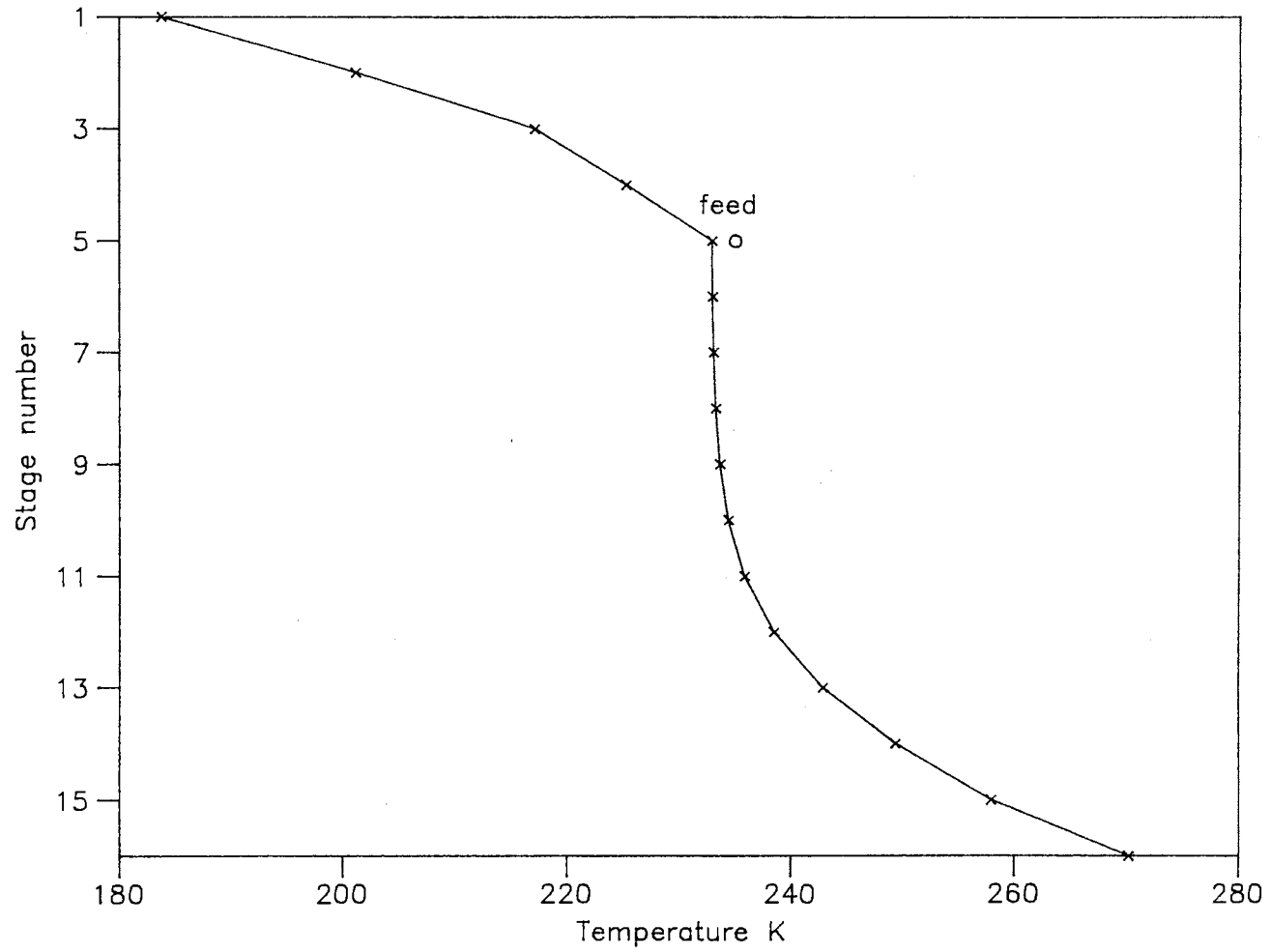


Figure 15: Converged Temperature Profile for Test Problem 3

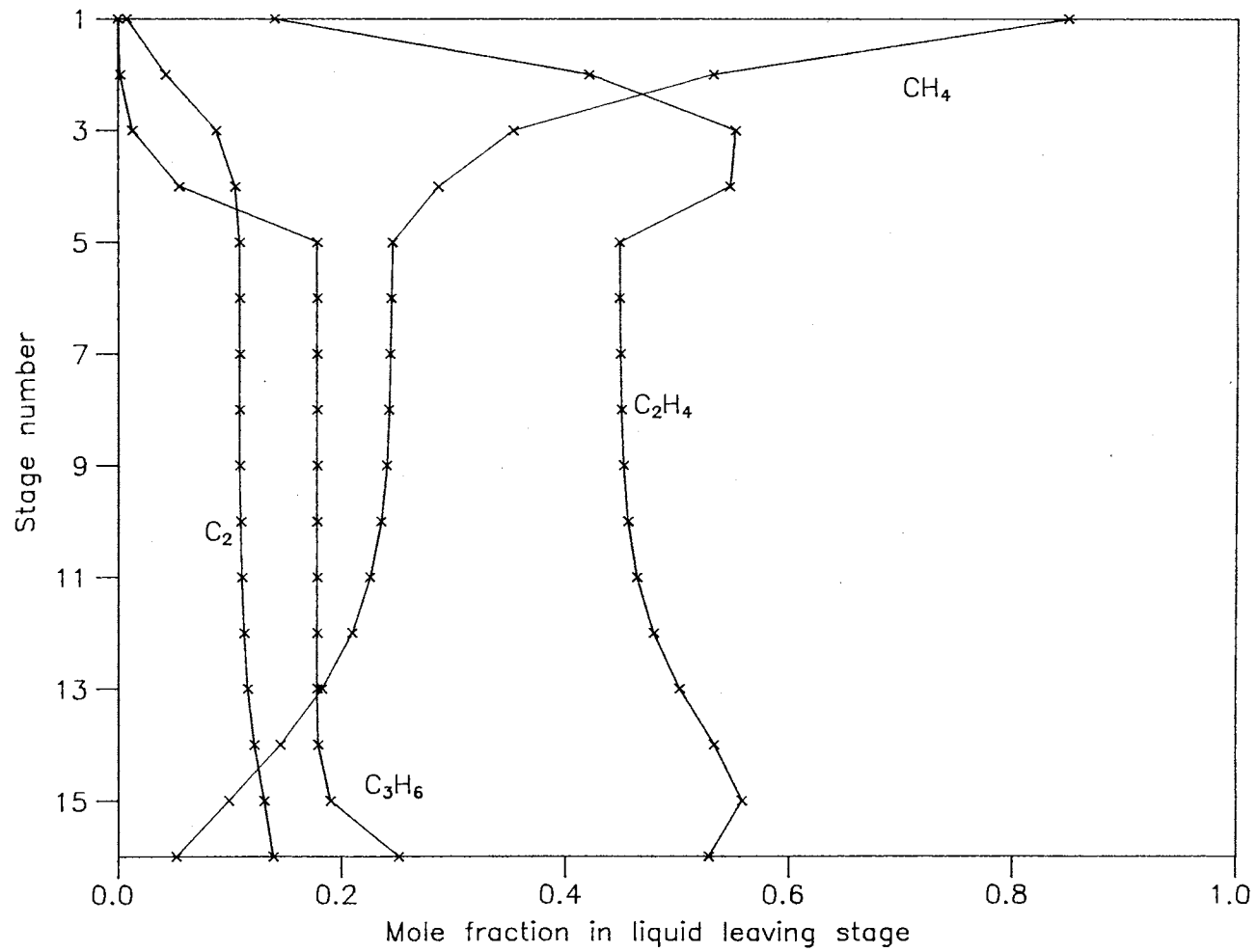


Figure 16: Converged Liquid Profile for Test Problem 3

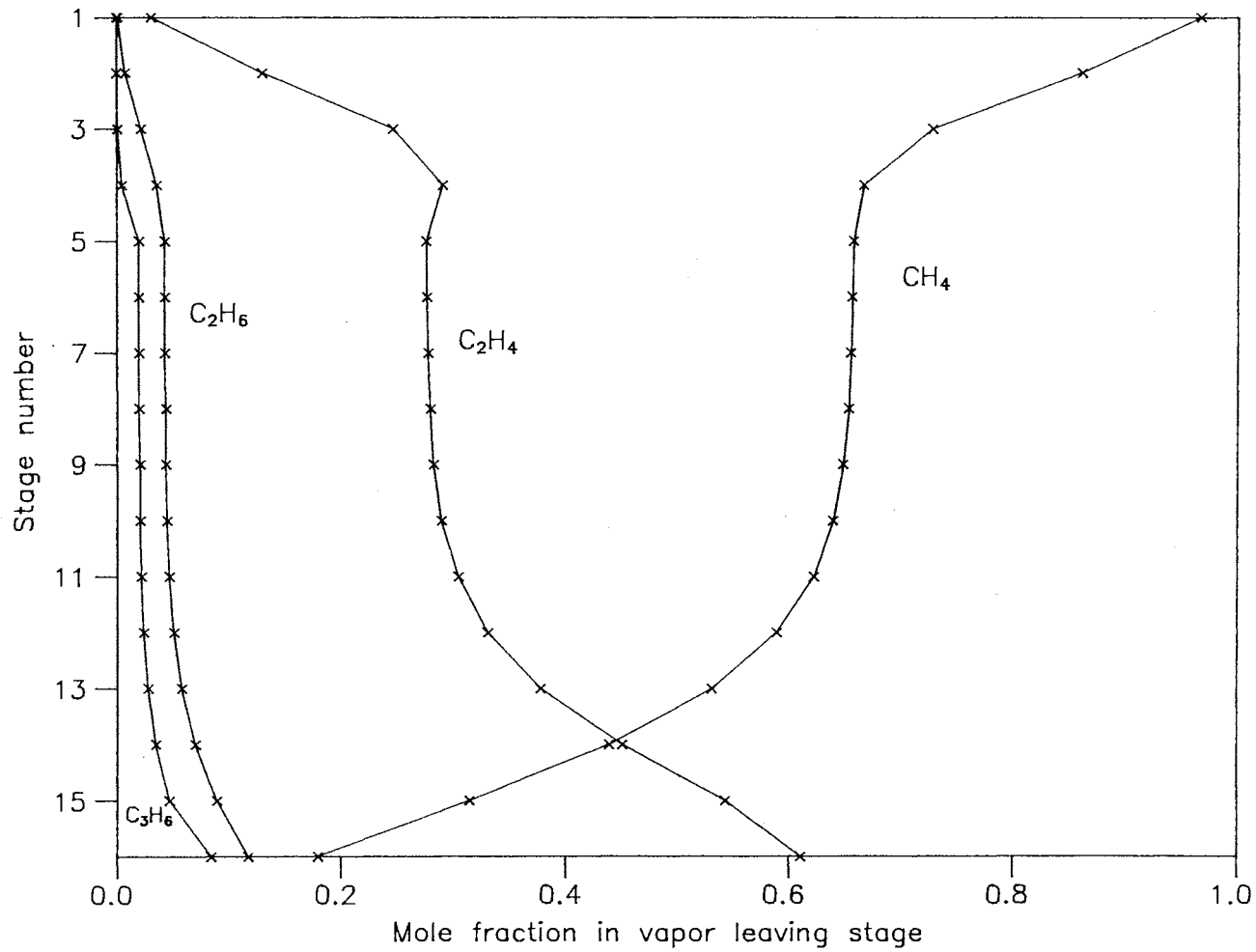


Figure 17: Converged Vapor Profile for Test Problem 3

TABLE XII  
TOP AND BOTTOM PRODUCT FLOW RATES  
FOR TEST PROBLEM 3

| Components                    | Top Product | Bottom Product |
|-------------------------------|-------------|----------------|
| CH <sub>4</sub>               | 32.9130     | 3.2974         |
| C <sub>2</sub> H <sub>4</sub> | 4.4640      | 32.9360        |
| C <sub>2</sub> H <sub>6</sub> | 0.2769      | 8.7227         |
| C <sub>3</sub> H <sub>6</sub> | 0.0035      | 15.6960        |
| C <sub>3</sub> H <sub>8</sub> | 0.00017     | 1.6998         |



(Poling et al., 1981) in evaluating the thermodynamic properties. Poling et al. have not reported the computation time for this problem.

This example illustrates how the homotopy, or path following, method can be used to accelerate the convergence on difficult problems.

## CHAPTER VIII

### CONCLUSIONS AND RECOMMENDATIONS

Simulation of multicomponent multistage separation processes involve solving a large number of nonlinear equations. These equations are solved by an iterative procedure and initial estimates of independent variables are needed. For a lack of any better information, these estimates are obtained by assuming ideal phase behavior. The major concerns in modeling these processes are computational efficiency and robustness.

Column oriented algorithms are used in this work for all matrix operations. In these methods, the matrix equations are solved column-by-column, instead of the more conventional row-by-row approach. These algorithms produce a savings in computation time and page faults in a virtual storage machine. Column oriented algorithms are recommended for all matrix operations, including addition, multiplication, and subtraction.

Convergence characteristics of problems depend on initial estimates of independent variables, and for some problems the domain of convergence becomes limited. This can be due to the specifications being a nonlinear

function of the independent variables, and/or the phase behavior of the mixture being highly nonideal. The domain of convergence of such problems is increased in this work by defining a homotopy, or path. In this method, the initial estimates are 'walked' to the final solution by following a path from ideal to nonideal thermodynamic properties.

Using the homotopy method, convergence has been obtained to difficult problems, and for some problems the convergence has been accelerated. Incorporation of homotopy has made the model robust. These classes of methods are relatively new to chemical engineering; and as more and more problems are solved, these methods will find a wider application.

As a next step, this work can be used as a basis to simulate linked columns and separation processes with chemical reactions. Extending this work to simulating linked columns involves incorporating the interconnecting streams in the material and heat balance equations. The matrix operations involved in simulating linked columns are much greater than for a single column. The computational efficiency, and reduction in page faults obtained by using column oriented algorithms will be greatly appreciated in these simulations.

Extending this work to separation processes with chemical reactions involves incorporating the generation

terms in the material and heat balance equations. A knowledge of reaction rates are needed to solve these problems.

The model developed in this work is computationally efficient, and the efficiency is obtained without sacrificing the robustness. The model is made robust by incorporating an homotopy for thermodynamic properties. The work done forms a sound basis for future work.

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## APPENDIX

### THERMODYNAMIC PROPERTIES AND DERIVATIVES FROM SRK EQUATION OF STATE

As discussed in Chapter IV, the thermodynamic properties and their derivatives are obtained from the SRK equation of state in this study. These derivatives are obtained analytically and the resulting equations are complex.

The number of mathematical operations needed to calculate these properties are reduced by efficient algebraic manipulations. The final form of the equations are given below. Some of the repeating terms are identified by a separate variable name in these equations.

#### Fugacity Coefficient

From Equations 4.1 and 4.6, the following expression is obtained for the fugacity coefficient.

$$\ln\phi_i = \left[ -\ln(Z-B) + \frac{B_i}{B}(Z-1) - \ln\left(\frac{Z+B}{Z}\right) (\text{FAC1}) \right] \quad (\text{A.1})$$

where

$$\text{FAC1} = \frac{A}{B} \left[ \frac{\sum_j x_j A_{ij}}{A} - \frac{B_i}{B} \right] \quad (\text{A.2})$$

The corresponding parameters for the liquid and vapor phases are used in these equations. The equilibrium constant,  $K_i$ , is then given by Equation 4.7.

#### Isothermal Enthalpy Departure

From Equations 4.1 and 4.12, the following expression is obtained for the isothermal enthalpy departure.

$$\Omega = RT \left[ (Z-1) - \frac{1}{B} \ln \left( \frac{Z+B}{Z} \right) (\text{FAC2}) \right] \quad (\text{A.3})$$

where

$$\text{FAC2} = \frac{P}{R^2 T^2} (a(T) - Ta'(T)) = \sum_i \sum_j x_i x_j A_{ij} \left( 1 + \frac{m_i T_{r,i}^{0.5}}{2\alpha_i^{0.5}} + \frac{m_j T_{r,j}^{0.5}}{2\alpha_j^{0.5}} \right) \quad (\text{A.4})$$

The corresponding parameters for the liquid and vapor phases are used in these equations. The liquid and vapor enthalpies are then obtained from Equations 4.8 and 4.9.

### Derivative Properties

The derivative properties,  $\partial \ln \phi_i / \partial T$ ,  $\partial \ln \phi_i / \partial x_i$ ,  $\partial \ln \phi_i / \partial y_i$  and  $\partial \Omega / \partial T$ , are needed in Equations 4.13 through 4.16. These are obtained by differentiating Equations A.1 and A.3 with respect to temperature and composition.

From Equation A.1, differentiating with respect to temperature, T

$$\frac{\partial \ln \phi_i}{\partial T} = \frac{Z'_T - B'_T}{B - Z} + \frac{B_i}{B} Z'_T - \left[ (\text{FAC1}) \left[ \frac{(ZB'_T - BZ'_T)}{Z(Z+B)} \right] + \frac{(\text{FAC3})/B}{T} \right] \quad (\text{A.5})$$

where

$$\text{FAC3} = \ln \left( \frac{Z+B}{Z} \right) \left[ 2 \sum_j x_j A_{ij} \left( 1 + \frac{m_i T_{r,i}^{0.5}}{2\alpha_i^{0.5}} + \frac{m_j T_{r,j}^{0.5}}{2\alpha_j^{0.5}} \right) + \frac{B_i}{B} (\text{FAC2}) \right] \quad (\text{A.6})$$

From Equation A.1, differentiating with respect to composition

$$\frac{\partial \ln \phi_i}{\partial x_i} = \frac{Z'_{x,i} - B_i}{B-Z} + \frac{B_i}{B} Z'_{x,i} - (Z-1) \left( \frac{B_i}{B} \right)^2 - \left[ (\text{FAC1}) \left( \frac{ZB_i - BZ'_{x,i}}{Z(Z+B)} \right) + 2 \ln \left( \frac{Z+B}{Z} \right) \left( (\text{FAC1}) \frac{B_i}{B} - \frac{A_i}{B} \right) \right] \quad (\text{A.7})$$

From Equation A.2, differentiating with respect to temperature, T

$$\frac{\partial \Omega}{\partial T} = R(Z-1) + RT Z'_T - \frac{RT}{B} (\text{FAC2}) \left[ \frac{(ZB'_T - BZ'_T)}{Z(Z+B)} \right] + \ln \left( \frac{Z+B}{Z} \right) \frac{R}{B} (\text{FAC4}) \quad (\text{A.8})$$

where

$$\text{FAC4} = \frac{P}{R^2 T^2} T^2 a''(T) = \frac{1}{2} \sum_i \sum_j x_i x_j A_{ij} \left( \frac{m_i^{T_{r,i}} 0.5}{2\alpha_i^{0.5}} + \frac{m_j^{T_{r,j}} 0.5}{2\alpha_j^{0.5}} + 4 \frac{m_i^{T_{r,i}} 0.5}{2\alpha_i^{0.5}} \frac{m_j^{T_{r,j}} 0.5}{2\alpha_j^{0.5}} \right) \quad (\text{A.9})$$

The corresponding parameters for the liquid and vapor phases are used in these equations.

In Equations A.5 and A.8,  $Z'_T$  is given by

$$Z'_T = \frac{A'_T(B-Z) + B'_T(A+Z+2BZ)}{3Z^2 - 2Z + (A-B-B^2)} \quad (\text{A.10})$$

where

$$A'_T = -\frac{1}{T} [A + (\text{FAC2})] \quad (\text{A.11})$$

and

$$B'_T = -B/T \quad (\text{A.12})$$

In Equation A.7,  $Z'_{X,i}$  is given by

$$Z'_{X,i} = \frac{A'_{X,i}(B-Z) + B'_{X,i}(A+Z+2BZ)}{3Z^2 - 2Z + (A-B-B^2)} \quad (\text{A.13})$$

where

$$A'_{X,i} = 2_j \Sigma x_j A_{ij} \quad (\text{A.14})$$

and

$$B'_{x,i} = B_i \quad (\text{A.15})$$

The derivative  $\partial H_i^{\circ}/\partial T$  is needed in Equations 4.15 and 4.16. These are obtained from Equations 4.10 and 4.11 as

$$\frac{\partial H_i^{\circ}}{\partial T} = C_{p,i} = a_i + b_i T + c_i T^2 + d_i T^3 \quad (\text{A.16})$$

The thermodynamic properties and their derivatives, discussed in Chapter IV, are obtained by using the corresponding parameters for the liquid and vapor phases in Equations A.1 through A.16.

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