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An Equilibrium Stage Model of the KALC Process

J. C. Mullins
R. W. Glass

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CHEMICAL TECHNOLOGY DIVISION
THORIUM UTILIZATION PROGRAM
Reprocessing Development - Task 200

AN EQUILIBRIUM STAGE MODEL OF THE KALC PROCESS

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AUGUST 1976

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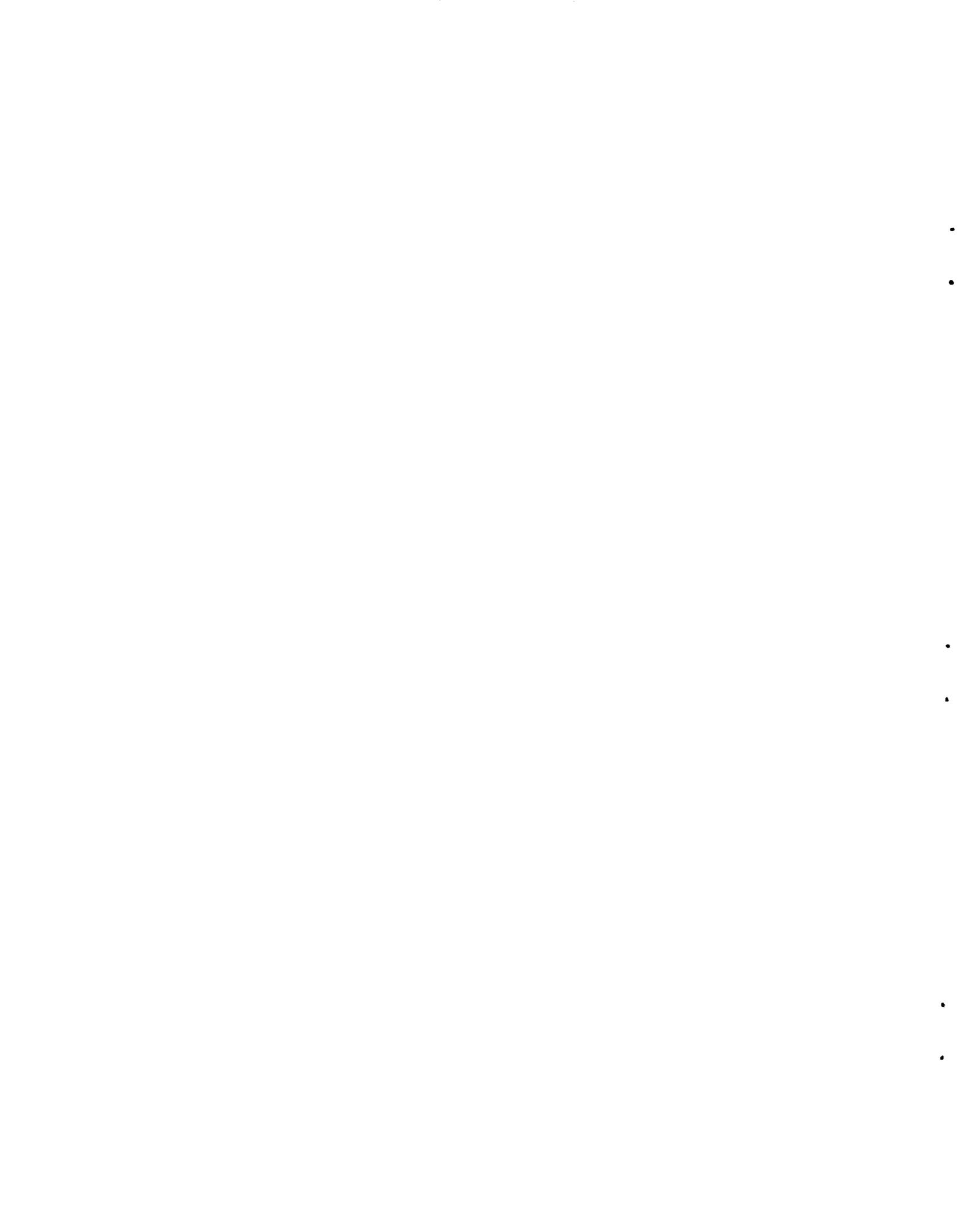
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AN EQUILIBRIUM STAGE MODEL OF THE KALC PROCESS

J. C. Mullins
R. W. Glass

ABSTRACT

A computer program has been written to solve equilibrium stage models of the KALC process in as exact a manner as presently available data will permit using matrix algebra techniques. A correlation is presented which represents the thermodynamic properties of the multicomponent system $\text{CO}_2\text{-Xe-O}_2\text{-CO-N}_2\text{-Kr}$ at temperatures of -55 to 0°C , pressures up to 70 atm, and over a range of concentrations of dissolved light gases likely to be of interest. The program has been tested for several possible system configurations with up to a total of 50 stages. A three-column configuration consisting of an absorber, a fractionator, and a stripper-rectifier column is used as an example.

1. INTRODUCTION

The need to remove ^{85}Kr from the gases evolved during the reprocessing of the fuel elements used in the high-temperature gas-cooled reactor (HTGR) led to the development of the KALC (Krypton Absorption in Liquid Carbon Dioxide) process.¹⁻³ The off-gases from the reprocessing consist typically of 90% carbon dioxide and 10% light gases

containing oxygen, carbon monoxide, nitrogen, and traces of xenon and krypton. A simplified flowsheet for the KALC process is shown in Fig. 1. The krypton, along with some of the other light gases, is removed in the absorber-fractionator. The liquid carbon dioxide containing the krypton and a small quantity of light gases then goes to a rectifier-stripper column, where the krypton and light gases accompanied by carbon dioxide are removed through two partial condensers at the top of the column. This small quantity of gas containing the majority of the krypton is processed to increase the concentration of krypton, and is eventually stored. The nearly pure, liquid carbon dioxide from the bottom of the stripper is recycled as scrub to the top of the absorber. Detailed descriptions of the proposed process are available in earlier reports.^{4,5}

The need to develop a mathematical model of the process was recognized early in the development of the KALC process. This led to the parametric study of the process by Whatley⁶ and to a solution of an equilibrium stage model by Mobley.⁷

Whatley's study of the KALC process also included the use of an equilibrium stage model and provided an extensive evaluation of the effects of various parameters such as pressure, scrub rate, number of stages, and reboiler duty on the decontamination factor (DF)* and concentration factor (CF)**,[†]. In his study, Whatley

* DF = amount of krypton entering in feed stream divided by the amount of krypton leaving the top of the absorber.

** CF = mole fraction of krypton in feed stream divided by the mole fraction of krypton in product stream leaving process.

[†] Whatley⁶ used a different definition of CF.

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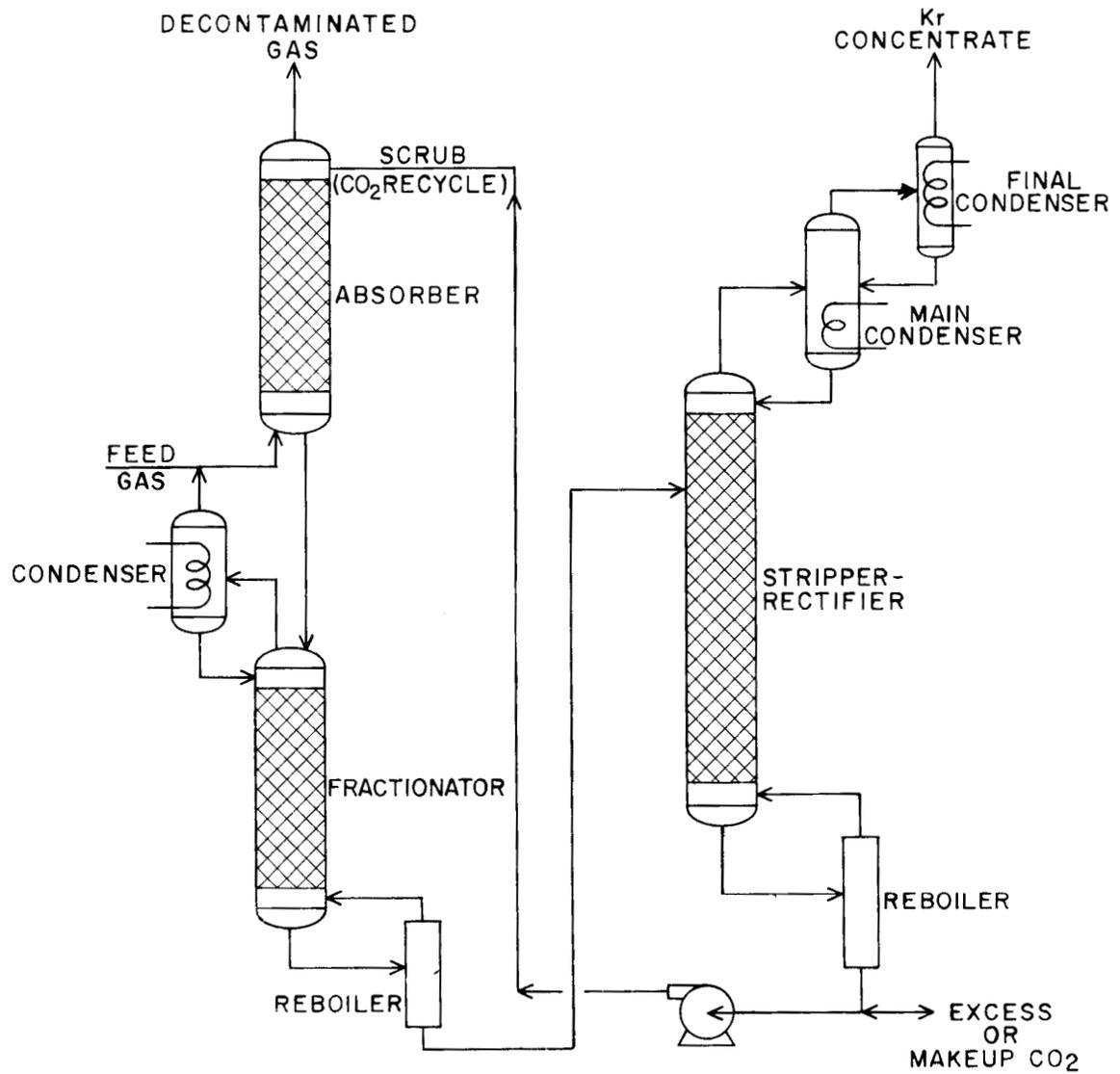


Fig. 1. Simplified flowsheet of the KALC process.

separated the absorber-fractionator from the stripper-rectifier column. His solution technique consisted of a stage-by-stage calculation beginning at each end of the column where conditions are specified. From assumed profiles of temperature, concentrations, and vapor and liquid rates, energy and material balances are imposed on each stage, along with the equilibrium requirement, to yield new values of the temperature, composition, and flow rates. Whatley represented the vapor-liquid equilibria of the system by an empirical fit to the available data for $\text{CO}_2\text{-O}_2$, $\text{CO}_2\text{-N}_2$, $\text{CO}_2\text{-CO}$, and $\text{CO}_2\text{-Kr}$ systems.

Mobley⁷ used a matrix technique developed by Tierney and co-workers^{8,9} to provide a solution to the model proposed by Whatley.⁶ Mobley's study, although not nearly as extensive as that of Whatley, appeared to provide a convenient solution technique which could be used to study the combined system or any number of different configurations.

These early studies led to the present work, which attempts to provide a more quantitative representation of the entire system with a thermodynamic correlation of all available data. This will permit investigation of the system over wider ranges of conditions than previously studied.

2. EQUILIBRIUM STAGE MODEL

2.1 Introduction

The equilibrium stage concept has been widely used in the modeling of distillation, absorption, and extraction processes; thus one often

overlooks the fact that it is a model. While a number of equilibrium stages can be associated with the separation achieved in a binary separation process, this is not always true of a multicomponent system involved in a real process such as that encountered here. In spite of this weakness, the model should prove useful in the design of the KALC process and in interpreting the data from the various experimental campaigns. Figure 2 shows the equilibrium stage model of the KALC process which may be solved by the computer program listed in Appendix E. With slight modifications discussed in more detail later, the program has also been used to model a one-column absorber and a two-column system consisting of an absorber column and a stripper-rectifier column. Almost any configuration can be modeled with minor changes in the basic program and one subroutine.

2.2 Solution of the Equilibrium Stage Model

2.2.1 Background

The solution to the equilibrium stage model as it has been modified with the acquisition of larger and faster electronic computers has been discussed by Smith¹⁰ and by Friday and Smith.¹¹

The solution of the equilibrium stage model for separation problems is obtained by finding a set of temperatures, phase rates, and compositions which satisfies all of the equations of the model. Denoting stage numbers by i and components by j , the equations of the model are:

(1) Equilibrium relations, that is,

$$y_{ij} = k_i^j x_{ij} \quad (1)$$

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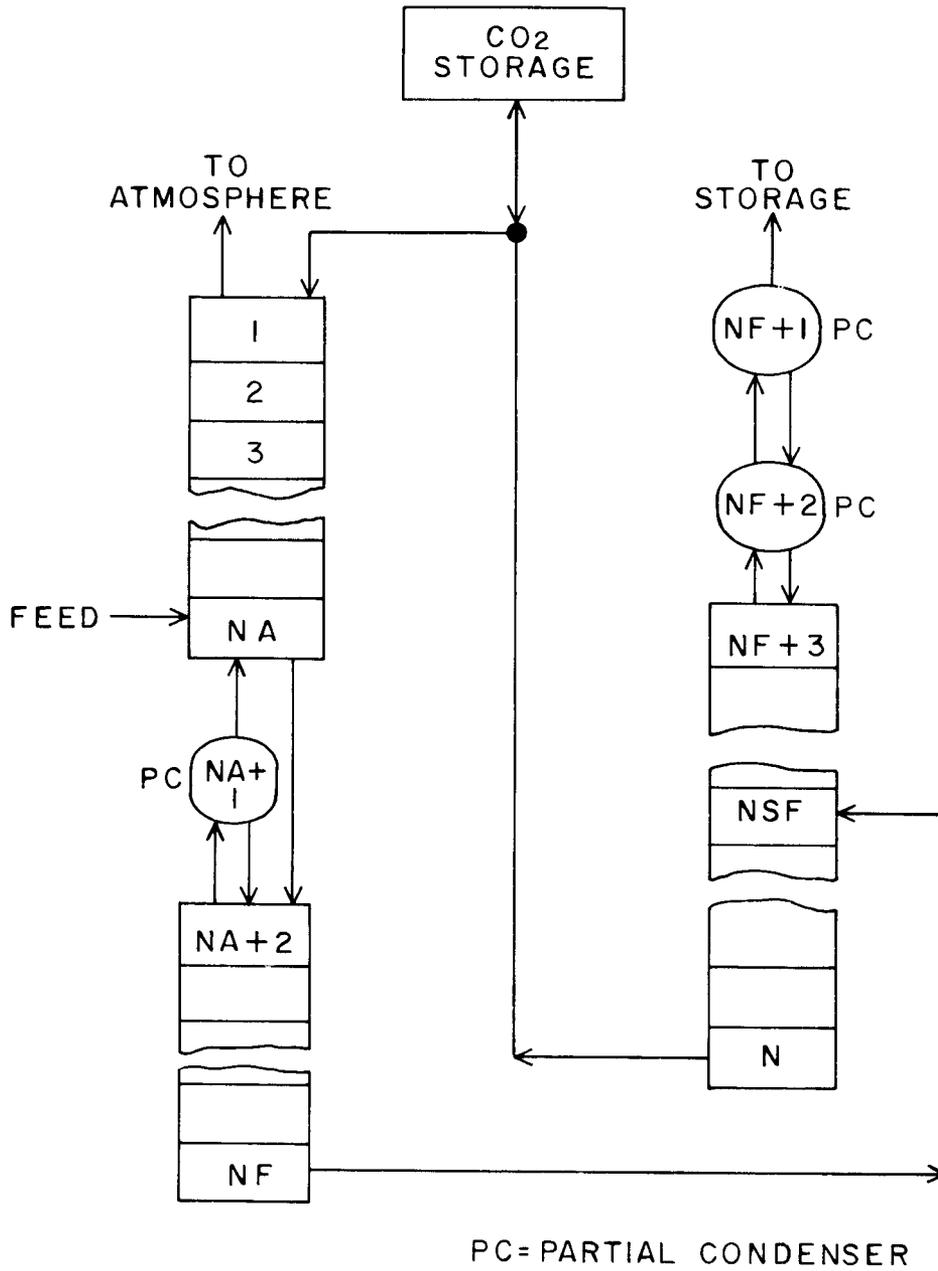


Fig. 2. Three-column equilibrium stage model of the KALC process.

- (2) Material balance equations around each stage for each component
- (3) Energy balance equation around each stage
- (4) Restrictive relation on concentrations, that is,

$$\sum_j x_{ij} = 1 = \sum_j k_i^j x_{ij}. \quad (2)$$

The normal procedure is to substitute Eq. (1) into Eq. (2) and, by an overall material balance, to eliminate the liquid flows in favor of the vapor flows as independent variables. The following three sets of relations remain:

$$C_{ij}(x_{ij}, v_i, t_i) = 0 \text{ (N times M relations)}, \quad (3)$$

$$E_i(x_{ij}, v_i, t_i) = 0 \text{ (N relations)}, \quad (4)$$

$$M_i(x_{ij}, v_i, t_i) = 0 \text{ (N relations)}, \quad (5)$$

where C_{ij} represents the material balance relations, E_i refers to the energy balance relations, and M_i designates the restrictive relations given by Eq. (2). The various methods used in the past for solving these three sets of relations are discussed by Friday and Smith.¹¹ They point out that almost all modern computer methods group the equations by components rather than by stages. One such method which has wide application to any stagewise operation is a general matrix technique developed and described by Tierney and co-workers.^{8,9} This method, as discussed below, originated from the earlier work of Amundson and co-workers.^{12,13}

2.2.2 General matrix method

The general matrix method for the solution to the equilibrium stage process as developed by Tierney and co-workers^{8,9} has been applied to the KALC process. Figure 2 specifies the feed stream and the number of stages in each column, as well as the interstage flow pattern. The numbering sequence begins at the top of the absorber and ends at the bottom of the stripper-rectifier, each partial condenser being considered as a stage. In the general formulation discussed below, the various heat streams will be considered to be specified, although in the sample calculation the amount of vapor leaving stages $NA + 1$ and $NF + 1$ will be specified and the heat stream in each of these two stages will be calculated. The amount of liquid carbon dioxide solvent returning to stage 1 is stipulated; the difference between that stream and the liquid stream leaving stage N is an additional product stream or a makeup stream, depending on the requirement.

Initially, N vapor flow rates and N stage temperatures are assumed. These assumed values can be corrected by N measures of energy balance error and N measures of material balance error. A linear correction process is defined as:

$$\Psi \Delta = - \Lambda, \quad (6)$$

where Δ is a $2N$ by 1 vector ($2N \times 1$) consisting of the N corrections to the assumed temperatures and the N corrections to the assumed flows. The vector Λ is $2N \times 1$ and contains the N material and N energy balance

errors. Ψ , which is the Jacobian matrix of errors, is $2N \times 2N$. An element of Ψ , ψ_{ij} , is defined as:

$$\psi_{ij} = \frac{\partial \lambda_i}{\partial \delta_j}, \quad (7)$$

where λ_i is an element of Λ and δ_j is an element of Δ . This is the familiar Newton-Raphson solution to nonlinear equations. These matrices and vectors can be partitioned and rewritten explicitly as:

$$\begin{bmatrix} E_t & E_v \\ J_t & J_v \end{bmatrix} \begin{bmatrix} C_t \\ C_v \end{bmatrix} = - \begin{bmatrix} D_m \\ D_e \end{bmatrix}. \quad (8)$$

Here the Ψ matrix has been partitioned into four $N \times N$ matrices, where

E_t = effect of temperature changes on composition on all stages
at constant flow,

$$e_{t,ij} = \partial d_{m,i} / \partial c_{t,j};$$

E_v = effect of flow changes on composition on all stages at
constant temperature,

$$e_{v,ij} = \partial d_{m,i} / \partial c_{v,j};$$

J_t = effect of temperature changes on energy balance on all
stages at constant flow,

$$j_{t,ij} = \partial d_{e,i} / \partial c_{t,j};$$

J_v = effect of flow changes on energy balance on all stages
at constant temperature,

$$j_{v,ij} = \partial d_{e,i} / \partial c_{v,j}.$$

The Δ vector has been partitioned into the temperature correction vector, C_t , and the flow correction vector, C_v . The Λ vector has been partitioned into the vector of material balance errors, D_m , and the vector of energy balance errors, D_e . The value of partitioning the Jacobian matrix of errors is discussed by Tierney and Bruno.⁸ For example, the constant model overflow problem reduces to:

$$E_t C_t = -D_m \quad (9)$$

Before proceeding with the analytical expressions for the matrices and vectors, it is necessary to define a number of matrices and vectors. After obtaining relations for Ψ , D_m , and D_e , the convergence technique is straightforward. From initial estimates of the stage temperatures and flow rates, energy balance and material balance errors are calculated along with the elements of Ψ . Corrections for the assumed values of temperature and flow rates are calculated from:

$$\begin{bmatrix} C_t \\ C_v \end{bmatrix} = - \begin{bmatrix} E_t & E_v \\ J_t & J_v \end{bmatrix}^{-1} \begin{bmatrix} D_m \\ D_e \end{bmatrix} \quad (10)$$

The process is repeated until D_m and D_e satisfy the convergence criteria.

Definitions. The basic matrices are defined here to precede a description of the material and energy balances for the equilibrium stage system.

- (1) Flow connection matrices, L and V. These are $N * N$ matrices denoting the flow of liquid and vapor streams between stages. The main diagonal is composed of negative numbers representing

the total flow of liquid or vapor leaving each stage. The other elements, v_{ij} or l_{ij} , are positive numbers giving the flow from stage j to stage i .

- (2) Composition matrices, X and Y. A matrix of size $N * M$ is developed for each phase. M is the number of components in the system. The ij elements of each matrix represent the composition of component j on stage i . For convenience, each composition matrix is partitioned into M column vectors, $X^{(j)}$ or $Y^{(j)}$.
- (3) Feed matrix, F. This $N * M$ matrix is used to represent the flows entering the system from outside sources. It is also partitioned into M column vectors, each one representing the feed rate of one component.
- (4) Equilibrium ratio matrices, K^j . One $N * N$ diagonal matrix is defined for each component, with the diagonal element k_i^j representing the equilibrium ratio of component j on stage i .
- (5) Heat vector, Q. One $N * 1$ vector of elements q_i is used to describe the addition (+) or removal (-) of heat from each stage, cal.
- (6) Liquid enthalpy vector, H. The element h_i = enthalpy, cal/g-mole of liquid stream leaving stage i . The vector is $N * 1$.
- (7) Vapor enthalpy vector, G. The element g_i = enthalpy, cal/g-mole of vapor stream leaving stage i . The vector is $N * 1$.

- (8) Feed enthalpy vector, Q_f . The element q_{fi} = total enthalpy, cal, of feed stream entering stage i . The vector is $N * 1$.

Material and energy balance equations. With the definitions above, a matrix formation of the equilibrium stage problem can easily be followed. The material balance for component j is given by:

$$LX^{(j)} + VY^{(j)} + F^{(j)} = 0. \quad (11)$$

The gas and liquid compositions for component j are related by:

$$Y^{(j)} = K_X^j X^{(j)}. \quad (12)$$

A substitution of Eq. (12) into Eq. (11) gives:

$$LX^{(j)} + VK_X^j X^{(j)} = -F^{(j)}. \quad (13)$$

Now let Z be defined by Eq. (14):

$$Z^j = L + VK_X^j. \quad (14)$$

Substituting Eq. (14) and rearranging Eq. (13) gives:

$$X^{(j)} = -(Z^j)^{-1} F^{(j)}. \quad (15)$$

With an assumed set of flow rates and temperatures, Eq. (15) can be used to calculate the liquid composition of component j on all N stages. Equation (12) will then give the compositions in the vapor phase. These calculations are made for each component of the system.

The overall material balance can be used to relate the liquid and vapor flow matrices:

$$LU + VU + FU = 0. \quad (16)$$

Here, U is an $N * 1$ or $M * 1$ unit vector, as appropriate.

The energy balance is written in a similar manner:

$$LH + VG + Q + Q_f = 0 . \quad (17)$$

The above equations are used to define the material and energy balance error vectors, which must be reduced to negligible values in the iterative solution:

$$D_m \equiv (X - Y)U = \sum_{j=1}^M x_{ij} - \sum_{j=1}^M y_{ij} \text{ for } i = 1 \dots N. \quad (18)$$

The energy error vector is defined from Eq. (17) as follows:

$$D_e \equiv LH + VG + Q + Q_f. \quad (19)$$

Independent flow variables. Earlier it was stated that each stage was considered to have two independent variables, a stage temperature and vapor flow rate (a liquid flow rate could have been used). As many as $N - 1$ vapor streams could be routed from each stage to other stages; however, only one is independent.

The flow variables are grouped into two classes: variable flows and fixed flows. If the flow rate of a stream is specified, then this stream has a fixed rate. This is the case for the scrub rate to the top of the absorber. If a reflux ratio is specified, the two streams are treated as variable flows; however, a restriction is introduced to keep the ratio constant. Although any one of the variable flows leaving a stage could be used as the independent variable, the sum of all variable flows is chosen as the independent flow variable. Later, a simple change will be made to let the heat term rather than a phase rate be the variable on a stage.

The vapor and liquid flow matrices are then rewritten as:

$$V = AV^* + V', \quad (20)$$

where

V^* = independent variable flow matrix, $(N * N)$ diagonal with v_i^* equal to total variable vapor flow leaving stage i ,

A = vapor flow restriction matrix, -1 for diagonal elements with a_{ij} ($i \neq j$) equal to the fraction of total variable vapor flow going from j to i ,

V' = fixed vapor flow matrix; contains flows not to be changed. Main diagonal elements are (-) and off-diagonal elements are (+).

Similarly, for the liquid flow matrix:

$$L = BL^* + L'. \quad (21)$$

These matrices are defined in an analogous manner to the vapor matrices. Neither L^* nor V^* is independent since both are related by an overall material balance. V^* is taken as the independent variable, while L^* is calculated from Eq. (16).

Temperature correction based on material balance errors (E_t).

To develop the necessary analytical relations, one starts from Eq. (18)

and differentiates:

$$\frac{\partial D_m}{\partial t_k} = \left(\frac{\partial X}{\partial t_k} - \frac{\partial Y}{\partial t_k} \right) U. \quad (22)$$

In order to evaluate the derivatives, consider the material balance for component j given by Eq. (13) and differentiate at constant flow rate:

$$Z^j \frac{\partial X^{(j)}}{\partial t_k} + V \frac{\partial K^j}{\partial t_k} X^{(j)} = 0. \quad (23)$$

Solving,

$$\frac{\partial X^{(j)}}{\partial t_k} = -(Z^j)^{-1} V \left(\frac{\partial K^j}{\partial t_k} \right) X^{(j)}. \quad (24)$$

One $N \times 1$ vector is obtained for each k from $k = 1$ to N . By grouping these terms, the matrix X_t^j is formed:

$$X_t^j = -(Z^j)^{-1} V M_o^j, \quad (25)$$

where M_o^j is a diagonal matrix with element

$$m_{o,i}^j = \frac{\partial k_i^j}{\partial t_i} x_{ij}. \quad (26)$$

For the other derivative in Eq. (22),

$$\frac{\partial Y^{(j)}}{\partial t_k} = K^j \frac{\partial X^{(j)}}{\partial t_k} + \frac{\partial K^j}{\partial t_k} X^{(j)}. \quad (27)$$

Grouping from $k = 1$ to N and using the definition of M_o^j above,

$$Y_t^j = K^j X_t^j + M_o^j. \quad (28)$$

Equation (22) can be written:

$$\frac{\partial D}{\partial t_k} = \left(\frac{\partial X}{\partial t_k} - \frac{\partial Y}{\partial t_k} \right) U = \sum_{j=1}^M \left(\frac{\partial X^{(j)}}{\partial t_k} - \frac{\partial Y^{(j)}}{\partial t_k} \right). \quad (29)$$

As k varies from 1 to N ,

$$E_t = \sum_{j=1}^M \left(X_t^j - Y_t^j \right). \quad (30)$$

Since the values of X_{ij} used in developing Eq. (30) do not necessarily sum to unity on each stage, it proves helpful to include a normalization factor. Let \bar{N} be a diagonal $N * N$ matrix with elements

$$n_{ii} = \frac{1}{\sum_{j=1}^M x_{ij}} . \quad (31)$$

The final equation for E_t as used in this work is:

$$E_t = \sum_j (X_t^j - Y_t^j) \bar{N} . \quad (32)$$

Flow-rate correction based on material balance errors (E_v).

Starting with the overall material balance, Eq. (16), and substituting for L and V using Eqs. (21) and (20), the following relation is obtained:

$$(BL^* + L' + AV^* + V') U = -FU. \quad (33)$$

Taking the partial derivative with respect to the independent flow variable, v_k^* :

$$B \frac{\partial L^*}{\partial v_k^*} U = -A \frac{\partial V^*}{\partial v_k^*} U . \quad (34)$$

Defining $R = B^{-1} A$ and solving yields:

$$\frac{\partial L^*}{\partial v_k^*} U = -R \frac{\partial V^*}{\partial v_k^*} U . \quad (35)$$

$\partial L^*/\partial v_k^*$ is an $N * N$ diagonal matrix, and $\partial V^*/\partial v_k^*$ is an $N * N$ diagonal matrix with a single nonzero element at k on the diagonal equal to unity. Thus, $R \partial V^*/\partial v_k^*$ is an $N * N$ matrix with all zeros except column

k; and since the left-hand side of Eq. (35) must equal the right-hand side,

$$\frac{\partial \ell_i}{\partial v_k^*} = -r_{ik} . \quad (36)$$

For component j, the material balance is given by:

$$Z^j X^{(j)} = -F^{(j)} . \quad (37)$$

Taking the partial derivative with respect to v_k^* ,

$$\frac{\partial Z_k^j}{\partial v_k^*} X^{(j)} + Z^j \frac{\partial X^{(j)}}{\partial v_k^*} = 0. \quad (38)$$

Using Eqs. (20), (21), and (14) to evaluate the term on the left-hand side of Eq. (38) gives:

$$\left(B \frac{\partial L^*}{\partial v_k^*} + A \frac{\partial V^*}{\partial v_k^*} K^j \right) X^{(j)} + Z^i \frac{\partial X^{(j)}}{\partial v_k^*} = 0. \quad (39)$$

Solving for $\partial X^{(j)} / \partial v_k^*$,

$$\frac{\partial X^{(j)}}{\partial v_k^*} = -(Z^j)^{-1} \left[B \frac{\partial L^*}{\partial v_k^*} X^{(j)} + A \frac{\partial V^*}{\partial v_k^*} Y^{(j)} \right]. \quad (40)$$

From Eq. (36), one sees that $(\partial L^* / \partial v_k^*) X^{(j)}$ is an $N * 1$ vector with elements $r_{ik} x_{ij}$. Let

$$M_1^{j(k)} = - \frac{\partial L^*}{\partial v_k^*} X^{(j)} \quad (41)$$

be an $N * 1$ column vector with elements

$$m_{1,ik}^j = r_{ik} x_{ij} . \quad (42)$$

If we let k vary from 1 to N , the matrix M_1^j is formed with elements given by Eq. (42). Similarly,

$$A \frac{\partial V^*}{\partial v_k^*} Y^{(j)} = M_2^{j(k)} \quad (43)$$

is a column vector with elements

$$m_{2,ik}^j = a_{ik} y_{kj} \quad (44)$$

Therefore, by varying k from 1 to N , the matrix M_2^j is formed; and from Eq. (40) the matrix X_v^j is given by:

$$X_v^j = (Z^j)^{-1} \left[B M_1^j - M_2^j \right] \quad (45)$$

From the definitions of the measure of error given by Eq. (18), we obtain:

$$\begin{aligned} \frac{\partial Dm}{\partial k^*} &= \left[\frac{\partial X}{\partial v_k^*} - \frac{\partial Y}{\partial v_k^*} \right] U \\ &= \sum_{j=1}^M X_v^{j(k)} - \sum_{j=1}^M Y_v^{j(k)} \quad , \end{aligned} \quad (46)$$

where

$$Y_v^j = K^j X_v^j \quad (47)$$

The following matrix for E_v is formed by grouping from $k = 1$ to N :

$$E_v = \sum_{j=1}^M (X_v^j - Y_v^j) \quad (48)$$

Temperature correction based on energy balance errors (J_t). In the k th column of J_t are the derivatives of De with respect to t_k . From the measure of error, Eq. (19), the derivative gives:

$$\frac{\partial De}{\partial t_k} = L \frac{\partial H}{\partial t_k} + V \frac{\partial G}{\partial t_k} \quad (49)$$

a column vector, the k th column of J_t . By varying k from 1 to N , J_t is generated:

$$J_t = LH_t + VG_t . \quad (50)$$

Here H_t and G_t are $N * N$ matrices whose k th columns are $\partial H/\partial t_k$ and $\partial G/\partial t_k$.

In order to determine these derivatives, let

$$H = \sum_{j=1}^M H^{*j} X^{(j)}, \quad (51)$$

and

$$G = \sum_{j=1}^M G^{*j} Y^{(j)} . \quad (52)$$

The H^{*j} and G^{*j} are $N * N$ diagonal matrices with the diagonal elements equal to the partial molar enthalpies of component j in the liquid and vapor, respectively:

$$\frac{\partial H}{\partial t_k} = \sum_{j=1}^M \left[\frac{\partial H^{*j}}{\partial t_k} X^{(j)} + H^{*j} \frac{\partial X^{(j)}}{\partial t_k} \right], \quad (53)$$

$$\frac{\partial G}{\partial t_k} = \sum_{j=1}^M \left[\frac{\partial G^{*j}}{\partial t_k} Y^{(j)} + G^{*j} \frac{\partial Y^{(j)}}{\partial t_k} \right]. \quad (54)$$

The partial derivatives shown at the far right were given previously by Eqs. (24) and (27) in the calculation of E_t . Here $\frac{\partial H^{*j}}{\partial t_k}$ is an $N * N$ matrix with only one element, on the diagonal at k (the partial molar heat capacity). Thus, $\left[\frac{\partial H^{*j}}{\partial t_k} \right] X^{(j)}$ is a column vector with one

nonzero element. By varying k from 1 to N , a diagonal matrix M_3^j is formed with elements

$$m_{3,i}^j = x_{ij} \frac{\partial h_i^{*j}}{\partial t_i} \quad (55)$$

In a similar manner for the vapor phase, the matrix M_4^j is formed with elements

$$m_{4,i}^j = y_{ij} \frac{\partial g_i^{*j}}{\partial t_i} \quad (56)$$

Substituting in Eqs. (53) and (54),

$$H_t = \sum_{j=1}^M (H^{*j} X_t^j + M_3^j) \quad (57)$$

and

$$G_t = \sum_{j=1}^M (G^{*j} Y_t^j + M_4^j). \quad (58)$$

These equations are substituted into Eq. (50) to yield J_t :

$$J_t = L \sum_{j=1}^M (H^{*j} X_t^j + M_3^j) + V \sum_{j=1}^M (G^{*j} Y_t^j + M_4^j). \quad (59)$$

The compositions used in Eq. (59) could be normalized as in the calculation of E_t . Tierney and Yanosik⁹ reported that little change was noted in any of the problems studied, and no normalization factors are included.

Flow-rate correction based on energy balance errors (J_v). Differentiating Eq. (19) with respect to the independent flow variable on stage k yields:

$$\frac{\partial De}{\partial v_k^*} = B \frac{\partial L^*}{\partial v_k^*} H + L \frac{\partial H}{\partial v_k^*} + A \frac{\partial V^*}{\partial v_k^*} G + V \frac{\partial G}{\partial v_k^*} \quad (60)$$

Using the results given earlier by Eq. (36), it is clear that the term $\left(\frac{\partial L^*}{\partial v_k^*}\right) H$ is a vector with elements $\left(\frac{\partial h_i}{\partial v_k^*}\right) h_i$, which is $-r_{ik} h_i$. If we let k vary from 1 to N , the matrix W_1 is formed with elements

$$W_{1,ik} = r_{ik} h_i . \quad (61)$$

In Eq. (60), $A(\partial V^*/\partial v_k^*) G$ is a column vector with elements $a_{ik} g_k$. If we let k vary from 1 to N , the matrix W_2 is formed with elements

$$W_{2,ij} = a_{ij} g_i . \quad (62)$$

Consider the term $L(\partial H/\partial v_k^*)$ in Eq. (60). From Eq. (51),

$$\frac{\partial H}{\partial v_k^*} = \sum_{j=1}^M H^{*j} \frac{\partial X^{(j)}}{\partial v_k^*} . \quad (63)$$

It is recognized that $\partial X^{(j)}/\partial v_k^*$ is the k th column of X_V^j , Eqs. (40) and (45). Therefore,

$$L \frac{\partial G}{\partial v_k^*} = L \sum_{j=1}^M H^{*j} X_V^{j(k)} . \quad (64)$$

Similarly, the term

$$V \frac{\partial G}{\partial v_k^*} = V \sum_{j=1}^M G^{*j} Y_V^{j(k)} . \quad (65)$$

The following final equation for J_V is obtained by varying k from 1 to N in Eqs. (60), (64), and (65):

$$J_V = -BW_1 + LH_V + W_2 + VG_V , \quad (66)$$

where the matrices H_V and G_V are defined by

$$H_V = \sum_{j=1}^M H^{*j} X_V^j \quad (67)$$

and

$$G_V = \sum_{j=1}^M G^{*j} Y_V^j . \quad (68)$$

Change of independent variable from heat to vapor flow. For the case of a partial condenser, it is often convenient to fix the rate of vapor leaving the stage and allow the heat stream to become the dependent variable. If the vapor rate is fixed and the heat stream is allowed to vary on stage i , then the elements of column i in both E_V and J_V will be zero except for the element corresponding to row i in J_V , which will be unity. This follows directly from Eq. (19) and the definition of the Ψ matrix. In the three-column KALC model shown in Fig. 2, this procedure was used for the partial condenser at the top of the fractionator and the small partial condenser at the top of the stripper-rectifier column.

2.3 Description of Computer Program

A computer program was written in PL/I language and tested on the IBM 360/91 system at ORNL. Figure 3 shows a flow diagram illustrating the main parts of the program. This diagram follows closely that of Tierney and Yanosik;⁹ only minor modifications have been made. Since both the gas phase and the liquid phase were known to be nonideal, it was necessary to iterate upon K_1 and the gas-phase enthalpy. This was done in a direct manner by assuming ideal behavior

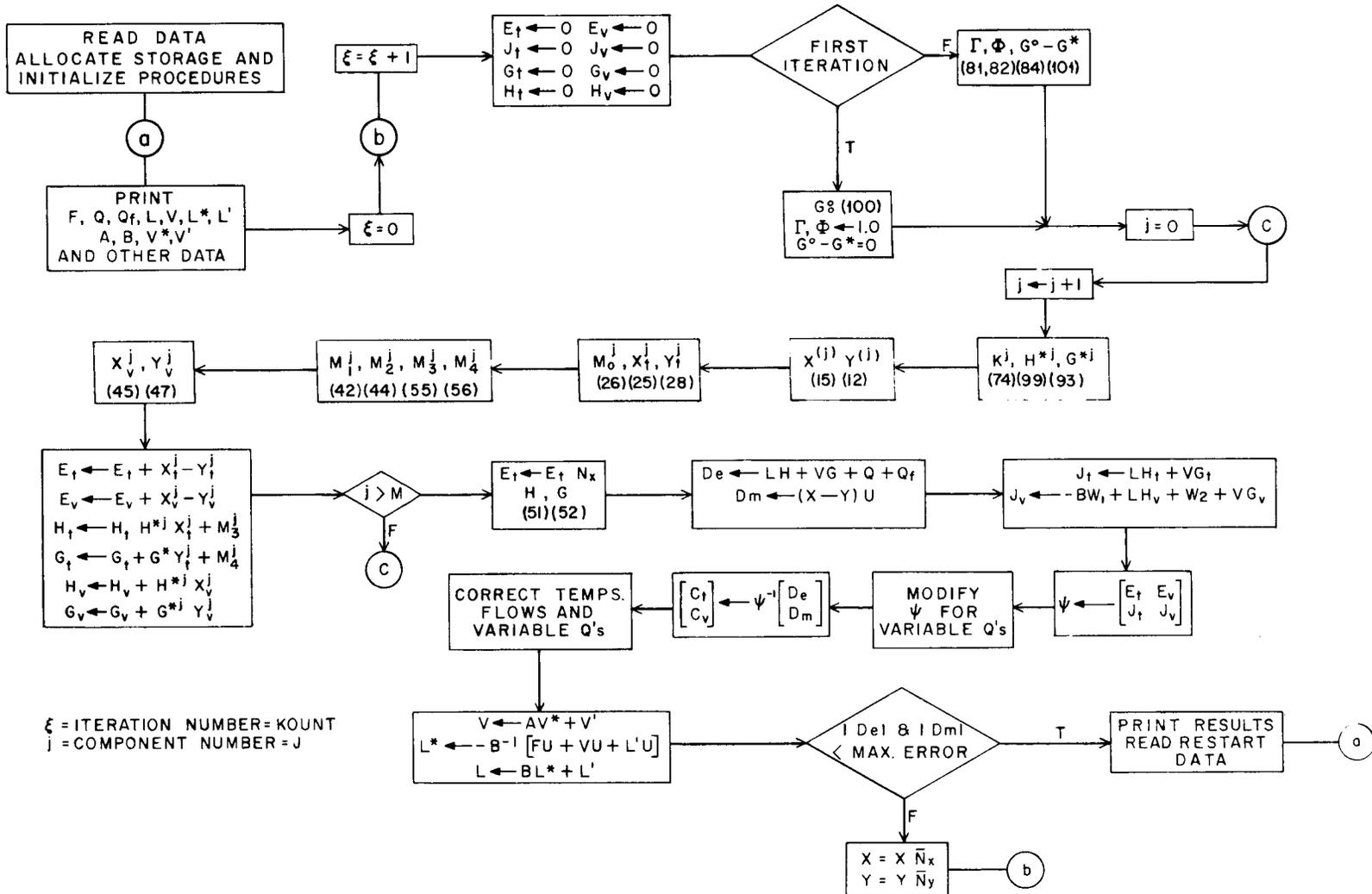


Fig. 3. Flow chart for computer program used to solve equilibrium stage model.

on the initial iteration (i.e., setting γ_{ij} and $\phi_{ij}^G = 1.0$, and $h_i^O - \bar{H}_i^G = 0$). On subsequent iterations, normalized values of x_{ij} and y_{ij} are used to calculate these values.

There are two major loops in the program: the component-by-component calculation of $X^{(j)}$ and $Y^{(j)}$, which begins at point c; and the overall iteration on the energy and material balance errors, which begins at point b. A number of computer runs may be run without recompiling the program if the following steps are taken at the completion of one calculation: a logic card is input, certain initial values are changed (e.g., the number of stages), and the program returns to a point near the beginning of the flow diagram. Appendix E contains details of this feature, along with a listing of the main program and the results of a sample calculation.

The program has been tested for several different operating conditions and initial estimates of flow rates and temperatures that were not very close to final conditions. Rapid convergence was obtained in almost every case. The results of two calculations are shown in Table 1. The first case is a three-column configuration with a total of nine stages: $NA = 2$, $NF = 5$, and $NSF = 8$. The configuration is that shown in Fig. 2. The second case is similar, except that the total number of stages is 36 with $NA = 14$, $NF = 26$, and $NSF = 29$. Six components are present in each case. As is seen in Table 1, convergence is rapid although not quite as good as reported by Tierney and Yanosik⁹ for a distillation column. This could be the result of nonideality in the calculations of enthalpy and K factors.

Table 1. Error measures for three-column configurations^a

Iteration number	36-stage configuration		9-stage configuration	
	$ D_m ^b$	$ D_e ^c$	$ D_m $	$ D_e $
0	2.79	2.07×10^6	1.10	2.08×10^6
1	1.48	1.25×10^6	0.735	1.11×10^6
2	0.537	4.31×10^5	0.216	3.07×10^5
3	0.139	1.60×10^5	0.0461	6.22×10^4
4	0.0310	2.31×10^4	0.0103	1.01×10^4
5	0.00656	2.91×10^3	0.00219	9.79×10^2
6	0.00138	5.07×10^2	0.000439	2.88×10^2
7	0.000304	1.25×10^2		

^aBasis: 100 g-moles of feed.

$${}^b |D_m| \equiv \left[\sum_{i=1}^N d_{m_i}^2 \right]^{1/2} .$$

$${}^c |D_e| \equiv \left[\sum_{i=1}^N d_{e_i}^2 \right]^{1/2} .$$

The program was also used to calculate results for a configuration with 50 stages, but the results are not shown here. In addition, the program, with minor modifications, was used to calculate results for a simple absorption column as well as a two-column configuration consisting of an absorber and a stripper.

The time required for the execution of the 9-stage example was 11 sec, whereas 456 sec was required for the 36 stages. Approximately 60 sec was required in addition to the execution time. Although storage requirements were not determined exactly, the 9- and 36-stage problems can be run with 270 K bytes and 600 K bytes of storage, respectively.

3. CORRELATION OF THERMODYNAMIC PROPERTIES FOR THE KALC SYSTEM

3.1 Introduction

In order to improve upon the earlier models used by Whatley⁶ and Mobley,⁷ it was necessary to estimate the thermodynamic properties of the vapor and liquid phases for the multicomponent system with greater accuracy. The overall objective was to introduce no additional uncertainty except that already inherent in the experimental data.

3.2 Vapor-Liquid Equilibrium Correlation

The correlation and prediction of vapor-liquid equilibrium data at high pressures constitute a field in which much work is being done with a diversity of approaches. The system under consideration is a relatively simple one consisting of one heavy component (xenon is treated here as a light component) and a number of light gases with

critical temperatures well below the temperatures of interest, namely -55 to 0°C. The objective of the correlation was to provide K factors ($K_i = y_i/x_i$) for all components over the temperature range of interest up to pressures in the neighborhood of 70 atm. A survey of the literature revealed a sufficient amount of data for CO₂-X systems to provide a correlation over the region of interest, providing that krypton and xenon exist only at low concentrations. The approach described below appears to satisfy the objective, but should not be expected to provide reasonable predictions outside the range intended.

3.2.1 Thermodynamic relations

The basic thermodynamic relations used in the computer model of the KALC process are shown below; they are given in more detail in Appendix A. The exact equilibrium relations are given by: (1) for components other than carbon dioxide, using the infinite dilute convention,

$$K_i = \frac{H_{i,1}^{(PO)} \gamma_i^{(PO)}}{P\phi_i^G} \exp \int_{PO}^P \frac{\bar{V}_i dP}{RT} \quad (i = 2, 3, \dots, M); \quad (69)$$

(2) for carbon dioxide (component 1), using the normal convention:

$$K_1 = \frac{f_1^{(PO)} \gamma_1^{(PO)}}{P\phi_1^G} \exp \int_{PO}^P \frac{\bar{V}_1 dP}{RT}; \quad (70)$$

where the distribution coefficient (or K factor) is defined by

$$K_i \equiv y_i/x_i. \quad (71)$$

The Henry's law constant for the light gases in carbon dioxide,

$H_{i,1}^{(PO)}$, is the reference fugacity for the light gases, including xenon.

For carbon dioxide, the normal convention is used and the reference fugacity is that of pure liquid carbon dioxide at a reference pressure P_0 . In this work, the reference pressure was taken as zero for convenience. The term ϕ_i^G is the fugacity coefficient defined by:

$$\phi_i^G \equiv \frac{\bar{f}_i^G}{P y_i}, \quad (72)$$

where \bar{f}_i^G is the fugacity of component i . Other variables have their usual meanings and are defined in Sect. 5.

If the concentrations of the dissolved gases are not excessively high and the temperature is well below the critical temperature of carbon dioxide (304.2°K), the partial molar volumes of the light components may be assumed to be incompressible, independent of concentration, and equal to the partial molar volume at infinite dilution. Likewise, the partial molar volume of pure carbon dioxide may be considered that of pure carbon dioxide, v_1^L , at the temperature in question.

In Eq. (70) the fugacity of the pure carbon dioxide at P_0 is given by:

$$f_1^{(P_0)} = f_1^s \exp \int_{P_1^s}^{P_0} \frac{v_1^L}{RT} dP, \quad (73)$$

where P_1^s is the vapor pressure of pure carbon dioxide at saturation. (14)

Since at saturation the fugacity of the pure liquid carbon dioxide is equal to that of the saturated vapor, it is calculated from the Redlich-Kwong equation of state as discussed in Sect. 7.2.1.

Substituting in Eq. (73) and making the assumptions discussed above, the final equations for the equilibrium constants are obtained:

$$K_i = \frac{H_{i,l}^{(PO)} \gamma_i^{(PO)}}{P \phi_i^G} \exp \left[\frac{\bar{V}_i^\infty (P - P_0)}{RT} \right] \quad i=2,3,\dots,M \quad (74)$$

$$K_1 = \frac{f_1^s \gamma_1^{(PO)}}{P \phi_1^G} \exp \left[\frac{V_1^L (P - P_1^s)}{RT} \right]. \quad (75)$$

In order to calculate the various terms in Eqs. (74) and (75), reasonable models must be assumed for the gas and liquid phase.

3.2.2 Liquid phase

The thermodynamic properties of a liquid are best derived from a representation of the excess Gibbs free energy. The excess free energy is assumed to be represented by a series expansion:¹⁵

$$g^{*EX} = -\alpha_{22}x_2^2 - \alpha_{33}x_3^2 - \alpha_{44}x_4^2 \dots \\ - 2\alpha_{23}x_2x_3 - 2\alpha_{24}x_2x_4 \dots, \quad (76)$$

where α_{ij} represent deviations from ideal behavior as a result of interactions between molecules i and j . Note that neither i nor j is one since the infinite dilute convention is being used. It is seen that g^{*EX} approaches zero as x_2, x_3, \dots, x_m approach zero, but not as the mole fractions approach one as in the normal convention. The general relation can be expressed as:

$$g^{*EX} = -\sum_{i,j=2}^M \alpha_{ij}x_i x_j. \quad (77)$$

The activity coefficients are directly related by the relation:

$$\left[\frac{\partial(\text{ng}^{\text{EX}})}{\partial n_k} \right]_{n_j \neq k, T, P} = RT \ln \gamma_k \quad k=1, 2, \dots, M. \quad (78)$$

Applying Eq. (78) to (77) leads directly to expressions for the activity coefficients,

$$RT \ln \gamma_k^{\square} = \sum_{i,j=2}^M \alpha_{ij} x_i x_j - 2 \sum_{i=2}^M \alpha_{ik} x_i \quad k=2, 3, \dots, M; \quad (79)$$

and for carbon dioxide,

$$RT \ln \gamma_1 = \sum_{i,j=2}^M \alpha_{ij} x_i x_j. \quad (80)$$

For a binary system, CO_2 -X, these reduce to:

$$RT \ln \gamma_2^{\square} = \alpha_{22} x_2^2 - 2\alpha_{22} x_2 = (x_1^2 - 1)\alpha_{22} \quad (81)$$

and

$$RT \ln \gamma_1 = \alpha_{22} x_2^2. \quad (82)$$

Note that both γ_2^{\square} and γ_1 approach one as x_2 approaches zero. In applying the above expression, the reference pressure will be taken as zero to provide the desired values of the activity coefficients.

The values of the α_{ij} in Eq. (76) or (80) for $i = j$ can thus be evaluated from an analysis of experimental data for binary systems. However, the values of the α_{ij} for $i \neq j$ cannot be determined without experimental ternary system data; for this reason, a simple estimate as suggested by Muirbrook¹⁶ is used in this work:

$$\alpha_{ij} = (\alpha_{ii} + \alpha_{jj})/2. \quad (83)$$

As noted in Appendix D, the type of mixing rule that is used will not affect the results since $\alpha_{ii} \approx \alpha_{jj}$ for the systems considered.

Other properties of the liquid phase which must be known in Eqs. (69) and (70) will be discussed later; these include \bar{V}_i , $H_{i,1}^{(PO)}$, and $f_{1,pure}^{(PO)}$.

3.2.3 Vapor phase

The properties of the vapor phase may be calculated from any equation of state which will adequately describe the properties of the gas over the range of interest. For pure component gases it is often desirable to fit the properties with an equation of state containing many constants; however, this is not desirable for mixtures since one must have constants for all components and valid mixing rules for the constants. One relationship which has been very successful in predicting properties of gases such as those encountered here is the Redlich-Kwong equation with mixture rules and constants as given by Prausnitz.¹⁵ This equation is also used to estimate the enthalpy deviations in the gas phase as discussed later. A summary of all pertinent equations and mixture rules is given in Appendix B. Here we are interested in the fugacity coefficient, which is given by:

$$\ln \phi_i^G = \ln \left(\frac{v}{v-b} \right) + \left(\frac{b_i}{v-b} \right) - 2 \sum_{j=1}^M \left[\frac{y_j a_{ij}}{RT^{3/2} b} \right] \ln \left(\frac{v+b}{v} \right) + \frac{ab_i}{RT^{3/2} b^2} \left[\ln \left(\frac{v+b}{v} \right) - \frac{b}{v+b} \right] - \ln \frac{Pv}{RT} \quad (84)$$

Equation (84) contains the constants of the Redlich-Kwong equation for the mixture, a and b , for the pure component, b_i , and the interaction

constant, a_{ij} . The various rules for calculating these constants for a mixture are given in Appendix B. This equation can also be used to calculate the fugacity of the pure component at the saturated vapor pressure.

3.2.4 Fitting parameters to binary vapor-liquid equilibrium data

Equations (69) and (72) can be rearranged and written for a binary system as follows:

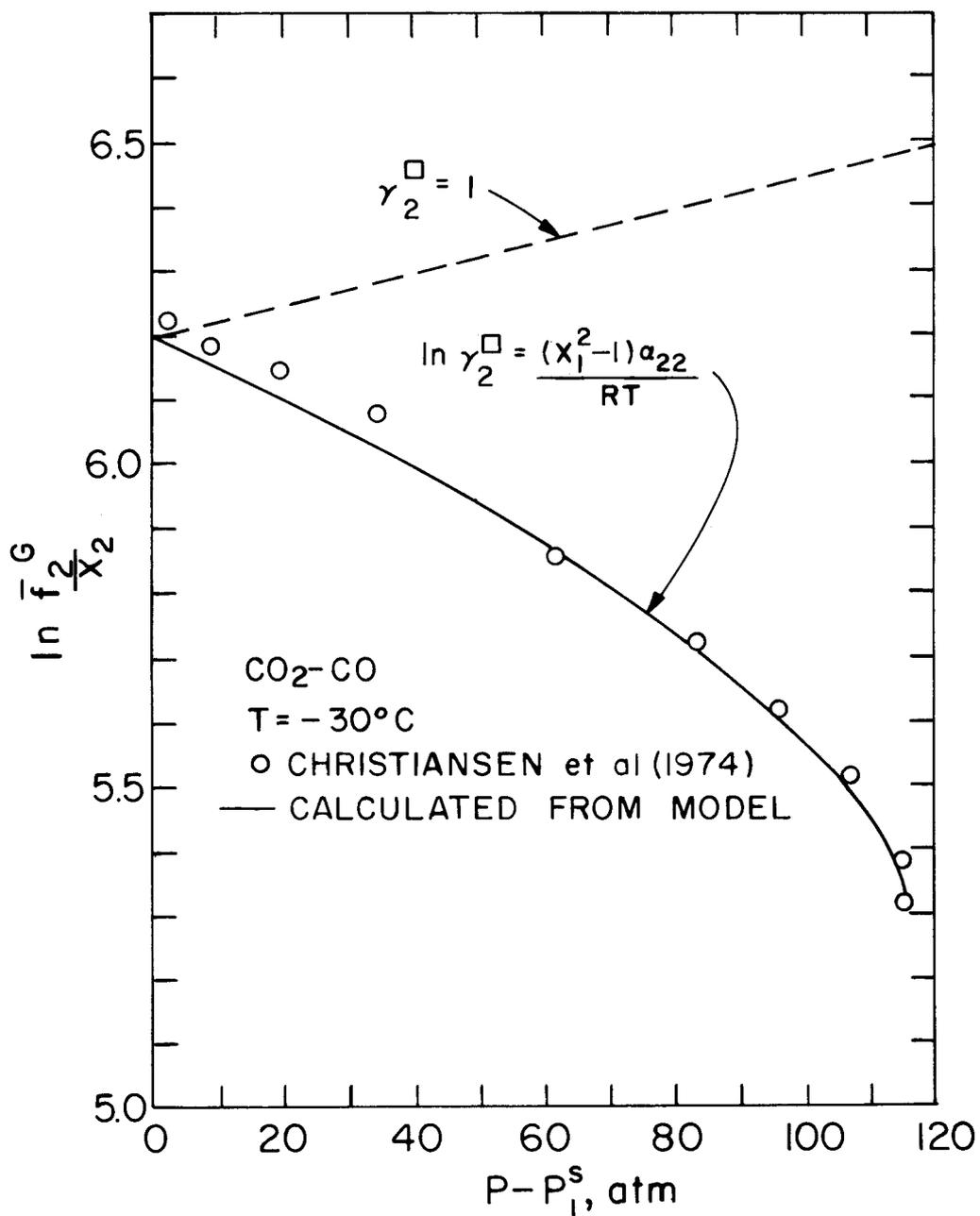
$$\ln \frac{\bar{f}_2^G}{x_2} = \ln H_{2,1}^{(PO)} + \ln \gamma_2^{\square(PO)} + \frac{\bar{V}_2^\infty (P - P_0)}{RT} . \quad (85)$$

If the solution were ideal, a plot of the quantity on the left-hand side of the equation vs $(P - P_0)$ should yield a straight line with slope \bar{V}_2^∞/RT and intercept $H_{2,1}^{(PO)}$. Equation (85) is known as the Krichevsky-Illinskaya equation; with $\gamma_2^{\square(PO)} = 1$, it is called the Krichevsky-Kasarnovsky equation.¹⁵ Figure 4 clearly shows that the activity coefficient must be included in the correlation. Equation (85) gives the final form of the equation used to correlate the binary vapor-liquid equilibrium data by substituting Eq. (81):

$$\ln \frac{\bar{f}_2^G}{x_2} = \ln H_{2,1}^{(PO)} + \frac{(x_1^2 - 1) \alpha_{22}}{RT} + \frac{\bar{V}_2^\infty (P - P_0)}{RT} . \quad (86)$$

At any given temperature, $H_{2,1}^{(PO)}$, α_{22} , and \bar{V}_2^∞ are constants; on the other hand, since it is desired to fit data over a fairly wide range of temperature, we must consider the variation of these quantities with temperature. The expression used for the natural logarithm of the activity coefficient, Eq. (81), provides that $\ln \gamma_2^{\square}$ is inversely proportional to absolute temperature if α_{22} is constant. If a solution is

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Fig. 4. Equilibrium data for the CO₂-CO system at -30°C.

regular,¹⁷ $\ln \gamma_2^\square$ varies inversely as the absolute temperature at constant composition and temperature; thus one might expect that α_{22} is invariant with temperature. Within the precision of the experimental data, this appeared to be the case for all systems considered here.

The effect of temperature on the partial molar volume of the light gas at infinite dilution was assumed to be given by:

$$\frac{1}{\bar{V}_i^\infty} \left(\frac{\partial \bar{V}_i^\infty}{\partial T} \right) = \bar{\beta}_i, \quad (87)$$

where $\bar{\beta}_i$ is an average coefficient of expansion. Integrating from a base temperature, T_0 , yields the final expression for \bar{V}_i^∞ :

$$\bar{V}_i^\infty = \bar{V}_{i0}^\infty \exp \left[\bar{\beta}_i (T - T_0) \right]. \quad (88)$$

A similar expression was used for the molar volume of pure carbon dioxide [see Eq. (75)].

$$v_1^L = v_{10}^L \exp \left[\bar{\beta}_1 (T - T_0) \right]. \quad (89)$$

The Henry's law constant $H_{2,1}^{(PO)}$ was fit to a correlation given by Preston and Prausnitz.¹⁸ This particular correlation requires two parameters, T_c^∞ and V_c^∞ . A description of this correlation, along with a printout of the subroutine used by the computer program, is included in Appendix C.

The final correlation used in fitting the binary vapor-liquid equilibrium data using Eq. (86) consisted of five parameters: $\bar{T}_{c_2}^\infty$,

$\bar{V}_{c_2}^\infty$, α_{22} , $\bar{V}_{O_2}^\infty$, and $\bar{\beta}_2$. Before fitting the data to the correlation, one must select the data points to be used.

3.2.5 Selection of experimental vapor-liquid equilibrium data

Table 2 provides a summary of the references considered in the selection of the vapor-liquid equilibrium data to be used in the correlation. Although the literature is filled with methods for testing vapor-liquid equilibrium data for thermodynamic consistency, none is entirely satisfactory for high-pressure data. This is not necessarily the fault of the method since insufficient data are usually measured. For example, terms involving the partial molar volume, \bar{V}_i , are unimportant at low pressures, but important at high pressures, and are usually not known. In addition, nonidealities in the gas phase, represented by ϕ_i^G , are not always known with sufficient accuracy. In spite of these difficulties, it is frequently easy to choose among the data of several different investigators and to eliminate some data points by making plots such as those shown in Fig. 5 for $\ln [(P - P_1^S)/x_2]$ vs $P - P_1^S$ and in Fig. 6 for $\ln (Py_1/P_1^S)$ vs $P - P_1^S$. These plots are convenient if, as was the case here, the investigators reported P , y_2 , x_2 at constant temperature. By preparing the two separate graphs, errors in y_2 and x_2 are separated. The intercept of $(P - P_1^S)/x_2$ can be used to obtain the Henry's law constant from the relation:

$$\lim_{\substack{P \rightarrow P_1^S \\ x_2 \rightarrow 0}} \left(\frac{P - P_1^S}{x_2} \right) = \frac{H_{2,1}^{(P_1^S)}}{\phi_2^G (P=P_1^S, y_2=0)}, \quad (90)$$

Table 2. Summary of vapor-liquid equilibrium data
for carbon dioxide-X systems

System	Temperature range (°C)	Pressure range (atm)	Reference	Investigator
CO ₂ - Xe		P _{CO₂} ^S	19	Notz et al. (1973)
CO ₂ - O ₂	0	41 to 116	20	Muirbrook and Prausnitz (1965)
	-55 to 0	21 to 146	21	Zenner and Dana (1963)
	-40 to 25	36 to 126	22	Kaminishi and Toriumi (1966)
	-50 to 10	10 to 130	23	Fredenslund and Sather (1970)
	-49.4 to -4	7 to 142	24	Fredenslund and Sather (1972)
CO ₂ - CO	-50 to 10	10 to 130	25	Kaminishi et al. (1968)
	-50 to 10	8 to 140	26	Christiansen et al. (1974)
CO ₂ - N ₂	0	48 to 116	20	Muirbrook and Prausnitz (1965)
	-55 to 0	12 to 137	21	Zenner and Dana (1963)
	-40 to 25	50 to 125	22	Kaminishi and Toriumi (1966)
	0 to 25	0 to 181	27	Abdullaev (1939)
	-55 to 0	41 to 155	28	Pollitzer and Strebel (1924)
CO ₂ - Kr	-53 to 22	P _{CO₂} ^S	19	Notz et al. (1973)
	-50 to 25	P _{CO₂} ^S	29	Beaujean et al. (1972)

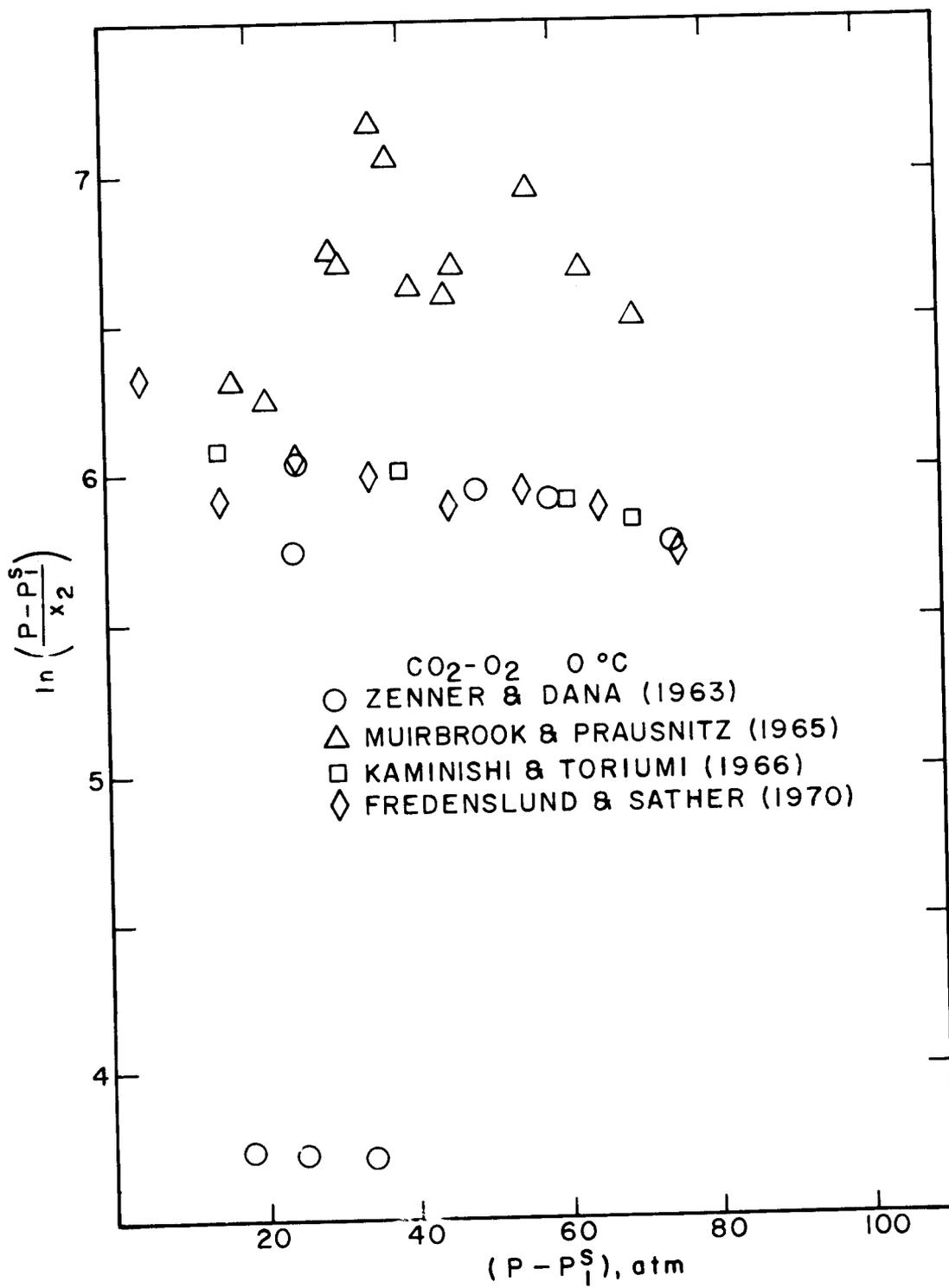


Fig. 5. Liquid-phase equilibrium data for the CO₂-O₂ system at 0°C.

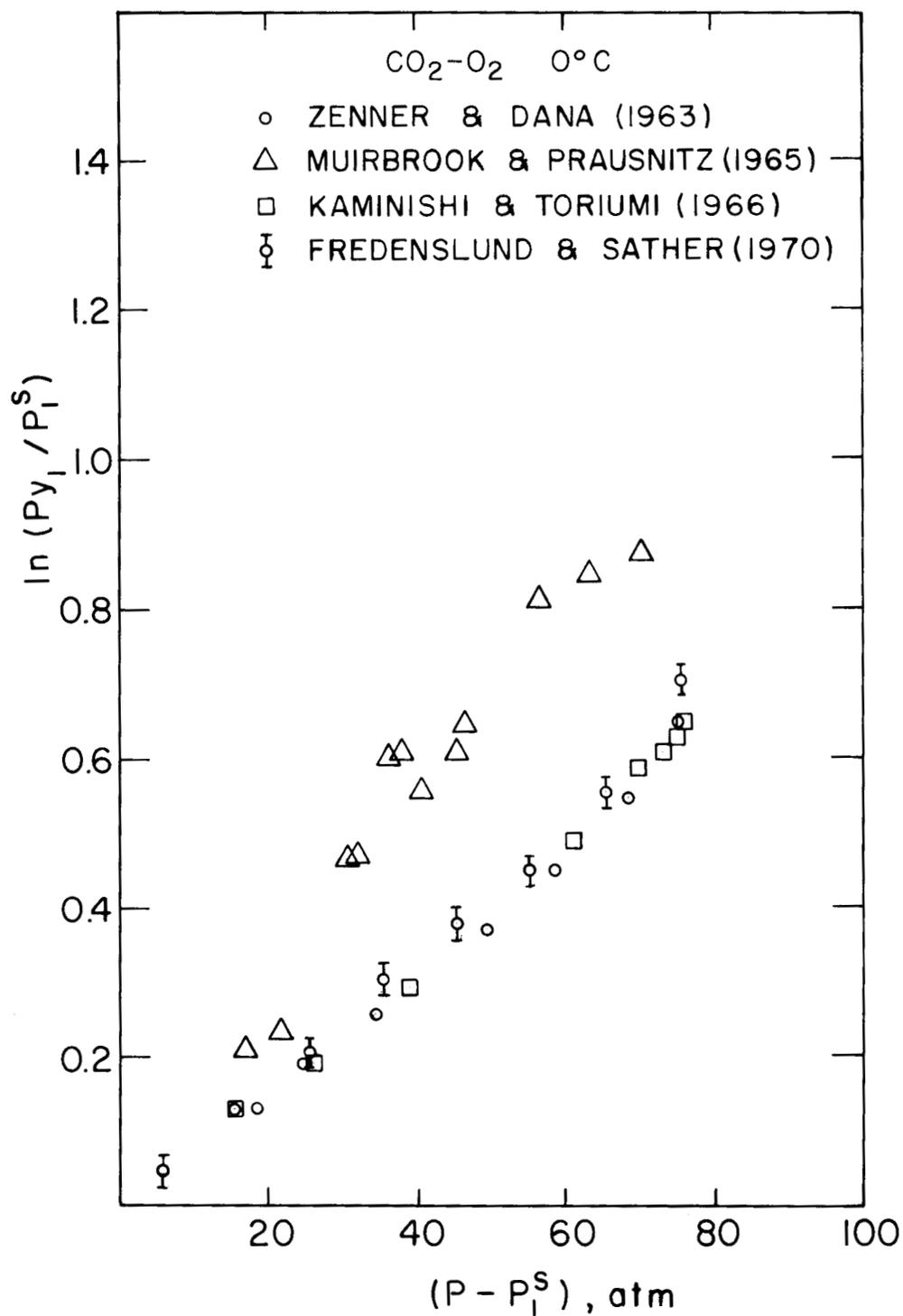


Fig. 6. Vapor-phase equilibrium data for the CO₂-O₂ system at 0°C.

where ϕ_2^G is the fugacity coefficient of the light gas evaluated at the vapor pressure of carbon dioxide and at infinite dilution. This value can be calculated accurately for many systems; hence the Henry's law constant can be evaluated without a knowledge of y_2 . To our knowledge, this relation has not been reported in the literature, where the quantity $\ln(\bar{f}_2^G/x_2)$ is usually plotted vs $(P - P_1^S)$. Calculation of \bar{f}_2^G , of course, requires a knowledge of y_2 .

The second type of plot, shown in Fig. 6, shows the natural logarithm of the enhancement factor, $\ln(Py_1/P_1^S)$, vs $(P - P_1^S)$. The enhancement factor must approach 1 as the pressure approaches P_1^S .

All of the data for the $\text{CO}_2\text{-O}_2$, $\text{CO}_2\text{-CO}$, and $\text{CO}_2\text{-N}_2$ systems were plotted, and selections were made of the data points to be used in the fit. Figures 5 and 6 illustrate data for the $\text{CO}_2\text{-O}_2$ system at 0°C for four different investigations. From these plots, it is apparent that the data of Muirbrook and Prausnitz²⁰ are grossly in error in the gas phase and somewhat inaccurate in the liquid as well. For this reason, they were eliminated from the correlation, as were the three very low points of Zenner and Dana²¹ shown at the bottom left of Fig. 5.

The surviving data points were then fitted to Eqs. (86) and (88) and the Henry's law correlation given in Appendix C by an optimization program described by Nedler and Mead.³⁰ The five parameters for each of the systems are reported in Table 3. Figure 4 illustrates a typical fit for the $\text{CO}_2\text{-CO}$ system at -30°C . Overall, the fit to these three systems appeared to be within the accuracy of the data, although not within the precision of individual investigators.

Table 3. Parameters for the vapor-liquid equilibrium correlation

System	Parameter				
	$T_{c_2}^{\infty}$ (°K)	$V_{c_2}^{\infty}$ (cc/g-mole)	α_{22} (cal/g-mole)	\bar{V}_o^{∞} (cc/g-mole)	$\bar{\beta} \times 10^5$ (°K ⁻¹)
CO ₂ - Xe	285.25	95.58		56.64	547
CO ₂ - O ₂	200.36	92.26	851.21	52.34	-7.8
CO ₂ - CO	180.44	86.48	863.47	48.59	-1810
CO ₂ - N ₂	197.66	93.93	885.60	50.03	137
CO ₂ - Kr	237.59	93.83		54.46	894

The available data for the CO₂-Kr and CO₂-Xe measured at ORNL and reported by Notz et al.¹⁹ were in the form of K factors at infinite dilution. These are directly related to the Henry's constant by:

$$\lim_{x_2 \rightarrow 0} \frac{y_2}{x_2} = \lim_{x_2 \rightarrow 0} \left(\frac{f_2^G}{x_2} \cdot \frac{1}{P\phi_2^G} \right) = \frac{H_{2,1}^{(P_1^S)}}{P_1^S \phi_2^G(x_2=0)} \quad (91)$$

After calculating the fugacity coefficient of krypton from the Redlich-Kwong equation of state, the Henry's law constant at the saturation pressure was obtained from xenon and krypton. A value of the partial molar volume must be known in order to obtain the value of the Henry's law constant at the reference pressure. These values were estimated, using a method described by Chueh and Prausnitz,³¹ at several temperatures and a value of $\bar{\beta}_1$ calculated (see Table 3). The Henry's law constants obtained at the vapor pressure were then corrected to the reference pressure, P₀,

$$\ln H_{2,1}^{(P_0)} = \ln H_{2,1}^{(P_1^S)} + \int_{P_1^S}^{(P_0)} \frac{\bar{V}_2}{RT} dP \quad (92)$$

The values of the Henry's law constants at the reference pressure were subsequently fitted to the correlation of Preston and Prausnitz,¹⁸ using the nonlinear fitting procedure discussed earlier. The values of T_{c2}^∞ and V_{c2}^∞ are reported in Table 3; the fit to the experimental data is shown in Fig. 7.

3.2.6 Correlation of Henry's law constants in a common solvent

Hildebrand et al.¹⁷ have suggested that the values of the Henry's law constant for gases dissolved in a common solvent are best correlated

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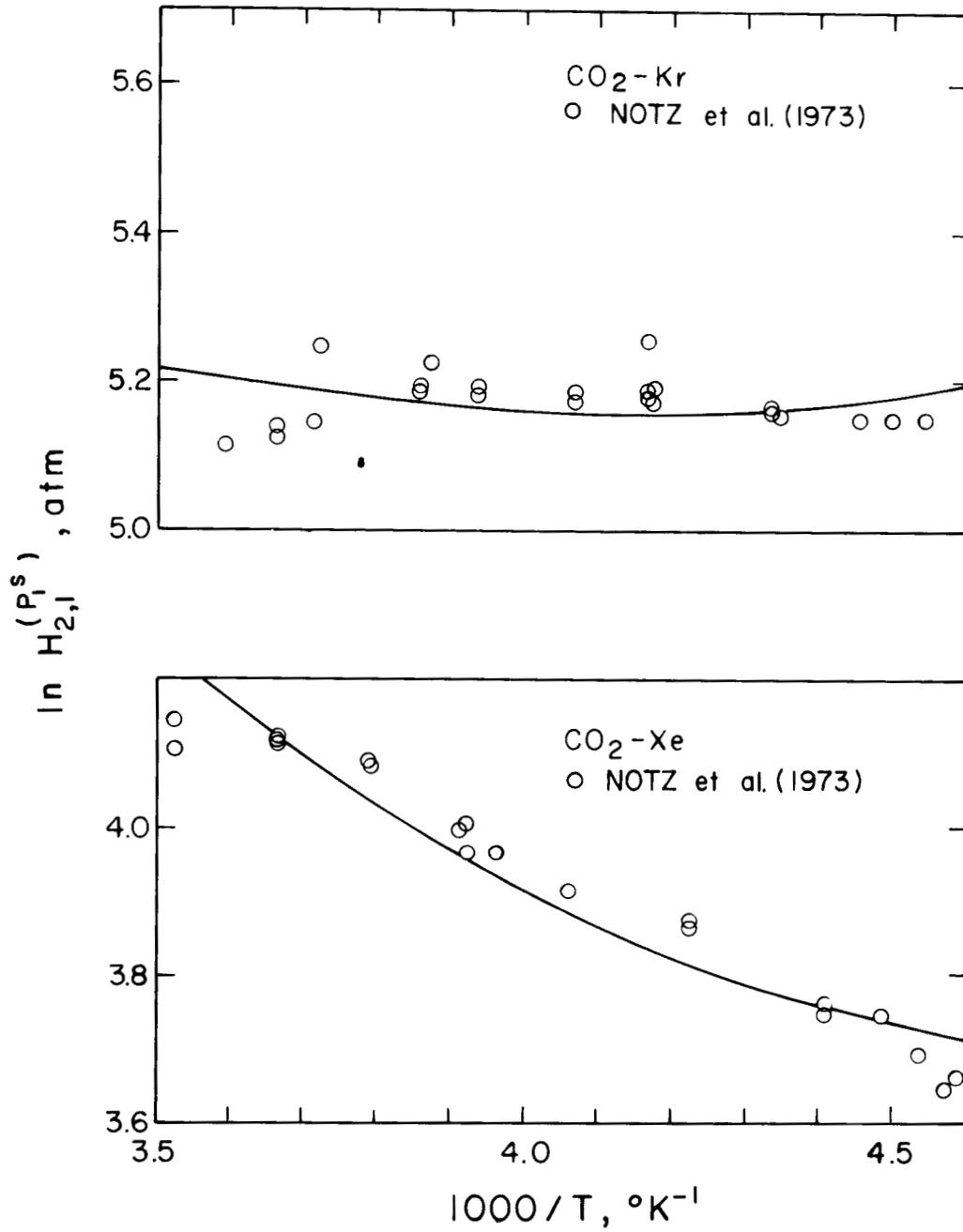


Fig. 7. Henry's law constants for the CO₂-Kr and CO₂-Xe systems as a function of temperature.

by plotting the logarithm of the Henry's law constant vs the energy of vaporization of the gas at its normal boiling point, ΔE_b^V . Using values of ΔE_b^V from Hildebrand et al.,¹⁷ the final results of the correlation were plotted at several temperatures as illustrated in Fig. 8 for -20°C .

Mobley⁷ previously analyzed all CO_2 -X binary systems available at that time using a plot similar to the one shown in Fig. 8 in order to distinguish between the two sets of krypton data available. He concluded that the KFA Jülich data²⁹ were in error, which was the same conclusion that Whatley⁶ reached by using other calculations as a basis. The value of the Henry's law constant as determined at KFA Jülich is reproduced in Fig. 8 for comparison. Mobley also concluded that the Henry's law constants based on the ORNL data were slightly high and chose to use values based on his own correlation.

New data for the CO_2 -CO system, as well as the measurements for the CO_2 -Xe system by ORNL, seem to indicate that all of the Henry's law constants for the system lie within about 10% of a straight line, as shown at -20°C . For this reason, the ORNL values were chosen to provide the "best" set of parameters. It is important to note that if the parameters are in error they will probably tend to predict conservative decontamination factors.*

3.3 Representation of Vapor and Liquid Enthalpy

3.3.1 Introduction

The enthalpy representation used in the equilibrium stage model, although simple, should be sufficiently accurate to provide quantitative

* Recent pilot-plant data of Glass et al.³² also confirm the CO_2 -Kr data of ORNL.

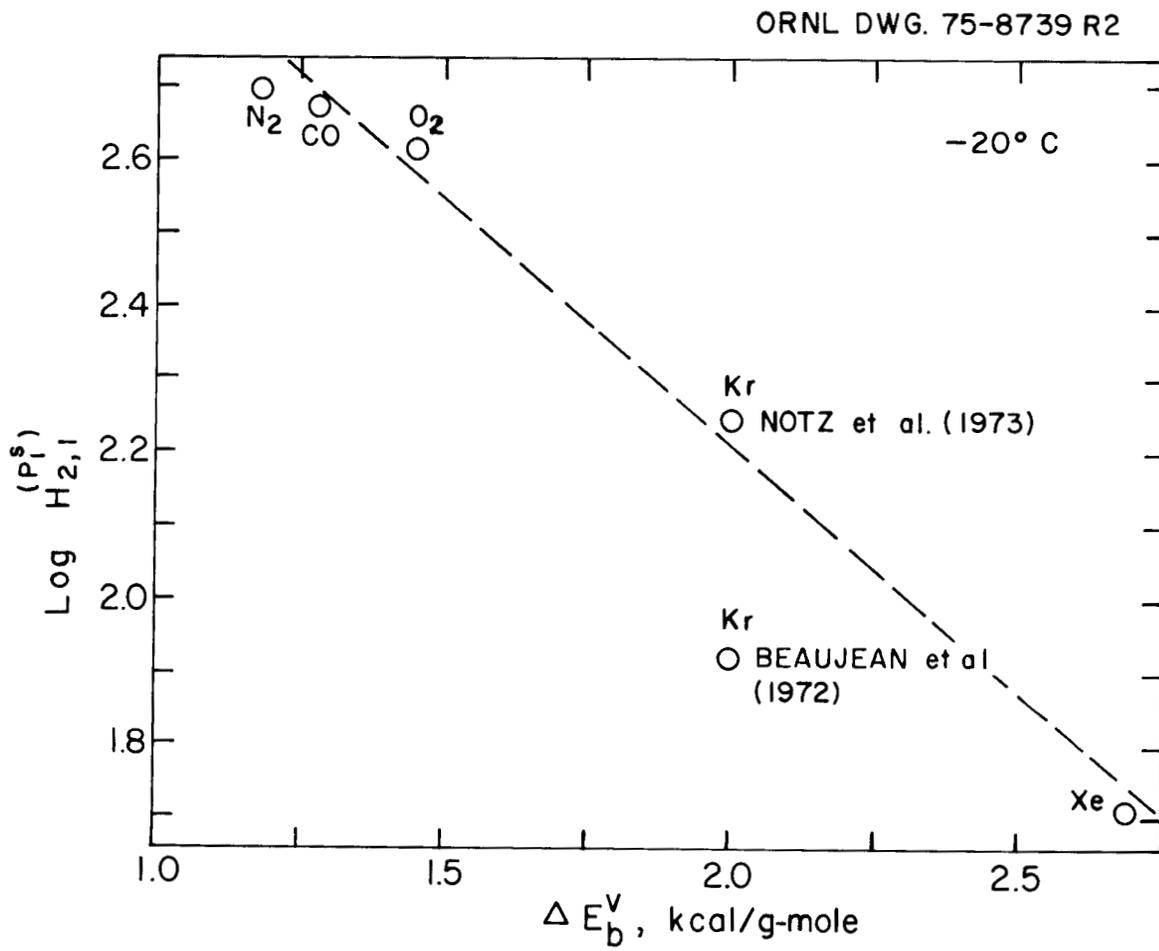


Fig. 8. Henry's law constants for the CO₂-X systems at -20°C.

agreement with actual system behavior. Adequate provision is made for nonidealities in the gas phase, but no attempt is made to consider the effect of pressure or concentration on the enthalpy of the liquid phase. The neglect of such effects is of little importance, particularly since the KALC process operates nearly isobarically and at low concentrations of dissolved gases.

The reference temperature for the enthalpy was chosen to be -40°C to conform with that given in published enthalpy tables for liquid carbon dioxide.

3.3.2 Correction for gas-phase nonideality

The corrections for the effect of gas-phase nonideality were taken into account by using the Redlich-Kwong equation of state with rules regarding mixtures as given by Prausnitz.¹⁵ A summary of those relations is given in Appendix B. The difference between the molar enthalpy of a component in an ideal gas state and the partial molar enthalpy in a gas mixture at the same temperature, pressure, and composition is:

$$h_k^o - \bar{H}_k^G = \frac{3/2}{T^{1/2}} \left\{ \frac{2}{b} \sum_{i=1}^M y_i a_{ik} \ln \left(\frac{v+b}{v} \right) - \frac{ab_k}{b^2} \ln \left(\frac{v+b}{v} \right) + \left(\frac{a}{b} \right) \left(\frac{vb_k - \bar{V}_k b}{v(v+b)} \right) \right\} + RT - P\bar{V}_k \quad (93)$$

This relation is applicable, of course, for a pure component as well as for a mixture. The enthalpy difference between an ideal gas mixture and a real gas mixture is given by:

$$h_m^o - h_m^G = \sum_{i=1}^M y_i (h_i^o - \bar{H}_i^G) \quad (94)$$

3.3.3 Enthalpy of carbon dioxide

The heat capacity of pure saturated liquid carbon dioxide was obtained from Glass et al.'s polynomial fit³³ to the liquid enthalpy:

$$C_s^L = 278.767 - 2.20936 T + 0.00471244 T^2 . \quad (95)$$

Integrating from T_0 and neglecting the effect of pressure,

$$h^L = 278.767 (T - T_0) - \frac{2.20936}{2} (T^2 - T_0^2) + \frac{0.00471244}{3} (T^3 - T_0^3). \quad (96)$$

The enthalpy of the carbon dioxide at any temperature in the ideal gas state was calculated from:

$$h^O = \Delta h_0^{\text{vap}} + (h_0^O - h_0^G) + \int_{T_0}^T C_p^O dT . \quad (97)$$

The heat of vaporization at T_0 , -40°C , was taken to be 3369.2 cal/g-mole from ref. 34. The value of $(h_0^O - h_0^G)$ was calculated from Eq. (93) applied to pure CO_2 at T_0 , and C_p^O was represented by:

$$C_p^O = \alpha + \beta T + \gamma T^2 . \quad (98)$$

The coefficients α , β , and γ are given in Table 4.

3.3.4 Enthalpy calculations for the light gases

The reference temperature for the light gases was also taken to be -40°C ; however, since the components do not exist as pure liquids at that temperature, the enthalpy was calculated relative to the partial molar enthalpy at infinite dilution in liquid carbon dioxide. The derivative of the Henry's law constant is used to relate this reference state to the ideal gas enthalpy, as follows:

Table 4. Coefficients for the ideal-gas heat-capacity polynomials^a and the enthalpy of the ideal gas at -40°C

Component	Coefficients			h_{i0}° (cal/g-mole)
	α	$\beta \times 10^3$	$\gamma \times 10^6$	
CO ₂	6.637	1.395	20.45	3513.05
Xe	4.968	0	0	521.93
O ₂	7.011	-0.810	2.8	-773.62
CO	6.962	-0.095	0.35	-194.51
N ₂	6.958	-0.035	0.15	-1199.32
Kr	4.968	0	0	-249.94

^aThe coefficients were evaluated by fitting the C_p° values at 100, 200, and 300°K. The latter values, except those for krypton and xenon, are taken from the JANAF Thermochemical Tables.³⁵ The values for krypton and xenon were obtained from Hultgren.³⁶

$$\frac{\partial \ln H_{i,1}^{(PO)}}{\partial(1/T)} = \frac{\bar{H}_i^\infty - h_i^o}{R}. \quad (99)$$

Since $\bar{H}_i^\infty = 0$ at T_o , evaluation of the derivative of the Henry's law constant using the correlation developed previously yielded the values of h_{i0}^o at -40°C given in Table 4. Values of h_i^o at other temperatures are calculated from:

$$h_i^o = h_{i0}^o + \int_{T_o}^T C_{pi}^o dT, \quad (100)$$

where h_{i0}^o is the value of the enthalpy of component i in the ideal gas state at -40°C . The heat capacity in the ideal gas state was given by a polynomial of the same form as Eq. (98). Table 4 gives the coefficients of the equation for the light gases, along with values for h_{i0}^o .

The values of \bar{H}_i^∞ at temperatures other than -40°C may be readily obtained from Eq. (99) after calculating the derivative of the Henry's constant from its correlation and h_i^o from Eq. (100).

3.3.5 Enthalpy calculation for the mixture

After the enthalpies of the pure components have been calculated for the ideal gas state, the enthalpy of the real gas mixture is given by:

$$h^G = \sum y_i \left[h_i^o - (h_i^o - \bar{H}_i^G) \right]. \quad (101)$$

The enthalpy of the liquid phase is calculated by assuming that $\bar{H}_{\text{CO}_2} = h_{\text{CO}_2}$ and that $\bar{H}_i = \bar{H}_i^\infty$ (i.e., that the solution is an ideal, infinitely dilute solution).

4. CONCLUSIONS

A computer program written for this study has been found to provide an "exact" solution to equilibrium stage models for the KALC process. This program, which uses the matrix techniques of Tierney and co-workers,^{8,9} is shown to be a convenient means for studying various column arrangements and specifications.

A thermodynamic correlation has been prepared using the Redlich-Kwong equation of state to represent the nonidealities of the gas phase and the unsymmetrical Margules equation to represent the nonidealities of the liquid phase. The values of the Margules constants, the Henry's law constants, and the partial molar volumes of the solute at infinite dilution have been determined for the CO₂-O₂, CO₂-N₂, CO₂-CO, CO₂-Xe, and CO₂-Kr systems from a careful selection of the best vapor-liquid equilibrium data. In the event that additional data for this system should become available or interest should develop in new systems, the form of the correlation will allow such information to be incorporated quite readily.

5. NOMENCLATURE

A = vapor recycle matrix; a_{ij} is fraction of total variable vapor leaving stage j that goes to stage i if $i \neq j$, and is -1 if $i = j$

a, a_i, a_{ij} = constants in Redlich-Kwong equation for the mixture, for pure i, and for the interaction

B = liquid recycle matrix; b_{ij} is fraction of total variable liquid leaving stage j that goes to stage i if $i \neq j$, and is -1 if $i = j$

- b, b_i = constants in Redlich-Kwong equation for the mixture and component i
- C_t, C_v = temperature and flow correction vectors; $c_{t,i}$ and $c_{v,i}$ are the temperature and flow corrections for stage i
- C_p^O = heat capacity in the ideal gas state, cal/g-mole-°K
- C_s^L = heat capacity of the saturated liquid, cal/g-mole-°K
- D_m, D_e = material and energy balance error vectors; $d_{m,i}$ and $d_{e,i}$ are the material and energy balance errors for stage i
- E_t, E_v = submatrices of Jacobian matrix ψ ; $e_{t,ij} = (\partial d_{m,i} / \partial t_j)$; $e_{v,ij} = (\partial d_{m,i} / \partial v_j^*)$
- ΔE_b^v = change in internal energy in going from liquid to the ideal gas state at the normal boiling point, kcal/g-mole
- $F, F^{(j)}$ = feed matrix and j th column of F ; f_{ij} is the amount of component j in feed to stage i , g-mole
- f_i^G = fugacity of component i in the gas phase, atm
- $f_1^{(PS)}$ = fugacity of pure liquid carbon dioxide at saturation, atm
- $f_1^{(PO)}$ = fugacity of pure liquid carbon dioxide at the reference pressure, atm
- G = vapor enthalpy vector; g_i is enthalpy of a mole of vapor in stage i
- G^{*j} = partial enthalpy of vapor (diagonal matrix); g_i^{*j} is the partial enthalpy of component j for vapor in stage i
- G_t = temperature dependence for vapor enthalpy (matrix); $g_{t,ij} = (\partial g_i / \partial t_j^*)$
- G_v = flow dependence for vapor enthalpy (matrix); $g_{v,ij} = (\partial g_i / \partial v_j^*)$
- g^{*EX} = excess molar Gibbs free energy based on an ideal dilute solution, cal/g-mole
- H = liquid enthalpy matrix; h_i is enthalpy of a mole of liquid in stage i
- H^{*j} = partial enthalpy of liquid (diagonal matrix); h_i^{*j} is the partial enthalpy of component j in stage i

- \bar{H}_i^G = partial molar enthalpy of component i in the gas state
 (same as an element g_i^{*j} in matrix G^{*j}), cal/g-mole
 \bar{H}_i^L = partial molar enthalpy of component i in the liquid
 state (same as an element h_i^{*j} in matrix H^{*j}),
 cal/g-mole
 $H_{i,l}^{(PO)}$ = Henry's law constant of component i in carbon dioxide
 at a reference pressure PO, atm
 H_t = temperature dependence for liquid enthalpy (matrix);
 $h_{t,ij} = (\partial h_i / \partial t_j)$
 H_v = flow dependence for liquid enthalpy (matrix); $h_{v,ij} =$
 $(\partial h_i / \partial v_j^*)$
 h_i^o = enthalpy of component i in the ideal gas state, cal/g-
 mole
 h_m^o = enthalpy of mixture in the ideal gas state, cal/g-mole
 h_o^G = enthalpy of gas at T_o , cal/g-mole
 Δh_o^{vap} = heat of vaporization at T_o , cal/g-mole
 h^o_L = enthalpy of liquid, cal/g-mole
 h_{io}^o = enthalpy of ideal gas component i at T_o , cal/g-mole
 J_{t,J_v}^J = submatrices of Ψ ; $j_{t,ik} = \partial d_{e,i} / \partial t_k$; $j_{v,ik} =$
 $\partial d_{e,i} / \partial v_k^*$
 K^j = equilibrium ratio matrix (diagonal); $k_i^j = y_{ij} / x_{ij}$
 K_i = equilibrium ratio, y_i / x_i
 L = liquid flow matrix, Eq. (21)
 L' = fixed liquid flow matrix, l_{ij} is a flow of liquid from
 stage j to i which is held constant
 $M_o^j, M_1^j, M_2^j, M_3^j, M_4^j$ = defined by Eqs. (26), (42), (44), (55), and (56)
 \bar{N} = normalization matrix (diagonal), Eq. (31)
 NA = stage number of bottom stage in absorber column
 NF = stage number of bottom stage in fractionator column
 NSF = stage number of feed stage in stripper-rectifier column
 n_i = number of moles of i

- n = total number of moles
 P = pressure, atm
 P_1^s = saturation vapor pressure of carbon dioxide, atm
 Q = vector of heat additions; q_i is heat energy added to stage i
 Q_f = feed enthalpy vector; $q_{f,i}$ is total enthalpy of all feeds to stage i
 R = matrix defined by $R = B^{-1}A$
 R = gas constant in appropriate units
 T = temperature vector; t_i is temperature of stage i
 T = temperature, °K
 T_0 = reference temperature of -40°C or 233.15°K
 T_c^∞ = parameter in Henry's law constant correlation, °K
 U = vector consisting of all 1's
 V = vapor flow matrix, Eq. (20)
 V' = fixed vapor flow matrix; v_{ij} is a flow of vapor from stage j to stage i which is held constant
 V^* = vapor flow variable (diagonal matrix); v_i^* is the sum of all vapor flows leaving stage i except those in V'
 V_c^∞ = parameter in Henry's law constant correlation, cc/g-mole
 \bar{V}_i = partial molar volume of component i , cc/g-mole
 \bar{V}_i^∞ = partial molar volume of component i at infinite dilution, cc/g-mole
 v = molar volume of gas, cc/g-mole
 v_1^L = molar volume of pure liquid carbon dioxide, cc/g-mole
 W_1, W_2 = matrices defined by Eqs. (61) and (62)
 $X, X^{(j)}$ = liquid composition matrix and j th column of X ; x_{ij} is composition of component j in liquid in stage i
 X_t^j = temperature dependence for liquid composition (matrix);
 $x_{t,ik}^j = (\partial x_{ij} / \partial t_k)$
 X_v^j = flow dependence for liquid composition (matrix); $x_{v,ik}^j =$
 $(\partial x_{ij} / \partial v_k^*)$

- x_i = mole fraction component i in liquid
 $Y, Y^{(j)}$ = vapor composition matrix and j th column of Y ; y_{ij} is composition of component j in vapor in stage i
 Y_t^j = temperature dependence for vapor composition (matrix);
 $y_{t,ik}^j = (\partial y_{ij} / \partial t_k)$
 Y_v^j = flow dependence for vapor composition (matrix); $j_{v,ik}^j = (\partial y_{ij} / \partial v_k^*)$
 y_i = mole fraction component i in vapor
 $Z^j = L + V K^j$

Greek Alphabet

- α_{ij} = coefficient in expansion of excess free energy representing interaction of components i and j
 α, β, γ = coefficients in heat capacity equation for ideal gas
 $\bar{\beta}_i$ = average coefficient of expansion for component i
 Γ = matrix of liquid-phase activity coefficients; γ_{ij} = activity coefficient of component j in stage i
 $\gamma_i^{\square}(P_0)$ = activity coefficient of component i corrected to the reference pressure, unsymmetric convention
 γ_1 = activity coefficient of carbon dioxide at system pressure
 $\gamma_1^{(P_0)}$ = activity coefficient of carbon dioxide corrected to the reference pressure
 Λ = vector of material and energy balance errors; λ_i is the material balance error for $i \leq N$ and energy balance error for $N < i \leq 2N$
 ξ = subscript indicating iteration number
 Φ = matrix of vapor-phase fugacity coefficients; ϕ_{ij}^G = fugacity coefficient of component j in stage i
 ϕ_i^G = gas-phase fugacity coefficient
 Ψ = Jacobian matrix of errors

Subscripts

e = energy balance

f = feed

i,j,k = indices for matrices; also used to indicate component or stage number

m = material balance

t = temperature

v = flow

o = evaluated at reference temperature of -40°C

c = critical conditions

s = saturated

Superscripts

j = component

G = gas

∞ = infinite dilution

P₀ = reference pressure

s = saturated

□ = convention of infinite dilution

o = ideal gas

6. REFERENCES

1. Don E. Ferguson, Paul A. Haas, and Rex E. Leuze, "Quantitative Recovery of Krypton from Gas Mixtures Mainly Comprising Carbon Dioxide," U.S. Patent No. 3,742,720 (July 3, 1973).

2. R. W. Glass et al., HTGR Head-End Processing: A Preliminary Evaluation of Processes for Decontaminating Burner Off-Gas, ORNL/TM-3527 (July 1972).
3. M. E. Whatley, R. W. Glass, P. A. Haas, A. B. Meservey, and K. J. Notz, "Decontamination of HTGR Reprocessing Off-Gases," pp. 86-101 in Proceedings of the 12th AEC Air Cleaning Conference, Oak Ridge, Tenn., Aug. 28-31, 1972, CONF-720823, Vol. 1 (Jan. 1973).
4. R. W. Glass, H. W. R. Beaujean, H. D. Cochran, Jr., P. A. Haas, D. M. Levins, and W. M. Woods, "Development of the Krypton Absorption in Liquid Carbon Dioxide (KALC) Process for HTGR Off-Gas Reprocessing," pp. 232-45 in Proceedings of the 13th AEC Air Cleaning Conference, San Francisco, Calif., Aug. 12-15, 1974, CONF-740807, Vol. 1 (March 1975).
5. R. W. Glass, H. D. Cochran, Jr., D. M. Levins, J. W. Snider, D. C. Watkin, W. M. Woods, and M. E. Whatley, System Features and Component Descriptions for the Unit Operations Off-Gas Decontamination Facility, ORNL/TM-4596 (February 1975).
6. M. E. Whatley, Calculations on the Performance of the KALC Process, ORNL-4859 (April 1973).
7. R. M. Mobley, Calculations for the Separation of Radioactive Krypton from the Off-Gas from the Reprocessing of High Temperature Gas-Cooled Reactor Fuel Elements, M.S. thesis, Clemson University, Clemson, S.C., 1973.
8. J. W. Tierney and J. A. Bruno, "Equilibrium Stage Calculations," A.I.Ch.E., J. 13, 556-63 (1967).

9. J. W. Tierney and J. L. Yanosik, "Simultaneous Flow and Temperature Correction in the Equilibrium Stage Problem," *A.I.Ch.E. J.* 15, 897-901 (1969).
10. B. D. Smith, Design of Equilibrium Stage Processes, McGraw-Hill, New York, 1963.
11. J. R. Friday and B. D. Smith, "An Analysis of the Equilibrium Stage Problem, Formulation and Convergence," *A.I.Ch.E. J.* 10, 698-706 (1964).
12. N. R. Amundson and A. J. Pontinen, "Multicomponent Distillation Calculations on a Large Digital Computer," *Ind. Eng. Chem.* 50, 730-36 (1958).
13. N. R. Amundson, A. J. Pontinen, and J. W. Tierney, "Multicomponent Distillation Calculations on a Large Digital Computer," *A.I.Ch.E. J.* 5, 295-300 (1959).
14. A. Michel, T. Wassenaar, T. Zwietering, and P. Smits, The Vapor Pressure of Liquid Carbon Dioxide, *Physica XVI* (5), 501-4 (May 1950).
15. J. M. Prausnitz, Molecular Thermodynamics of Fluid-Phase Equilibria, Prentice-Hall, Inc., Englewood Cliffs, N.J., 1969.
16. N. K. Muirbrook, Experimental and Thermodynamic Study of the High-Pressure Vapor-Liquid Equilibria for the Nitrogen-Oxygen-Carbon Dioxide System, Ph.D. thesis, University of California, Berkeley, 1964.
17. J. H. Hildebrand, J. M. Prausnitz, and R. L. Scott, Regular and Related Solutions (The Solubility of Gases, Liquids, and Solids), Van Nostrand-Reinhold, New York, 1970.

18. G. T. Preston and J. M. Prausnitz, "A Generalized Correlation for Henry's Constants in Nonpolar Systems," *Ind. Eng. Chem., Fundamentals* 10, 389-97 (1971).
19. K. J. Notz, A. B. Meservey, and R. D. Ackley, "The Solubility of Krypton and Xenon in Liquid CO₂," *Trans. Am. Nucl. Soc.* 17, 318-19 (1973).
20. N. K. Muirbrook and J. M. Prausnitz, "Multicomponent Vapor-Liquid Equilibria at High Pressures: Part I. Experimental Study of the Nitrogen-Oxygen-Carbon Dioxide System at 0°C," *A.I.Ch.E. J.* 11, 1092-96 (1965).
21. G. H. Zenner and L. I. Dana, "Liquid-Vapor Equilibrium Compositions of Carbon Dioxide-Oxygen-Nitrogen Mixtures," *Chem. Eng. Progr., Symp. Ser.* 59(44), 36-41 (1963).
22. G. Kaminishi and T. Toriumi, "Vapor-Liquid Equilibria Between Liquid Carbon Dioxide and Hydrogen, Nitrogen and Oxygen," *Kogyo Kagaku Zasshi* 69(2), 175-78 (1966).
23. A. Fredenslund and G. A. Sather, "Gas-Liquid Equilibrium of the Oxygen-Carbon Dioxide System," *J. Chem. Eng. Data* 15, 17-22 (1970).
24. A. Fredenslund, J. Mollerup, and O. Persson, "Gas-Liquid Equilibrium of the Oxygen-Carbon Dioxide System," *J. Chem. Eng. Data* 17, 440-43 (1972).
25. G. Kaminishi et al., "Vapor-Liquid Equilibria for Binary and Ternary Systems Containing Carbon Dioxide," *J. Chem. Eng. (Japan)* 1(2), 109-16 (1968).
26. L. J. Christiansen, A. Fredenslund, and N. Gardner, "Gas-Liquid Equilibria of the CO₂-CO and CO₂-CH₄-CO Systems," *Advan. Cryog. Eng.* 19, 309-19 (1974).

27. Y. A. Abdullaev, "Equilibrium in the Liquid Carbon Dioxide System in the Presence of Technical Gases," *J. Chem. Eng. (USSR)* 16, 37-40 (1939).
28. F. Pollitzer and Z. Strebel, "The Influence of an Indifferent Gas on the Saturation Vapor Concentration of a Liquid," *Z. Phys. Chem.* 110, 768-85 (1924).
29. H. Beaujean, M. Laser, J. Bohnenstingl, P. Filss, M. Heidendael, St. Mastera, E. Merz, and H. Vygen, "Off-Gas Treatment and Krypton in HTGR-Fuel Element Reprocessing," presented at the Symposium on Management of Radioactive Waste from Fuel Reprocessing, Paris, France, Nov. 18, 1972.
30. J. A. Nelder and R. Mead, "A Simplex Method for Function Minimization," *Comp. J.* 7, 308-13 (1965).
31. P. L. Chueh and J. M. Prausnitz, "Vapor-Liquid Equilibria at High Pressures: Calculation of Partial Molar Volumes in Nonpolar Liquid Mixtures," *A.I.Ch.E. J.* 13, 1099-1107 (1967).
32. R. W. Glass, H. W. R. Beaujean, V. L. Fowler, T. M. Gilliam, D. J. Inman, and D. M. Levins, Krypton Absorption in Liquid CO₂ (KALC): Campaign II in the Experimental Engineering Section Off-Gas Decontamination Facility, ORNL/TM-5095 (February 1976).
33. R. W. Glass, T. M. Gilliam, and V. L. Fowler, An Empirical Model for Calculating Vapor-Liquid Equilibrium and Associated Phase Enthalpy for the CO₂-O₂-Kr-Xe System for Application to the KALC Process, ORNL/TM-4947 (January 1976).
34. R. H. Perry, C. H. Chilton, and S. D. Kirkpatrick (Eds.), Chemical Engineers Handbook, 4th ed., Sect. 3-159, McGraw-Hill, New York, 1963.

35. D. R. Stull (Project Director), JANAF Thermochemical Tables, Dept. of Commerce, National Bureau of Standards, Prepared by The Thermal Research Laboratory, Dow Chemical Company, Midland, Mich. (1965).
36. R. R. Hultgren, Selected Values of the Thermodynamic Properties of the Elements, American Society for Metals, Metals Park, Ohio, 1973.
37. K. S. Pitzer et al., "The Volumetric and Thermodynamic Properties of Fluids. II. Compressibility Factor, Vapor Pressure and Entropy of Vaporization," J. Am. Chem. Soc. 77, 3433-40 (1955).
38. J. M. Prausnitz and P. L. Chueh, Computer Calculations for High-Pressure Vapor-Liquid Equilibria, Prentice-Hall, Inc., Englewood Cliffs, N.J., 1968.



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7. APPENDIXES

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7.1 Appendix A: Basic Thermodynamic Relations

For systems such as the one under consideration in this report, it is normally most convenient to use the unsymmetric convention to represent the activity coefficients. The Henry's law convention is used for all light components. At equilibrium,

$$\mu_i^L = \mu_i^G \quad (A-1)$$

If we let P^0 represent a reference pressure which is taken to be zero here, the activity coefficient of the light components is defined by:

$$\mu_i^L = \mu_i^\square(P^0, T) + RT \ln \gamma_i^\square x_i; \quad (A-2)$$

and

$$\lim_{x_i \rightarrow 0} \gamma_i^\square = 1.0 \quad \text{for } i=2,3,\dots,M. \quad (A-3)$$

For component 1, the normal convention is used:

$$\mu_1^L = \mu_1^*(P^0, T) + RT \ln \gamma_1 x_1; \quad (A-4)$$

and

$$\lim_{x_1 \rightarrow 1} \gamma_1 = 1.0. \quad (A-5)$$

The reference state refers to the pure liquid at P^0 and T . For the gas phase, the usual equation¹⁵ relating fugacity and chemical potential

is used for all components with a reference state, the ideal gas at 1 atm:

$$\mu_i^G = \mu_i^O(T) + RT \ln \bar{f}_i^G. \quad (\text{A-6})$$

Substituting Eqs. (A-6) and (A-2) into Eq. (A-1) and rearranging, we obtain

$$\ln \frac{\bar{f}_i^G}{\gamma_i^\square x_i} = \frac{\mu_i^\square(\text{PO}, T) - \mu_i^O(T)}{RT}. \quad (\text{A-7})$$

At constant temperature the right-hand side (and hence the left-hand side) of the equation is constant and may be used to define the Henry's law constant at the reference pressure PO , as follows:

$$\ln H_{i,1}^{(\text{PO})} = \ln \frac{\bar{f}_i^G}{\gamma_i^\square x_i} = \frac{\mu_i^\square(\text{PO}, T) - \mu_i^O(T)}{RT}. \quad (\text{A-8})$$

The effects of temperature and pressure on the Henry's law constant follow directly from Eq. (A-8) by partial differentiation:¹⁵

$$\frac{\partial \ln H_{i,1}^{(\text{P})}}{\partial P} = \bar{V}_i^\infty \quad (\text{A-9})$$

and

$$\frac{\partial \ln H_{i,1}^{(\text{PO})}}{\partial (1/T)} = \frac{\bar{H}_i^\infty - h_i^O}{R}. \quad (\text{A-10})$$

Returning to Eq. (A-8) and writing the fugacity in terms of the fugacity coefficient,

$$\phi_i^G \equiv \frac{\bar{f}_i^G}{P y_i}, \quad (\text{A-11})$$

the following relation is obtained:

$$H_{i,1}^{(PO)} = Py_i \phi_i^G / \gamma_i^\square x_i \quad . \quad (A-12)$$

Rewriting Eq. (A-12) in terms of K factors gives:

$$K_i = \frac{y_i}{x_i} = \frac{H_{i,1}^{(PO)} \gamma_i^\square}{P \phi_i^G} \quad \text{for } i=2,3,\dots,M \quad . \quad (A-13)$$

In a similar manner for component 1 (carbon dioxide), Eqs. (A-4) and (A-6) are substituted into (A-1); rearranging, then, yields:

$$\ln \frac{\bar{f}_1^G}{\gamma_1 x_1} = \frac{\mu_1^*(PO, T) - \mu_1^o(T)}{RT} \quad . \quad (A-14)$$

Again, the right-hand side is independent of composition and must equal the natural logarithm of the fugacity of pure liquid carbon dioxide at PO, $\ln f_1^{(PO)}$. Rewriting as before in terms of the K factor using the definition of ϕ_1^G yields:

$$K_1 = \frac{f_1^{(PO)} \gamma_1}{P \phi_1^G} \quad . \quad (A-15)$$

The effect of pressure on activity coefficients defined with a reference state at a fixed pressure is:¹⁵

$$\frac{\partial \ln \gamma_i}{\partial P} = \frac{\bar{V}_i}{RT} \quad . \quad (A-16)$$

Equation (A-16) follows directly from differentiating Eqs. (A-2) and (A-4). Using this relation, the K factor equations are rewritten as:

$$K_i = \frac{H_{i,1}^{(PO)} \gamma_i^\square(PO)}{P \phi_i^G} \exp \int_{PO}^P \frac{\bar{V}_i}{RT} dP \quad i=2,3,\dots,M \quad , \quad (A-17)$$

and

$$K_1 = \frac{f_1^{(PO)} \gamma_1^{(PO)}}{P \phi_1^G} \exp \int_{P_0}^P \frac{\bar{v}_1 dP}{RT} \quad (A-18)$$

Equations (A-17) and (A-18) are exact thermodynamic relations for the K factors expressed in terms of quantities that are more easily correlated than x and y.

7.2 Appendix B: Redlich-Kwong Equation of State and Procedure RKWONG

7.2.1 The equation of state

The Redlich-Kwong equation of state with mixture rules as given by Prausnitz¹⁵ was used to represent the properties of the gas phase. The basic equation of state is:

$$\frac{Pv}{RT} = \frac{v}{v-b} - \frac{a}{RT^{3/2}(v+b)} \quad (B-1)$$

In the case of a pure component, the constants a and b are related to the critical temperature and pressure by:

$$a = \frac{\Omega_a R^2 T_c^{2.5}}{P_c} \quad (B-2)$$

and

$$b = \frac{\Omega_b RT_c}{P_c} \quad (B-3)$$

If the equation is fitted such that the first and second partial derivatives of pressure with respect to volume are zero at the critical point, $\Omega_a = 0.4278$ and $\Omega_b = 0.0867$. For a number of substances, including carbon dioxide, Prausnitz reports values of Ω_a and Ω_b that were adjusted to fit the saturated vapor curve; the

corresponding values for carbon dioxide were 0.4470 and 0.0911 respectively. The universal values of Ω_a and Ω_b were used for the light gases.

To predict the properties of the mixture, Prausnitz gives the following rules with regard to mixtures:

$$a = \sum_{i,j=1}^M y_i y_j a_{ij}, \quad (\text{B-4})$$

$$b = \sum_{i=1}^M y_i b_i, \quad (\text{B-5})$$

$$a_{ij} = \frac{(\Omega a_i + \Omega a_j) R^2 T_{cij}^{2.5}}{2P_{cij}} \quad (\text{B-6})$$

$$P_{cij} = \frac{Z_{cij} R T_{cij}}{v_{cij}}, \quad (\text{B-7})$$

$$v_{cij}^{1/3} = 1/2 (v_{ci}^{1/3} + v_{cj}^{1/3}), \quad (\text{B-8})$$

$$Z_{cij} = 0.291 - 0.08 \frac{(\omega_i + \omega_j)}{2}, \quad (\text{B-9})$$

$$T_{cij} = (T_{ci} T_{cj})^{1/2} (1 - k_{ij}). \quad (\text{B-10})$$

In Eqs. (B-4) through (B-10) the symbols have their usual meaning; the subscript c refers to the critical point for the pure component, but not for $i \neq j$. Here ω is the acentric factor defined by Pitzer.³⁷ If the values of T_c , P_c , and V_c are used to evaluate the constants, ω is not needed. However, Eq. (B-9) is usually more reliable for calculating Z_c for the pure component than directly from P_c , V_c , and T_c .

Values of Ω_a , Ω_b , ω , T_c , and P_c (see Table 5) were input for the systems considered in this work. Values of a and b were then determined by using Eq. (B-9) to calculate Z_c for the pure components and Eq. (B-7) as written for the pure component to calculate V_c . The calculations then proceeded sequentially with Eqs. (B-8), (B-9), (B-10), (B-7), (B-6), and (B-4) to calculate a . The value of b was calculated directly from Eqs. (B-3) and (B-5).

The Redlich-Kwong equation of state was used to calculate the fugacity coefficient in the gas phase, as well as the deviation of the enthalpy of the real gas mixture from the ideal gas mixture. The fugacity coefficient is given by:¹⁵

$$\ln \phi_k = \ln\left(\frac{v}{v-b}\right) + \frac{b_k}{v-b} - 2 \sum_{i=1}^M \left[\frac{y_i a_{ik}}{RT^{3/2} b} \right] \ln\left(\frac{v+b}{v}\right) + \frac{ab_k}{RT^{3/2} b^2} \left[\ln\left(\frac{v+b}{v}\right) - \frac{b}{v+b} \right] - \ln \frac{Pv}{RT} \quad (B-11)$$

In order to carry out the component-by-component computations of the equilibrium stage model, it was convenient to calculate the quantity $(h_k^o - \bar{H}_k)$ for each component. An equation for use in calculating this quantity can be obtained as follows.

The Redlich-Kwong equation is substituted into the exact thermodynamic relation¹⁵

$$H - \sum_{i=1}^M n_i h_i^o = \int_V^\infty \left[P - T \left(\frac{\partial P}{\partial T} \right)_{V,N} \right] dV + PV - nRT \quad (B-12)$$

The resulting equation may be differentiated with respect to M_k at constant P , T , and $M_{j \neq k}$ to obtain:

Table 5. Parameters for the Redlich-Kwong equation of state

Component	Ω_a	Ω_b	ω	T_c (°K)	P_c (atm)
CO ₂	0.4470	0.0911	0.225	304.2	72.8
Xe	0.4278	0.0867	0	289.7	57.6
O ₂	0.4278	0.0867	0.021	154.6	49.8
CO	0.4278	0.0867	0.041	132.9	34.5
N ₂	0.4278	0.0867	0.04	126.2	33.5
Kr	0.4278	0.0867	0	209.4	54.3

$$h_k^o - \bar{H}_k = \frac{3/2}{T^{1/2}} \left\{ \frac{2}{b} \left[\sum_{i=1}^M y_i a_{ik} \right] \ln \left(\frac{v+b}{v} \right) - \frac{ab_k}{b^2} \ln \left(\frac{v+b}{v} \right) \right. \\ \left. + \left(\frac{a}{b} \right) \left(\frac{vb_k - \bar{v}_k b}{v(v+b)} \right) \right\} + RT - P \bar{v}_k \quad (B-13)$$

In Eq. (B-13) the partial molar volume, \bar{v}_k was calculated from the relation given by Prausnitz and Chueh:³⁸

$$\bar{v}_k = \frac{\frac{RT}{v-b} + \frac{RTb_k}{(v-b)^2} - \frac{2 \sum_{i=1}^M y_i a_{ik}}{T^{1/2} v(v+b)} + \frac{ab_k}{T^{1/2} v(v+b)^2}}{\frac{RT}{(v-b)^2} - \frac{a}{T^{1/2}} \left[\frac{2v+b}{v^2(v+b)^2} \right]} \quad (B-14)$$

The difference between the enthalpy of the ideal gas and that of the mixture is calculated from:

$$h^o - h = \sum_{i=1}^M y_i (h_i^o - \bar{H}_i) \quad (B-15)$$

These values were calculated using the procedure RKWONG described in Sect. 7.2.2.

7.2.2 Procedure RKWONG

RKWONG: PROC(L, M, Y, P, T, PHIG, DELHBAR, DELH);

The procedure was linked to the main program by the parameters:

L = logic parameter with values of 1, 2, and 3, binary fixed

- 1 - reads input data (see below).
- 2 - (this option is presently inoperative)
- 3 - calculates PHIG, DELHBAR, and DELH

M = number of components, binary fixed

Y = vector of vapor mole fractions, binary float

P = pressure, atm, binary float

T = temperature, °K, float

PHIG = vector of fugacity coefficients, ϕ_i^G , binary float

DELHBAR = vector of $(h_i^O - \bar{H}_i)$, cal/g-mole, binary float

DELH = $\sum_{i=1}^M y_i (h_i^O - \bar{H}_i)$, cal/g-mole, binary float

Input:

(1) $\Omega_a \Omega_b \omega T_c P_c V_c$ IDENT

Card (1) is repeated M times. V_c is normally input as zero;

in this case, it is calculated from Eqs. (B-9) and (B-7). IDENT

is an eight-character string variable used to identify a component.

(2) k_{ij} for values of i from 1 to M-1 and j

from 2 to M. The order is:

$k_{12}, k_{13} \dots k_{1M}; k_{23}, k_{24} \dots k_{2M}$, etc.

The values of k_{ij} have been input as zero.

7.3 Appendix C: Henry's Law Constant Correlation and Procedure HENRY'S

7.3.1 Henry's law constant correlation

The Henry's constant correlation used in the model of the KALC process is a generalized correlation of Preston and Prausnitz¹⁸ based on the statistical mechanics of dilute solutions in conjunction with the two-fluid theory of Scott and a reduced empirical equation of state. The resulting generalized equation for the Henry's constant is:

```

RKWCNG: PROC (L,M,Y,E,T,FEIG,DELHEAR, DELH) ;
DCL F BINARY FICAT ;
DCL RT ;
DCL EX,AM,BM ;
DCL R STATIC ;
DCL (Y(*), PHIG(*), VEAR(M), DELHEAR(*) ) BINARY FLOAT ;
DCL Z STATIC ;
DCL I, J ;
DCL S(3) IAEFI ;
DCL (A(M,M), E(M), OMEGA(M) FLOAT, OMEGB(M) FLOAT,
ZC(M,M), W(M), PC(M,M), VC(M,M), TC(M,M), K(M,M) ) FLOAT,
IDENT(M) CHAR(8) ) CIL ;
R = 0.0820574 ; EX = 1/3 ;
GO TO S(L) ;
S(1): PUT SKIP(2) FLIT('INPUT PARAMETERS FOR R_K EQUATION',
'OMEGA', 'CMEGE', 'W', 'TC, DEGK', 'PC, ATM', 'VC, LITER',
'COMPONENT')
(X(10), A, SKIP, X(15), A, X(5), A, X(8), A, X(4), A, X(5),
A, X(2), A, X(1), A) ;
ALLOCATE A, E, CMEGA, CMEGE, ZC, W, PC, VC, TC, K, IDENT ;
DO I = 1 TC M ;
GET LIST (OMEGA(I), CMEGB(I), W(I), TC(I,I), PC(I,I),
VC(I,I), IDENT(I) ) ;
PUT SKIP EDIT (OMEGA(I), CMEGE(I), W(I), TC(I,I), PC(I,I),
VC(I,I), IDENT(I))
(X(10), F(10,5), F(10,5), F(10,3), F(10,2), F(10,2), F(10,5), X(2),
A(8) ) ;
END ;
PUT SKIP(2) EDIT('CORRECTICNS FOR GEOM MEAN, KIJ') (X(10), A) ;
DO I = 1 TC M-1 ;
PUT SKIP EDIT (I) (X(10), F(2) ) ;
DO J = I+1 TO M ;
GET LIST (K(I,J)) ;
PUT EDIT (K(I,J)) (F(10,3)) ;
END ; END ;
DO I = 1 TC M ;
DO J = I TO M ;
ZC(I,J) = 0.291-0.06*(W(I) + W(J))/2 ;
END ;
IF VC(I,I) > C THEN ZC(I,I) = PC(I,I)*VC(I,I)/(R*TC(I,I)) ;
ELSE ; VC(I,I) = ZC(I,I)*R*TC(I,I)/PC(I,I) ;
B(I) = OMEGB(I)*R*TC(I,I)/PC(I,I) ;
END ;
DO I = 1 TO M ;
DO J=I+1 TC M ;
VC(I,J) = (((VC(I,I)**EX+ VC(J,J)**EX)/2))**3 ;
TC(I,J) = SQRT(TC(I,I)*TC(J,J))*(1-K(I,J)) ;
PC(I,J) = ZC(I,J)*R*TC(I,J)/VC(I,J) ;
END ; END ;
DO I = 1 TO M ; DO J = I TC M ;
A(I,J) = (OMEGA(I) + OMEGA(J))*R*R*(TC(I,J)**2.5)/(2*PC(I,J)) ;
A(J,I) = A(I,J) ;
END ; END ;
RETURN ;
S(2): Z = 1.0 ;
RETURN ;
S(3): AM = 0 ;
RT = R*T ;

```

```

BM = 0 ;
DO I = 1 TO M ;
BM = BM + Y(I)*E(I) ;
DO J = 1 TO M ;
AM = AM+Y(I)*Y(J)*A(I,J) ;
END ; END ;
CALL VCLG ;
DELH = RT*(1.5*AM/(EM*RT*I**0.5)*LOG((VG+EM)/VG)+1-P*VG/RT) ;
DELH = (1.9E726/C.0E20574)*DELH ;
DO I = 1 TO M ;
PHIG(I) = FUNCT(I) ;
VBAR(I) = VFUNCT(I) ;
DELHBAE(I) = HFUNCT(I) ; END ;
FUNCT: PROC(I) ;
DCL X ;
X = 0 ; DO J = 1 TO M ; X = X+Y(J)*A(J,I) ; END ;
X = -2*X ;
X = (X/(R*EM*I**1.5))*ICG((VG+EM)/VG) + ICG(VG/(VG-EM))
+ B(I)/(VG-EM) + AM*E(I)*(LOG((VG+EM)/VG)-EM/(VG+EM))/
(R*I**1.5*EM*EM) - ICG(P*VG/(R*I)) ;
X = EXP(X) ;
RETURN(X) ;
END FUNCT ;
VFUNCT: PRCC(I) ;
DCL X,J,XX ;
T12 = SQRT(T) ; RT = R*I ;
X = 0 ;
DO J = 1 TO M ; X = X + Y(J)*A(J,I) ; END ;
X = -2*X/(T12*VG*(VG+EM)) ;
X = X + (RT/(VG-EM))*(1+E(I)/(VG-EM)) ;
X = X + AM*E(I)/(T12*VG*(VG+EM)**2) ;
XX = RT/(VG-EM)**2 ;
XX = XX-(AM/T12)*(2*VG+EM)/(VG*VG*(VG+EM)**2) ;
X = X/XX ;
RETURN(X) ;
END VFUNCT ;
HFUNCT: PROC(I) ;
DCL X,J ;
X = 0 ; DO J = 1 TO M ; X = X + Y(J)*A(J,I) ; END ;
X = (2*X-AM*B(I)/EM)/EM ;
X = X*LOG((VG+EM)/VG) ;
X = X + (AM/EM)*(VG*B(I)-VEAR(I)*EM)/(VG*(VG+EM)) ;
X = 1.5*X/SQRT(T) + RT - P*VBAR(I) ;
X = X * 1.9E726/R ;
RETURN(X) ;
END HFUNCT ;
VCLG: PROC ; /* SOLVES RK USING CUBIC SOLUTION */
DCL A,B,C(4),L(4),PHI,RT,VGAS(3),A3,B3,L,M,N,MM,RR,K,T12 ;
L = 2 ; M = 3 ; RT = R*I ; T12 = SQRT(T) ; C(1) = 1 ;
C(2) = -RT/P ; C(3) = -EM**2-RT*BM/P+AM/(T12*P) ; C(4) = -AM*BM/(P*
T12) ; D(1) = 1 ; D(2) = C ; D(3) = (3*C(3)-C(2)**L)/3 ;
D(4) = (27*C(4)-9*C(2)*C(3)+2*C(2)**M)/27 ;
RR = (D(3)/3)**M + (L(4)/2)**L ; IF RR<0 THEN DO ; MM=1 ;
PHI = ATAN(SQRT(-L(3)**M/27 + D(4)**L/4) / (D(4)**L/4)) ;
DO K = 0 TO 2 ;
VGAS(K+1) = 2*SQRT(-L(3)/3)*COSD(PHI/3 + 120*K) ;
VGAS(K+1) = VGAS(K+1) - C(2)/3 ; END ;
VG = MAX(VGAS(1),VGAS(2),VGAS(3)) ; END ;

```

```
ELSE DC ; MM= 0 ; A3=(-L(4)/2+SQRT(RR)) ; B3=(-D(4)/2-SQRT(RR)) ;  
A = ABS(A3)**(1/3) ;  
IF A3<0 THEN A = -A ; E = ABS(B3)**(1/3) ; IF B3<0 THEN E=-B ;  
VG = A + E -C(2)/3 ;      END ;  
RETURN ; ENC      VCIG ;  
END RKWCNG      ;
```

$$\ln \frac{H_1^{(P_1^s)} v_1^s}{RT} = \frac{2C_{1T}}{v_r} + \frac{3C_{2T}}{2v_r^2} + \frac{4C_8}{3v_r^3} + \frac{6C_{3T}}{5v_r^5} + \left(C_{4T} + \frac{C_{5T}}{v_r^2} - \frac{C_{5T}}{2C_{16}} \right) \frac{e^{-C_{16}/v_r^2}}{v_r^2} - \left(\frac{C_{4T}}{2C_{16}} + \frac{C_{5T}}{2C_{16}^2} \right) \left(e^{-C_{16}/v_r^2} - 1 \right), \quad (C-1)$$

where

$$C_{1T} = C_1 + \frac{C_2}{T_r} + \frac{C_3}{T_r^2} + \frac{C_4}{T_r^3} + \frac{C_5}{T_r^5}, \quad (C-2)$$

$$C_{2T} = C_6 + \frac{C_7}{T_r} \quad (C-3)$$

$$C_{3T} = \frac{C_{15}}{T_r}, \quad (C-4)$$

$$C_{4T} = \frac{C_9}{T_r^3} + \frac{C_{10}}{T_r^4} + \frac{C_{11}}{T_r^5}, \quad (C-5)$$

$$C_{5T} = \frac{C_{12}}{T_r^3} + \frac{C_{13}}{T_r^4} + \frac{C_{14}}{T_r^5}, \quad (C-6)$$

$$T_r = \frac{T}{T_{c2}^{\infty}}, \quad (C-7)$$

$$v_r = \frac{v_1^s}{v_{c2}^{\infty}}. \quad (C-8)$$

Although the correlation is given above for the Henry's law constant at saturation, it was used as a fitting equation only; and the two parameters,

$T_{C_2}^{\infty}$ and $v_{C_2}^{\infty}$, were determined for the Henry's constants at the reference pressure, which was taken to be zero. Values of the 16 constants can be seen in the printout of the procedure HENRY'S given below. Values of $T_{C_2}^{\infty}$ and $v_{C_2}^{\infty}$ that were determined for the five binary systems studied here are given in Table 3. Values of v_1^s , the molar volume of the saturated liquid heavy component, are calculated using the reduced correlation of Lyckman as presented by Prausnitz and Chueh.³⁸ The subroutine VOLSAT shown in the printout below accomplishes this calculation.

7.3.2 Procedure HENRY'S

```
HENRY'S: PROC(L, N, NH, T, H);
```

The parameters connecting the procedure have the following definitions and attributes:

L = logic parameter of value 1 or 2, binary

1 - reads data used by procedure; see list below

2 - calculates Henry's constants

N = number of components, binary

NH = number of heavy components (one for this work), binary

T = temperature, °K, float

H = matrix of Henry's law constants N by NH, binary float

Calling HENRY'S with L = 1 results in the following data being input:

```
1. TC(I) PC(I) VC(I) W(I) IDENT(I)
```

TC = critical temperature, °K,

PC = critical pressure, atm,

VC = critical volume, cc/g-mole.

(If VC is input as zero, then VC is calculated as described in Sect. 7.2.)

ω = acentric factor

IDENT = eight-character string used to identify the components

This input is repeated for each component, I = 1 to N.

2. IDENT(NH+1) IDENT(NH+2) - - - IDENT(N)

These are the light components.

3. TCI(J,I) VCI(J,I)

TCI = parameter $T_{C_2}^{\infty}$, °K

VCI = parameter $v_{C_2}^{\infty}$, °K

This card is repeated for each binary pair. In the case here, I = 1 and J has values of 2,3---N.

7.4 Appendix D: Activity Coefficient Correlation and Procedure ACTCO

7.4.1 Activity coefficient correlation

The activity coefficients of each component can be calculated directly from an expression for the excess Gibbs free energy. The Gibbs excess free energy is assumed to follow the expansion

$$g^{*EX} = - \sum_{i,j=2}^M \alpha_{ij} x_i x_j \quad (D-1)$$

From the relation between excess free energy and activity coefficient,¹⁴

$$RT \ln \gamma_k = \frac{\partial (ng^{*EX})}{\partial n_k}, \quad (D-2)$$

```

/*GENERALIZED CORRELATION FOR HENFY'S CONSTANT, PRESTON & PRAUSNITZ*/
HENFYS: PRCC(L,N,NH,T,E);
        DCL R,V,Q,K,X,Y,Z,U,TR,VR,T,I,J;
        DCL C(16) STATIC INITIAL(
        0.42457138, -C.57214424, -0.48309824, -0.12611504, 0.02042006,
        0.15446554, -C.06794337, C.06654287, 0.30730388, 0.27319810,
        -0.32214081, -C.07442808,
        0.35402549, 0.05514906, C.02432847, 0.86320302 ) ;
        DCL LCGC FLCAT, LOGH FLCAT;
        DCL (IDENT(N) CHAR(E));
        DCL (VS(N), TC(N), VC(N), PC(N), W(N)) CONTROLLED;
        DCL (TCI(N,N), VCI(N,N)) CONTROLLED;
        DCL H(*,*);
        DCL S(2) IAEFI;
        R = 82.0574 ;
        GO TO S(1);
S(1):  ALLOCATE VS,TC,VC,PC,W,TCI,VCI;
        PUT SKIP EDIT ('TC', 'FC', 'VC', 'W', 'COMP') (X(10),A,X(10),A,X(10),
        A,X(10),A,X(10),A);
        PUT SKIP;
        DO I=1 TC N ;
        GET LIST (TC(I),FC(I),VC(I),W(I),IDENT(I));
        IF VC(I)=0 THEN VC(I)=(R*TC(I)/PC(I))*(0.291-0.08*W(I));
        PUT SKIP EDIT (TC(I),FC(I),VC(I),W(I),IDENT(I)) (X(8),F(6,2),X(6)
        ,F(6,2),X(6),F(6,2),X(6),F(5,3),X(7),A(8));
        END;
        PUT SKIP(2);
        DO J=(NH+1) TC N;
        GET LIST (IDENT(J));
        PUT SKIP EDIT ('IDENT(' ,J, ')', IDENT(J)) (X(8),A,F(2),A,A(8));
        END;
        PUT SKIP(2);
        PUT SKIP EDIT ('MATRIX OF TCI') (X(15),A);
        PUT SKIP;
        TCI=0; VCI=C; H=C;
        DO I=1 TC NH; DC J=(NH+1) TC N;
        GET LIST (TCI(J,I),VCI(J,I));
        IF VCI(J,I)=0 THEN VCI(J,I)=21.888+0.79E27*VC(I);
        END; END;
        DO J=1 TC N;
        PUT SKIP EDIT ((TCI(J,I) DC I=1 TO N) (X(10), (N) F(5,1));
        END;
        PUT SKIP(2);
        PUT SKIP EDIT ('MATRIX OF VCI') (X(15),A);
        PUT SKIP;
        DO J=1 TC N;
        PUT SKIP EDIT ((VCI(J,I) DC I=1 TO N) (X(10), (N) F(5,1));
        END;
        PUT PAGE;
        RETURN;
S(2):  DO I=1 TC NH; DC J=(NH+1) TC N;
        TR=T/TCI(J,I);
        CALL VCISAT(T,TC(I));
        VR=VS(I)/VCI(J,I);
        C1T=C(1)+C(2)/TR+C(3)/(TR*TR)+C(4)/TR**3+C(5)/TR**5;
        C2T=C(6)+C(7)/TF;
        C3T=C(15)/TF;
        C4T=C(9)/TR**3+C(10)/TR**4+C(11)/TR**5;

```

```

C5T=C(12)/TR**3+C(13)/TR**4+C(14)/TR**5;
V=2*C1T/VR+3*C2T/(2*VR*VR)+4*C(8)/(3*VR**3)+6*C3T/(5*(VR**5));
U=C4T+C5T/(VR*VR)-C5T/(2*C(16));
X=EXP(-C(16)/(VR*VR))/(VR*VR);
Y=C4T/(2*C(16))+C5T/(2*(C(16)**2));
Z=EXP(-C(16)/(VR*VR))-1;
LOGQ=V+U*X-Y*2;
Q=EXP(LOGQ);
H(J,I)=Q*F**I/VS(I);
END; END;
RETURN;
/*CORRELATION FOR MCIAR LIQUID VOLUMES, LYCKMAN, ECKERT & PRAUSNITZ*/
VCLSAT: PROC(TT,TC);
DCL TT,TC,TR1;
DCL VR(3);
DCL K;
DCL A(3) STATIC INITIAL(0.11917,0.98465,-0.55314);
DCL B(3) STATIC INITIAL(0.009513,-1.60378,-0.15793);
DCL C(3) STATIC INITIAL(0.21091,1.82484,-1.01601);
DCL D(3) STATIC INITIAL(-0.06922,-0.61432,0.34095);
DCL E(3) STATIC INITIAL(0.07480,-0.34546,0.46795);
DCL F(3) STATIC INITIAL(-0.084476,0.087037,-0.239938);
TR1=TT/TC;      DIF=1-TR1;
DO K=1 TO 3;
VR(K)=A(K)+E(K)*TR1+C(K)*TR1*TR1+D(K)*(TR1**3)+E(K)/TR1+F(K)*
LOG(DIF);
END;
VS(I)=VC(I)*(VR(1)+VR(2)*W(I)+VR(3)*W(I)*W(I));
END VCLSAT;
END HENRYS;

```

the following equations were obtained:

(1) for $k = 2, 3 \dots M$,

$$RT \ln \gamma_k = \sum_{i,j=2}^M x_i x_j \alpha_{ij} - 2 \sum_{i=2}^M x_i \alpha_{ik} ; \quad (D-3)$$

(2) for component 1,

$$RT \ln \gamma_1 = \sum_{i,j=2}^M x_i x_j \alpha_{ij} . \quad (D-4)$$

Since only the values of α_{ij} for $i = j$ are found from experimental data on binary systems, it is necessary to formulate a rule regarding mixtures for $i \neq j$. Muirbrook¹⁶ proposed

$$\alpha_{ij} = \frac{\alpha_{ii} + \alpha_{jj}}{2} . \quad (D-5)$$

This seemed to be adequate for the system encountered here since all the values of α_{ii} were similar.

7.4.2 Procedure ACTCO

ACTCO: PROC(L, M, T, X, GAM);

The procedure was linked to the main program by the following parameters:

L = logic parameter with values of 1 or 2, binary fixed

1 - reads input data (see below)

2 - calculates the activity coefficients

M = number of components, binary fixed

T = temperature, °K, float

```

ACTCC:  PRCC(L,M,T,X,GAM)
        DCL RT ;
        DCL I,J,K ;
        DCL S(2) IAEFI ;
        DCL A(M,M) CTI ; ICL(GAM(*),X(*) ) BINARY FLOAT
        GO TO S(L) ;
S(1):  ALLOCATE A ; A = C ;
        GET LIST((A(I,I) DO I = 2 TC M)) ;
        DO I = 2 TO M ;
        DO J = I+1 TO M ; A(I,J) = (A(I,I) + A(J,J))/ 2 ;
        A(J,I) = A(I,J) ; ENI ; END ;
        PUT SKIP(2) ELIT('MATRIX CF MARGULES CONSTANTS')
        (X(10),A) ;
        PUT SKIP(1) ELIT((( A(I,J) DC I = 1 TO M) DO J = 1 TO M))
        (SKIP,X(8),(M)F(10,5)) ;
        RETURN ;
S(2):  RT = 1.98726*T ;
        SUM1 = 0 ; SUM2 = 0 ;
        DO J = 2 TC M ;
        DO I = 2 TC M ;
        SUM1 = SUM1 + A(I,J) * X(I)*X(J) ; END ; END;
        DO K = 2 TC M ;
        SUM2 = 0 ; DC I = 2 TC M ;
        SUM2 = SUM2 + X(I) * A(I,K) ; END ;
        GAM(K) = EXP((SUM1-2*SUM2 )/RT) ;
        END ;
        GAM(1) = EXP(SUM1/RT) ;
        RETURN ;
        END ACTCO ;

```

X = vector of M mole fractions, binary float

GAM = vector of M activity coefficients, binary float

Calling ACTCO with L = 1 results in the following data being input:

1. A(I,I), where A(I,I) = the Margules constant α_{ii} , cal/g-mole.

This input is repeated for i = 2---M.

7.5 Appendix E: Listing of Main Program for Three-Column KALC Process and the Results of a Sample Calculation

A listing of the main program and the results for a sample calculation are provided here. The program uses a number of internal procedures which have not been described. With the exception of SETUP, none of these has input and their functions can be determined from the program listing. SETUP is an internal procedure which establishes the configuration of the columns. The only alterations necessary in the program in order to modify the configuration are a change in this procedure and a change in the makeup of the Ψ matrix for any variable heat streams. This change in the Ψ matrix has been discussed in Sect. 2.2.2. The PROGRAM Statements affecting the Ψ matrix because of the two variable heat streams used in the three-column example are clearly marked in the listing of the main program. An explanation of the input for the program is given below.

7.5.1 Input for program

1. N, M

N = total number of stages, see Fig. 2

M = number of components

2. Input for subroutine SETUP

(a) NA, NF, NSF

NA = last stage on absorber

NF = last stage on fractionator

NSF = feed stage in stripper

(b) TC(1) TC(NA) TC(NA+1) TC(NF) TC(NF+1) TC(N)

These are initial estimates of temperatures, in °C, on the stages as numbered.

(c) P(1), P(NA), P(NA+1), P(NF), P(NF+1), P(N)

These are pressures, in atmospheres, on the stages as numbered.

Pressures are assumed to vary linearly between P(1) and P(NA),

P(NA+1) and P(NF), and P(NF+1) and P(N).

(d) F(NA,1), F(NA,2), ---F(NA,M)

Feed entering stage NA, g-moles

(e) QF(NA,1)

Total enthalpy of feed entering stage NA, cal.

(f) Q(1,1), Q(NA+1,1), Q(NF,1), Q(NF+1,1), Q(NF+2,1), Q(N,1)

Q(1,1) = heat added or removed on stage 1, cal

(This is the value added or removed in recycle stream between stage N and 1.)

Q(NA+1,1) = initial estimate of heat removed by partial condenser, cal

Q(NF,1) = heat added in fractionator reboiler, cal

Q(NF+1,1) = initial estimate of heat removed by final partial condenser on stripper, cal

$Q(NF+2,1)$ = heat removed in large partial condenser on
stripper, cal

$Q(N,1)$ = heat added in stripper reboiler, cal

(All heats are positive if added, negative if removed.)

(g) $LS(1,1)$, $LS(NA+1, NA+1)$, $LS(NF+1, NF+1)$, $LS(NF+2, NF+2)$

Initial estimates of total variable liquid flows leaving the
stages indicated, g-moles.

(h) $VS(1,1)$, $VS(NF,NF)$, $VS(NF+2, NF+2)$, $VS(N,N)$

Initial estimates of total variable vapor flows leaving the
stages indicated, g-moles.

(i) $VP(NA+1, NA+1)$, $VP(NA, NA+1)$

$VP(NA+1, NA+1)$ = fixed vapor flow leaving partial condenser
on fractionator, g-moles (negative)

$VP(NA, NA+1)$ = fixed vapor flow leaving partial condenser
and entering stage NA, g-moles (positive)

(j) $VP(NF+1, NF+1)$

Total fixed vapor flow leaving final partial condenser, g-
moles (negative)

(k) $LP(N,N)$, $LP(1,N)$

$LP(N,N)$ = total fixed liquid flow leaving stage N, g-moles
(negative)

$LP(1,N)$ = fixed liquid flow leaving stage N and going to
stage 1, g-moles (positive)

3. Input for HENRY'S (see Appendix C).
4. Input for RKWONG (see Appendix B).
5. Input for ACTCO (see Appendix D).

6. ALPHA(J), BETA(J), GAMMA(J)

Coefficients of ideal gas heat capacity equation from Table 4.

(6) is repeated M times.

7. VOBAR(J) BETABAR(J)

VOBAR(J) = partial molar volume, \bar{V}_{oj}^{∞} , cc/g-mole

BETABAR(J) = coefficient of expansion, $\bar{\beta}_j$, $^{\circ}\text{K}^{-1}$ (These values, which are given in Table 3, are repeated M times.)

8. LOGIC(1), LOGIC(2), LOGIC(3), LOGIC(4)

These are logic parameters that control reading in data for another computation. Values are read as 0 or 1.

LOGIC(1) = 1

(a) N

Reads total number of stages

SETUP is then called, and all input listed under (2) is read into the computer.

LOGIC(2) = 1

HENRY'S is called, and new input is read into the computer (see Appendix C).

LOGIC(3) = 1

RKWONG is called, and new input is read into the computer (see Appendix B).

LOGIC(4) = 1

ACTCO is called, and new input is read into the computer (see Appendix D).

/*SIMULIANEOUS FLOW AND TEMPEERATURE CORRECTION IN THE EQUILIBRIUM
STAGE PROEIEEM-TIERNEY ET AL*/

```

STAGE:PROC OPTICNS(MAIN);
SETUP:  PROC(N,M) ;
        /* SETUP FOR THREE CCLUMN KALC PROCESS
        NA = NO. CF STAGES IN AESCRBER
        NF = NC. CF BCITCM STAGE IN FRACTIONATOR
        NSF = NC. OF FEED STAGE IN STRIPPER
        NA+1 = PARTIAL CCNDENSER
        NF+2 = PARTIAL CCNDENSER
        NF+1 = PARTIAL CCNDENSER
        F = 0 ;
        Q,QF = 0 ;
        A,B,VS,VP,LS,IP = 0 ;
        GET LIST(NA,NF,NSF) ;
        GET LIST(TC(1),TC(NA),TC(NA+1),TC(NF),TC(NF+1),TC(N)) ;
        GET LIST(P(1),P(NA),P(NA+1),P(NF),P(NF+1),P(N)) ;
        GET LIST((F(N),J) DC J=1 TC M)) ;
        GET LIST(QF(NA,1)) ;
        GET LIST(Q(1,1),Q(NA+1,1),Q(NF,1),Q(NF+1,1),Q(NF+2,1),Q(N,1)) ;
        GET LIST(LS(1,1),LS(NA+1,NA+1),LS(NF+1,NF+1),LS(NF+2,NF+2)) ;
        GET LIST(VS(1,1),VS(NF,NF),VS(NF+2,NF+2),VS(N,N)) ;
        GET LIST(VP(NA+1,NA+1),VE(NA,NA+1)) ;/* FOR FIXED FLOWS*/
        GET LIST(VP(NF+1,NF+1)) ;
        GET LIST(LF(N,N),LP(1,N)) ;/*LF(N,N) IS NEG*/
        DO I = 2 TC NA-1 ;
        TC(I) = TC(1) + (I-1)*(TC(NA)-TC(1))/(NA-1) ;
        P(I) = P(1) + (I-1)*(P(NA)-P(1))/(NA-1) ; END ;
        DO I = NA+2 TC NF-1 ;
        P(I) = P(NA+1) + (I-NA-1)*(P(NF)-P(NA+1))/(NF-NA-1) ;
        TC(I) = TC(NA+1) + (I-NA-1)*(TC(NF)-TC(NA+1))/(NF-NA-1) ; END ;
        DO I = NF+2 TC N-1 ;
        P(I) = P(NF+1) + (I-NF-1)*(P(N)-P(NF+1))/(N-NF-1) ;
        TC(I) = TC(NF+1) + (I-NF-1)*(TC(N)-TC(NF+1))/(N-NF-1) ; END ;
        DO I = 1 TC N-1 ; A(I,I) = -1 ; B(I,I) = -1 ;
        A(I,I+1) = 1 ; E(I+1,I) = 1 ; END ;
        A(N,N) = -1 ; E(N,N) = -1 ;
        A(NF,NF+1) = C ; B(NF+1,NF) = 0 ; B(NSF,NF) = 1 ;
        DO I = 2 TO NA ; LS(I,I) = LS(1,1) ;
        VS(I,I) = 100-VP(NA+1,NA+1) ; END ;
        DO I = NA+2 TC NF ; LS(I,I) = LS(NA+1,NA+1) + LS(NA,NA) ;
        VS(I,I) = VS(NF,NF) ; FNC ;
        LS(NF,NF) = LS(NF,NF) - VS(NF,NF) ;
        DO I = NF+3 TC N ; LS(I,I) = LS(NF+2,NF+2) ;
        VS(I,I) = VS(N,N) ; END ;
        DO I = NSF TO N ; LS(I,I) = LS(I,I) + LS(NF,NF) ; END ;
        VS(NA+1,NA+1)=0; /* FOR FIXED COND FLOW*/
        VS(NF+1,NF+1) = 0 ;
        B(NA+2,NA) = 1 ; /* FOR BYPASSING CONDENSER */
        B(NA+1,NA) = C ; /* FOR BYPASSING CONDENSER*/
        LS(N,N) = 0 ;
        END SETUP ;
        DCL LOGIC(4) ;
        NH=1;
        GET LIST(N,M) ;
        NDIM=2*N;
        DCL (LCGP,LOGF1,K1) FLCAT ;
        DCL P1S BINARY FLOAT ;

```

```

DCL TC(N) BINARY FLCAT CTL ;
ALLOCATE TC ;
DCL (HE(M,M),HE1(M,M),HE2(M,M)) FLOAT CTL ;
ALLOCATE HE,HE1,HE2 ;
DCL (PSI(NDIM,NIIM),TSDNN(N,N)) BINARY FLOAT(53) CTL ;
ALLOCATE TSDNN ;
DCL TNDIM(NDIM,1) BINARY FLCAT(53) CTL ;
ALLOCATE PSI;
ALLOCATE TNDIM ;
DCL (PHIG(N,M),GAM(N,M),DELHBAR(N,M)) BINARY FLOAT CTL ;
ALLOCATE PHIG,GAM,DELHBAR ;
DCL (GSC(M),VCEAR(M),EETABAR(M)) BINARY FLOAT CTL ;
ALLOCATE GSC,VCEAR,EETABAR ;
DCL (L(N,N),V(N,N),C(N,1),QF(N,1),ET(N,N),EV(N,N),JT(N,N),
JV(N,N),GT(N,N),GV(N,N),HT(N,N),HV(N,N),F(N,M),XX(N,M),YY(N,M),
ALPHA(M),BETA(M),GAMMA(M),
K(N,N),HS(N,N),GS(N,N),DK(N,N),DH(N,N),DG
(N,N),FF(N,1),X(N,1),Y(N,1),MO(N,N),XT(N,N),
SUMM(N,1),P(N,N),A(N,N),R(N,N),M1(N,N),M2(N,N),M3(N,N),
M4(N,N),
XV(N,N),YV(N,N),
H(N,1),G(N,1),
DM(N,1),DE(N,1),UN(N,1),UM(M,1), W1(N,N)
,W2(N,N), C(NDIM,1),
DEL(NDIM,1),VS(N,N),VP(N,N),IS(N,N),LP(N,N),ITZ(N,N),ITB(N,N)
,NORM(N,N),IPSI(NDIM,NDIM),SUMX(N,1),Z(N,N),YT(N,N),
SUMY(N,1),TSNN(N,N),TSNM(N,M),TSN1(N,1),TSM(M),
P(N)) BINARY FLCAT CTL;
ALLOCATE L,V,C,QF,ET,EV,JT,JV,GT,GV,HT,HV,F,XX,YY,ALPHA,EETA,
GAMMA, K,HS,GS,DK,DH,DG,FF,
X,Y,MO, XT, SUMM,E,A,R,M1,M2,M3,M4, XV,YV
,H,G,DM,DE,UN,UM,W1,W2,
C,DEL,VS,VP,IS,IP,ITZ, ITB, TSNN,TSNM,TSN1, TSM,
NCFM,IPSI,SUMX,Z,YI, SUMY ,P ;
DCL DF,CF ;
DCL AIM,AIF;
DCL (D,ED,EDC,CCN) BINARY FLCAT(53);
CON=0.;
CALL SETUP(N,M) ;
/* SETSUP THE MATRICES FOR THE OAK RIDGE PROBLEM */
LL=1; CALL HENFYS(IL,M,NE,TK,HE) ;
LL=1; CALL RKWCNG(LL,M,Y(*,1),P(1),TK,PHIG(1,*),DELHBAR(1,*),
DELH) ;
CALL ACTCC(IL,M,TK,XX(1,*),GAM(1,*)) ;
GET LIST((ALPHA(J),EETA(J),GAMMA(J) DC J = 1 TO M)) ;
GET LIST((VCEAR(J),EETABAR(J) DO J= 1 TO M)) ;
PUT SKIP(2) ELIT('CCMP','VCEAR','EETABAR','ALPHA','BETA',
'GAMMA')(X(10),A,X(4),A,X(3),A,X(3),A,X(5),A,X(8),A) ;
PUT SKIP(2) ELIT((J,VCEAR(J),EETABAR(J),ALPHA(J),BETA(J),
GAMMA(J) DC J = 1 TO M))
(SKIP,F(11),F(11,2),E(11,3),F(9,3) (2)E(12,3));
START: CALL MMGG(A,VS,N,N,N,TSNN) ;
V = TSNN + VE ;
CALL MMGG(B,IS,N,N,N,TSNN) ;
L = TSNN + IP ;
MM=1;
KCOUNT=0;
PUT PAGE ;
PUT SKIP(5) ELIT('N','F','Q','QF')(X(5),A,(M)X(6),A,(M)X(6),

```

```

X(4),A,X(10),A)      ;
PUT SKIP(2);
DO I = 1 TO N;
PUT SKIP(2) EDIT(I,(F(I,J) DC J= 1 TO M),Q(I,1),QF(I,1)      ) ;
(X(4),F(2), (M)F(12,2),F(12,0),F(12,0) ) ;
END ;
PUT PAGE ;
PUT SKIP(5) EDIT('L')(X(34),A) ;
PUT SKIP(2);
DO I = 1 TO N ;
PUT SKIP(2) EDIT((L(I,J) DC J = 1 TO N )) (F(10,2)) ;
END ;
PUT SKIP(5) EDIT('V')(X(34),A) ;
PUT SKIP(2) ;
DO I = 1 TO N ;
PUT SKIP(2) EDIT((V(I,J) DC J = 1 TO N)) (F(10,2)) ;
END ;
PUT PAGE ;
PUT SKIP(5) EDIT('LS')(X(34),A) ;
PUT SKIP(2) ;
DO I = 1 TO N;
PUT SKIP(2) EDIT((LS(I,J) DC J = 1 TO N)) (F(10,2)) ;
END ;
PUT SKIP(5) EDIT('LF')(X(34),A) ;
PUT SKIP(2) ;
DO I = 1 TO N;
PUT SKIP(2) EDIT((LF(I,J) DC J = 1 TO N)) (F(10,2));
END ;
PUT PAGE ;
PUT SKIP(5) EDIT('A')(X(34),A);
PUT SKIP(2);
DO I = 1 TO N;
PUT SKIP(2) EDIT((A(I,J) DC J= 1 TO N)) (F(8,2));
END ;
PUT SKIP(5) EDIT('B')(X(34),A) ;
PUT SKIP(2) ;
DO I = 1 TO N;
PUT SKIP(2) EDIT((B(I,J) DC J = 1 TO N)) (F(8,2));
END ;
PUT PAGE;
PUT SKIP(5) EDIT('VS')(X(34),A) ;
PUT SKIP(2) ;
DO I = 1 TO N;
PUT SKIP(2) EDIT((VS(I,J) DC J= 1 TO N)) (F(10,2)) ;
END ;
PUT SKIP(5) EDIT('VE')(X(34),A) ;
PUT SKIP(2) ;
DO I = 1 TO N;
PUT SKIP(2) EDIT((VE(I,J) DC J = 1 TO N)) (F(10,2)) ;
END ;
PUT PAGE ;
PUT SKIP(2) EDIT('FEED STAGES = ', NA,NSF,'FEED ENTHALPY =',
QF( NA, 1)) (X(5),A,F(2),X(3),F(2),X(3),A,E(13,6)) ;
PUT SKIP(2) EDIT('FEED','COMP','RATE')(X(5),A,SKIP,X(5),A,X(4),
A) ;
PUT SKIP EDIT((I,F( NA,I) DO I = 1 TO M))
(SKIP,X(7),F(2),F(10,6)) ;
PUT SKIP EDIT('RECIPIER LUTY IN FR = ',Q(NF,1)) (X(5),A,E(16,6))

```

```

;
PUT SKIP EDIT('REBCIIR DUTY IN STRIPPER = ',Q(N ,1))
(X(5),A,F(16,6)) ;
START1: ET,EV,JI,JV,GT,GV,HT,HV,F=0;
KOUNT=KCOUNT+1;
IF KOUNT = 1 THEN DC ;
TO = 233.15 ;
LL = 2 ; CALL HENRYS(LL,M,NH,TO-.5,HE1) ;
LL = 2 ; CALL HENRYS(LL,M,NH,TO+.5,HE2) ;
DO I = 2 TC M ;
GSO(I) = -(LOG(HE2(I,1))-ICG(HE1(I,1)))/(1/(TO+.5)-1/(TO-.5))
*1.98726 ;
END ;
TSM = 0 ; TSM(1) = 1 ; P1S= VPFUNCT(TO) ;
LL = 2 ;
CALL RKWONG(LL,P,TSM,P1S,TO,PHIG(1,*),DELHBAR(1,*),DELH) ;
LL = 3 ;
CALL RKWONG(LL,P,TSM,P1S,TO,PHIG(1,*),DELHBAR(1,*),DELH) ;
GSC(1) = DELH + 3369.2 ; /* HEAT OF VAP FROM PERRY*/
PUT SKIP ;
PUT SKIP EDIT('IDEAL GAS ENTHALPIES AT -40 C')(X(5),A) ;
PUT SKIP EDIT('CCMPCNENT NC', 'ENTHALPY, CAL/GM MOLE',(I,
GSO(I) DO I=1 TC M))(X(10),A,X(5),A,(M)(SKIP,X(15),F(2),X(6),
F(12,2) ) ) ;
END ;
FF=0;
DEL=0;
PSI=0;
K,HS,GS,DK,IH,DC=0;
UM=1;
UN=1;
J=0;
NORM=0;
SUMY = 0 ;
SUMX=0;
H,G=0;
IF KCUNT = 1 THEN DC;
PHIG = 1; DELHBAR = C; GAM = 1.0 ; END ;
ELSE DC ; LL= 2 ;
CALL RKWONG(LL,M,YY(1,*),F(1),TK,PHIG(1,*),DELHBAR(1,*),DELH) ;
DO I = 1 TC N ;
TK = TC(I) + 273.15 ;
LL= 3 ;
CALL RKWONG(LL,M,YY(I,*),F(I),TK,PHIG(I,*),DELHBAR(I,*),DELH) ;
LL=2; CALL ACTCO(LL,M,TK,XX(I,*),GAM(I,*)) ; ;
END ; END ;
START2: J=J+1;
M0,M1,M2,M3,M4=C;
DO I=1 TC N;
FF(I,1)=F(I,J);
TC1 =TC(I)+1.0;
TK =TC(I)+273.15;
RT = 82.0574*TK ;
TK1 =TC(I)+274.15;
TK2 =TC(I)+275.15;
IF J=1 THEN DC;
P1S = VPFUNCT(TK) ;
VBAR = EXP((TK-TO)*EETAPEAR(1))*VOBAR(1) ;

```

```

TSM = 0 ; TSM(1) = 1 ; II = 2 ;
CALL RKWNG(LI,M,TSM,PIS,TK,TSM,TSNM(I,*),DELH) ;
LL = 3 ;
CALL RKWNG(LL,M,TSM,PIS,TK,TSM,TSNM(I,*),DELH) ;
FS = TSM(1)*PIS ;
K(I,I) = GAM(I,1)*FS*EXP(VBAR*(P(I)-PIS)/RT)/(P(I)*PHIG(I,1)) ;
DK(I,I) = EVPFUNCT(TK)/F(I) ;
END;
ELSE DC;
LL=2; CALL HENRYS(LI,M,NH,TK,HE);
LL=2; CALL HENFYS(LI,M,NH,TK1,HE1);
LL=2; CALL HENRYS(LI,M,NH,TK2,HE2);
K(I,I)=HE(J,1)/F(I) ; /* FOR DERIVATIVE USE ONLY */
K1 =HE1(J,1)/P(I) ;
DK(I,I)=K1 -K(I,I);
VBAR = VOEAF(J)*EXP((TK-T0)*EETABAR(J)) ;
K(I,I) = K(I,I)*GAM(I,J)*EXP(VBAR *P(I)/RT)/(PHIG(I,J));
END;
GS(I,I) = ALPEA(J)*(TK-T0) + BETA(J)*(TK**2-T0**2)/2 +
GAMMA(J)*(TK**3-T0**3)/3 + GSO(J) -DELHBAR(I,J) ;
DG(I,I) = BETA(J) +2*GAMMA(J)*TK ;
IF J=1 THEN DC;
HS(I,I) = 278.767*(TK-T0) -2.20936*(TK**2-T0**2)/2
+0.00471244*(TK**3-T0**3)/3 ;
DH(I,I) = 278.767-2.20936*TK+0.00471244*TK*TK ;
END;
ELSE DC;
HS(I,I) = (LOG(HE1(J,1)) -LOG(HE(J,1)))/(1/TK1 -1/TK) *1.9872
+GS(I,I) ;
HS1 = (LOG(HE2(J,1)) -LOG(HE1(J,1)))/(1/TK2 -1/TK1) *
1.9872+GS(I,I) ;
DH(I,I)=HS1 -HS(I,I) ;
END;
END;
CALL MMGG(V,K,N,N,N,TSNN) ;
Z = L + TSNN ;
TSDNN = Z ;
CALL MINV#(TSINN,N,I,CCN) ;
ITZ = -TSDNN ;
CALL MMGG(ITZ,FF,N,N,MM,X) ;
CALL MMGG(K,X,N,K,MM,Y) ;
DO I=1 TC N ;
M0(I,I)=DK(I,I)*X(I,1) ;
END;
CALL MMGG(ITZ,V,N,N,K,TSNN) ;
CALL MMGG(TSNN,M0,N,N,N,XI) ;
CALL MMGG(K,XI,K,N,K,TSNN) ;
YT = M0+TSNN ;
TSDNN = B ;
CALL MINV#(TSINN,N,IL,CCN) ;
ITB = TSDNN ;
CALL MMGG(ITE,A,N,N,N,R) ;
DO I=1 TC N ;
DO II=1 TC N ;
M1(I,II)=F(I,II)*X(I,1) ;
M2(I,II)=A(I,II)*Y(II,1) ;
END;
M3(I,I)=DH(I,I)*X(I,1) ;

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M4(I,I)=DG(I,I)*Y(I,1);
END;
CALL MMGG(B,M1,N,N,N,TSNN) ;
TSNN = TSNN - M2 ;
ITZ = -ITZ ;
CALL MMGG(ITZ,TSNN ,N,N,N,XV);
CALL MMGG(K,XV,N,N,N,YV ) ;
ET=ET+XT-YT;
EV=EV+XV-YV;
CALL MMGG(HS,XT,N,N,N,TSNN) ;
HT=HT+TSNN+M3;
CALL MMGG(GS,YT,N,N,N,TSNN) ;
GT=GT+TSNN+M4;
CALL MMGG(HS,XV,N,N,N,TSNN) ;
HV=HV+TSNN ;
CALL MMGG(GS,YV,N,N,N,TSNN) ;
GV=GV+TSNN ;
DO I=1 TC N;
XX(I,J)=X(I,1);
YY(I,J)=Y(I,1);
END;
SUMX=SUMX+X;
SUMY = SUMY +Y ;
CALL MMGG(HS,X,N,N,MM,TSN1) ;
H = H + TSN1 ;
CALL MMGG(GS,Y,N,N,MM,TSN1) ;
G = G + TSN1 ;
IF J<M THEN GC TC START2;
DO I=1 TC N;
NORM(I,I)=1/SUMX(I,1);
END;
CALL MMGG(ET,NCFM,N,N,N,TSNN) ;
ET = TSNN ;
TSNM = XX-YY;
CALL MMGG(TSNM ,UM,N,M,MM,DM);
CALL MMGG(L,H,N,N,MM,TSN1) ;
DE = TSN1+Q+QE ;
CALL MMGG(V,G,N,N,MM,TSN1) ;
DE = DE + TSN1 ;
ADM =SUM(DM**2);
ADE =SUM(DE**2);
ADM=SQRT(ADM );
ADE=SQRT(ADE );
CALL MMGG(L,HT,N,N,N,TSNN) ;
JT = TSNN ;
CALL MMGG(V,GT,N,N,N,TSNN) ;
JI = TSNN + JT ;
DO I=1 TC N; LC II=1 TC N;
W1(I,II)=E(I,II)*H(I,1);
W2(I,II)=A(I,II)*G(I,1);
END; END;
CALL MMGG(B,W1,N,N,N,TSNN) ;
JV = -TSNN ;
CALL MMGG(L,HV,N,N,N,TSNN) ;
JV = JV + TSNM ;
CALL MMGG(V,GV,N,N,N,TSNN) ;
JV = JV + TSNN + W2 ;
DO I=1 TC N; LC II=1 TC N;

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PSI(I,II)=EI(I,II);
PSI(I,II+N)=EV(I,II);
PSI(I+N,II)=JI(I,II);
PSI(I+N,II+N)=JV(I,II);
END;
PSI(I,N+NA+1) = C ; /* FOR VARIABLE Q(NA+1) */
PSI(I,N+NF+1) = 0 ; /* FOR VARIABLE Q(NF+1) */
PSI(I+N,N+NA+1) = 0 ; /* FOR VARIABLE Q(NA+1) */
PSI(I+N,N+NF+1) = 0 ; /* FOR VARIABLE Q(NF+1) */
DEL(I,1)=DM(I,1);
DEL(I+N,1)=DE(I,1);
END;
PSI(N+NA+1,N+NA+1) = 1; /* FOR VARIABLE Q(NA+1) */
PSI(N+NF+1,N+NF+1) = 1 ; /* FOR VARIABLE Q(NF+1) */
CALL MINV#(PSI,NDIM,DED,CCN);
IPSI=PSI; DEL = -DEI ;
CALL MMGG(IPSI,DEL,NDIM,NDIM,MM,C) ;
DO I=1 TC N;
TC(I) = TC(I) + C(I,1) ;
END;
DO I = 1 TC NA, NA+2 TC NF, NF+2 TO N ; /* FOR VARIABLE CCND */
VS(I,I)=VS(I,I)+C(I+N,1) ;
END;
Q(NA+1,1)=C(NA+1,1) + C(N+NA+1,1) ; /* FOR VARIABLE Q'S */
Q(NF+1,1) = Q(NF+1,1) +C(N+NF+1,1) ; /* FOR VARIABLE Q'S */
CALL MMGG(A,VS,N,N,N,TSNN) ;
V = TSNN + VE ;
CALL MMGG(P,UP,N,N,MM,SUMM) ;
CALL MMGG(V,UN,N,N,MM,TSN1) ;
SUMM = SUMM + TSN1 ;
CALL MMGG(LP,CN,N,N,MM,TSN1) ;
SUMM = SUMM + TSN1 ; SUMM = -SUMM ;
CALL MMGG(ITB,SUMM,N,N,MM,TSN1) ;
DO I=1 TC N;
LS(I,I)=TSN1(I,1) ;
END;
CALL MMGG(B,LS,N,N,N,TSNN) ;
L = TSNN + IP ;
PUT PAGE ;
PUT SKIP DATA(ADE,ALM);
PUT SKIP EDIT('ITERATION NO. =',KOUNT)(X(5),A,F(4)) ;
PUT SKIP(2) EDIT('STAGE','T,C','L','V','L/V','H IIQ','H VAPOR',
'P,ATM')
(X(3),A,X(2),A,X(8),A,X(9),A,X(6),A,X(5),A,X(3),A,X(3),A) ;
PUT SKIP ;
DO I=1 TC N;
ALV = L(I,I)/V(I,I) ;
PUT SKIP EDIT(I,TC(I),-L(I,I),-V(I,I),ALV,H(I,1),G(I,1),P(I))
(X(5),F(2),F(8,2),F(10,2),F(10,2),F(9,2),F(8,2),F(9,2),F(9,2));
END ;
PUT SKIP(4) ;
PUT SKIP(2) EDIT('COMPONENT')(X(5),(M/2)X(10),A) ;
PUT SKIP EDIT('STAGE',(I DC I = 1 TO M),'SUM')(X(5),A,X(5),
(M)F(2),X(9)),A) ;
DO I=1 TO N;
PUT SKIP EDIT(I,'X=',(XX(I,J) DO J=1 TO M),SUMX(I,1))
(X(5),F(2),A,(M)F(11,4),F(8,5)) ;
PUT SKIP EDIT('Y=',(YY(I,J) DC J = 1 TO M),SUMY(I,1))

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(X(8),A,(M)E(11,4),F(8,5)) ;
PUT SKIP EDIT('K=',(YY(I,J)/XX(I,J) DO J = 1 TO M))
(X(8),A,(M)E(11,4)) ;
END ;
IF ADM<1E-3 THEN IF ADE<1E+3 THEN GO TO PRINT;
ELSE; ELSE;
CALL MMGG(NCRM,XX,N,N,M,TSNM) ;
XX = TSNM ;
DO I = 1 TC N ; NORM(I,I)=1/SUMY(I,1);END ;
CALL MMGG(NCRM,YY,N,N,M,TSNM);
YY = TSNM ;
GO TO STARI1;
PRINT: PUT SKIP(2) EDIT('CONVERGED')(X(10),A) ;
DF = F(NA,M)/(-YY(1,M)*V(1,1)) ;
SLGF,SLGE = 0 ;
DO J = 2 TC M ; SLGF = SLGF +F(NA,J) ;
SLGP = SLGE-V(NF+1,NF+1)*YY(NF+1,J) ; END ;
FEED = 0 ; DO J = 1 TO M; FEED = FEED + F(NA,J); END ;
CFKR = FEED*YY(NF+1,M)/F(NA,M) ;
CFLG = SLGF/SIGF ;
PUT PAGE ;
PUT SKIP EDIT('ITERATION NO. =',KCUNT)(X(5),A,F(4)) ;
PUT SKIP(2) EDIT('STAGE','T,C','L','V','L/V','H IIQ','H VAPOR',
'P,ATM')
(X(3),A,X(2),A,X(8),A,X(9),A,X(6),A,X(5),A,X(3),A,X(3),A) ;
PUT SKIP ;
DO I=1 TC N;
ALV = L(I,I)/V(I,I) ;
PUT SKIP EDIT(I,TC(I),-L(I,I),-V(I,I),ALV,H(I,1),G(I,1),P(I))
(X(5),F(2),F(8,2),F(10,2),F(10,2),F(9,2),F(8,2),F(9,2),F(9,2));
END ;
PUT SKIP(4) ;
PUT SKIP(2) EDIT('COMPONENT')(X(5),(M/2)X(10),A) ;
PUT SKIP EDIT('STAGE',(I DO I = 1 TO M),'SUM')(X(5),A,X(5),
(M)F(2),X(9)),A) ;
DO I=1 TC N;
PUT SKIP EDIT(I,'X=',(XX(I,J) DO J=1 TO M),SUMX(I,1))
(X(5),F(2),A,(M)E(11,4),F(8,5)) ;
PUT SKIP EDIT('Y=',(YY(I,J) DO J = 1 TO M),SUMY(I,1))
(X(8),A,(M)E(11,4),F(8,5)) ;
PUT SKIP EDIT('K=',(YY(I,J)/XX(I,J) DO J = 1 TO M))
(X(8),A,(M)E(11,4)) ;
END ;
PUT SKIP(2) EDIT('DES=',ADE,'DMS=',ADM)(X(5),A,F(12,4)) ;
PUT SKIP;
PUT SKIP;
PUT SKIP(2) EDIT('HEAT LOAD ON CONDENSER = ',Q(NA+1,1))
(X(5),A,F(16,6)) ;
PUT SKIP(2) EDIT('HEAT LOAD ON CONDENSER = ',Q(NF+1,1))
(A,F(16,6));
PUT SKIP(2) EDIT('D. F. =',DF)(X(5),A,F(12,2)) ;
PUT SKIP(2) EDIT('C.F. KR = ',CFKR)(X(5),A,F(12,2)) ;
PUT SKIP(2) EDIT('C.F. IG = ',CFLG)(X(5),A,F(12,2)) ;
RESTART: PUT PAGE;
LL= 1 ;
GET LIST (LOGIC) ;
IF LOGIC(1)=1 THEN IC;
FREE TC,PSI,TSN,N,TNDIM,PHIG,GAM,DELHBAR,L,V,Q,QF,ET,

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EV, JT, JV, GT, GV, HT, HV, F, XX, YY, K, HS, GS, DK, DH, DG, FF, X, Y, MO, XI,
SUMM, B, A, F, M1, M2, M3, M4, XV, YV, H, G, DM, DE, UN, UM, W1, W2, C, DEL,
VS, VP, IS, IP, ITZ, ITE, NORM, IESI, SUMX, Z, YT, SUMY, TSNN, TSNM,
TSN1, P
;
GET LIST (N) ; NDIM=2*N ;
ALLOCATE TC, PSI, TSDNN, TNDIM, PHIG, GAM, DELHBAR, L, V, Q, QF, EI,
EV, JT, JV, GT, GV, HT, HV, F, XX, YY, K, HS, GS, DK, DH, DG, FF, X, Y, MO, XT,
SUMM, B, A, R, M1, M2, M3, M4, XV, YV, H, G, DM, DE, UN, UM, W1, W2, C, DEL,
VS, VP, IS, IP, ITZ, ITE, NORM, IESI, SUMX, Z, YT, SUMY, TSNN, TSNM,
TSN1, P
;
CALL SETUP (N, M) ; END;
IF LOGIC (2) = 1 THEN CALL FENRYS (LL, M, NH, TK, HE) ;
IF LOGIC (3) = 1 THEN CALL RKWONG (LL, M, Y (*, 1), P (1), TK, PHIG (1, *),
DELHBAR (1, *), DELH) ;
IF LOGIC (4) = 1 THEN CALL ACTCO (LL, M, TK, XX (1, *), GAM (1, *));
/* NO PROVISION FOR CHANGING M, HEAT CAPACITIES OR PARTIAL
MOLAR VOLUMES */
GO TO START ;
VPPUNCT: PROC (T) ;
/* CALCULATES VE OF CO2 FROM EQ OF MICHELS */
DCL LOGVE FICAT, T, VP ;
LOGVP = 24.61930 - 1353.202/T - 8.142537*LOG10 (T) + .006259156*T ;
VP = 10**LOGVE ; RETURN (VE) ;
END VPPUNCT ;
DVPUNCT: PROC (T) ;
/* CALCULATES VE DERIVATIVE */
DCL T, DPDT, LN10 FICAT ;
LN10 = LCG (10) ;
DPDT = VPPUNCT (T) ;
DPDT = DEFT*(LN10*1353.202/(T*T) - 8.142537/T + LN10*.006259156) ;
RETURN (DEFT) ;
END DVPUNCT ;
MMGG: PROCEDURE (A, B, K, I, M, C) ;
/* GENERAL MATRIX MULT OF C = A X B COPIED FROM PL1 SSR */
DECLARE (A (*, *), B (*, *), C (*, *)) BINARY FLCAT ;
DECLARE S BINARY FLCAT (53) ;
DECLARE (K, L, M, I, J, N) BINARY FIXED ;
DECLARE ERROR EXTERNAL CHARACTER (1) ;
ERROR = 'D' ;
IF K > 0 THEN IF L > 0 THEN IF M > 0 THEN DO ;
I = 0 ;
NEXTI: I = I + 1 ;
J = 0 ;
NEXTJ: J = J + 1 ;
S = 0 ;
DO N = 1 TO L ; S = S+MULTIPLY (A (I, N), B (N, J), 53) ;
END ;
C (I, J) = S ;
IF J < M THEN GO TO NEXTJ ;
ELSE IF I < K THEN GO TO NEXTI ;
ERROR = 'C' ;
END ;
END MMGG ;
/*MINV# IS THE DOUBLE PRECISION MATRIX INVERSION SUBROUTINE FROM THE
SCIENTIFIC SUBROUTINE PACKAGE. THE CALCULATION OF THE DETERMINANT
HAS BEEN OMITTED.*/
MINV#: PROC (A, N, I, CON) ;
DCL ERROR EXTERNAL CHARACTER (1) ;

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DCL (I,J,K,N,I(N),M(N)) FIXED BINARY;
DCL (A(*,*),EIGA,HOLD,I,CCN,S) BINARY FLOAT(53);
ERROR='0';
IF N<=0 THEN DC;
ERROR='1';
GO TO FIN;
END;
IF CON=C THEN S=1.0E-15;
ELSE S=CCN;
IF N=1 THEN DC;
D=A(1,1);
IF ABS(D)<=S THEN DC;
ERROR='2';
END;
ELSE A(1,1)=1/D;
GO TO FIN;
END;
D=1.0;
DO K=1 TC N;
L(K)=K;
M(K)=K;
BIGA=A(K,K);
DO I=K TC N;
DO J=K TC N;
IF ABS(BIGA)<ABS(A(I,J)) THEN DO;
BIGA=A(I,J);
L(K)=I;
M(K)=J;
END;
END;
END;
J=L(K);
IF L(K)>K THEN DC;
DO I=1 TC N;
HOLD=-A(K,I);
A(K,I)=A(J,I);
A(J,I)=HOLD;
END;
END;
I=M(K);
IF M(K)>K THEN DC;
DO J=1 TC N;
HOLD=-A(J,K);
A(J,K)=A(J,I);
A(J,I)=HOLD;
END;
END;
IF ABS(BIGA)<=S THEN DC;
D=0.0;
END;
DO I=1 TC N;
IF I /= K THEN A(I,K)=A(I,K)/(-A(K,K));
END;
DO I=1 TC N;
IF I /= K THEN DC;
DO J=1 TC N;
IF J /= K THEN A(I,J)=A(I,K)*A(K,J)+A(I,J);
END;

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      END;
      END;
      DO J=1 TO N;
      IF J /= K THEN A (K,J)=A (K,J)/A (K,K);
      END;
CCMP:  /* CONTINUE */
      A (K,K)=1.C/A (K,K);
      END;
      K=N;
LCOE:  K=K-1;
      IF K>0 THEN DC;
      I=L (K);
      IF I>K THEN DC;
      DO J=1 TC N;
      HOLD=A (J,K);
      A (J,K)=-A (J,I);
      A (J,I)=HOLD;
      END;
      END;
      J=M (K);
      IF J>K THEN DC;
      DO I=1 TC N;
      HOLD=A (K,I);
      A (K,I)=-A (J,I);
      A (J,I)=HOLD;
      END;
      END;
      GO TC LCOE;
      END;
FIN:   RETURN;
END MINV#;
END STAGE;

```

TC	PC	VC	W	COMP
304.20	72.80	93.61	0.225	CO2
289.70	57.60	120.10	0.000	XE
154.60	49.80	73.70	0.021	O2
132.90	34.50	90.95	0.041	CO
125.20	33.50	88.97	0.040	N2
209.40	54.30	92.08	0.000	KB

IDENT(2) XE
 IDENT(3) O2
 IDENT(4) CO
 IDENT(5) N2
 IDENT(6) KB

MATRIX OF ICI

0.0	0.0	0.0	0.0	0.0	0.0
285.3	0.0	0.0	0.0	0.0	0.0
207.4	0.0	0.0	0.0	0.0	0.0
180.4	0.0	0.0	0.0	0.0	0.0
197.7	0.0	0.0	0.0	0.0	0.0
237.6	0.0	0.0	0.0	0.0	0.0

MATRIX OF VCI

0.0	0.0	0.0	0.0	0.0	0.0
95.6	0.0	0.0	0.0	0.0	0.0
92.3	0.0	0.0	0.0	0.0	0.0
86.5	0.0	0.0	0.0	0.0	0.0
93.9	0.0	0.0	0.0	0.0	0.0
93.8	0.0	0.0	0.0	0.0	0.0

INPUT PARAMETERS FOR R_K EQUATION

OMEGA	OMEGA B	W	TC, DEGK	PC, ATM	VC, LITER	COMPONENT
0.44700	0.09110	0.225	304.20	72.80	0.00000	CO2
0.42780	0.08670	0.000	289.70	57.60	0.00000	XE
0.42780	0.08670	0.021	154.60	49.80	0.00000	O2
0.42780	0.08670	0.041	132.90	34.50	0.00000	CO
0.42780	0.08670	0.040	126.20	33.50	0.00000	N2
0.42780	0.08670	0.000	209.40	54.30	0.00000	KR

CORRECTIONS FOR GEOM MEAN, KIJ

1	0.000	0.000	0.000	0.000	0.000
2	0.000	0.000	0.000	0.000	
3	0.000	0.000	0.000		
4	0.000	0.000			
5	0.000				

MATRIX OF MARGULES CONSTANTS

0.00000	0.00000	0.00000	0.00000	0.00000	0.00000
0.00000	0.00000	425.60498	431.74487	442.79980	0.00000
0.00000	425.60498	851.20996	857.34985	868.40479	425.60498
0.00000	431.74487	857.34985	863.48999	874.54492	431.74487
0.00000	442.79980	868.40479	874.54492	885.59985	442.79980
0.00000	0.00000	425.60498	431.74487	442.79980	0.00000

COMP	VOBAR	BETABAR	ALPHA	BETA	GAMMA
1	39.48	4.680E-03	6.637	1.395E-03	2.045E-05
2	56.64	5.470E-03	4.968	0.000E+00	0.000E+00
3	52.34	-7.800E-05	7.011	-8.100E-04	2.800E-06
4	48.59	-1.810E-02	6.962	-9.500E-05	3.500E-07
5	50.03	1.370E-03	6.958	-3.500E-05	1.500E-07
6	54.46	8.940E-03	4.968	0.000E+00	0.000E+00

N	P						Q	QP
1	0.00	0.00	0.00	0.00	0.00	0.00	-165000	0
2	90.98	0.01	3.00	3.00	3.00	0.01	0	386220
3	0.00	0.00	0.00	0.00	0.00	0.00	-333340	0
4	0.00	0.00	0.00	0.00	0.00	0.00	0	0
5	0.00	0.00	0.00	0.00	0.00	0.00	365600	0
6	0.00	0.00	0.00	0.00	0.00	0.00	-200000	0
7	0.00	0.00	0.00	0.00	0.00	0.00	-1900000	0
8	0.00	0.00	0.00	0.00	0.00	0.00	0	0
9	0.00	0.00	0.00	0.00	0.00	0.00	2077000	0

L

-1430.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	1350.00
1430.00	-1430.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
0.00	0.00	-86.50	0.00	0.00	0.00	0.00	0.00	0.00
0.00	1430.00	86.50	-1516.50	0.00	0.00	0.00	0.00	0.00
0.00	0.00	0.00	1516.50	-1406.50	0.00	0.00	0.00	0.00
0.00	0.00	0.00	0.00	0.00	-104.00	0.00	0.00	0.00
0.00	0.00	0.00	0.00	0.00	104.00	-646.00	0.00	0.00
0.00	0.00	0.00	0.00	1406.50	0.00	646.00	-2052.50	0.00
0.00	0.00	0.00	0.00	0.00	0.00	0.00	2052.50	-1350.00

V

-57.00	122.50	0.00	0.00	0.00	0.00	0.00	0.00	0.00
0.00	-122.50	22.50	0.00	0.00	0.00	0.00	0.00	0.00
0.00	0.00	-22.50	110.00	0.00	0.00	0.00	0.00	0.00
0.00	0.00	0.00	-110.00	110.00	0.00	0.00	0.00	0.00
0.00	0.00	0.00	0.00	-110.00	0.00	0.00	0.00	0.00
0.00	0.00	0.00	0.00	0.00	-3.75	108.00	0.00	0.00
0.00	0.00	0.00	0.00	0.00	0.00	-108.00	625.00	0.00
0.00	0.00	0.00	0.00	0.00	0.00	0.00	-625.00	625.00
0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	-625.00

LS

1430.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
0.00	1430.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
0.00	0.00	86.50	0.00	0.00	0.00	0.00	0.00	0.00
0.00	0.00	0.00	1516.50	0.00	0.00	0.00	0.00	0.00
0.00	0.00	0.00	0.00	1406.50	0.00	0.00	0.00	0.00
0.00	0.00	0.00	0.00	0.00	104.00	0.00	0.00	0.00
0.00	0.00	0.00	0.00	0.00	0.00	646.00	0.00	0.00
0.00	0.00	0.00	0.00	0.00	0.00	0.00	2052.50	0.00
0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00

IP

0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	1350.00
0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	-1350.00

A

-1.00	1.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
0.00	-1.00	1.00	0.00	0.00	0.00	0.00	0.00	0.00
0.00	0.00	-1.00	1.00	0.00	0.00	0.00	0.00	0.00
0.00	0.00	0.00	-1.00	1.00	0.00	0.00	0.00	0.00
0.00	0.00	0.00	0.00	-1.00	0.00	0.00	0.00	0.00
0.00	0.00	0.00	0.00	0.00	-1.00	1.00	0.00	0.00
0.00	0.00	0.00	0.00	0.00	0.00	-1.00	1.00	0.00
0.00	0.00	0.00	0.00	0.00	0.00	0.00	-1.00	1.00
0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	-1.00

B

-1.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
1.00	-1.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
0.00	0.00	-1.00	0.00	0.00	0.00	0.00	0.00	0.00
0.00	1.00	1.00	-1.00	0.00	0.00	0.00	0.00	0.00
0.00	0.00	0.00	1.00	-1.00	0.00	0.00	0.00	0.00
0.00	0.00	0.00	0.00	0.00	-1.00	0.00	0.00	0.00
0.00	0.00	0.00	0.00	0.00	1.00	-1.00	0.00	0.00
0.00	0.00	0.00	0.00	1.00	0.00	1.00	-1.00	0.00
0.00	0.00	0.00	0.00	0.00	0.00	0.00	1.00	-1.00

VS

57.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
0.00	122.50	0.00	0.00	0.00	0.00	0.00	0.00	0.00
0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
0.00	0.00	0.00	110.00	0.00	0.00	0.00	0.00	0.00
0.00	0.00	0.00	0.00	110.00	0.00	0.00	0.00	0.00
0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
0.00	0.00	0.00	0.00	0.00	0.00	108.00	0.00	0.00
0.00	0.00	0.00	0.00	0.00	0.00	0.00	625.00	0.00
0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	625.00

VP

0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
0.00	0.00	22.50	0.00	0.00	0.00	0.00	0.00	0.00
0.00	0.00	-22.50	0.00	0.00	0.00	0.00	0.00	0.00
0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
0.00	0.00	0.00	0.00	0.00	-3.75	0.00	0.00	0.00
0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00

FEED STAGES = 2 8 FEED ENTHALPY = 3.862200E+05

FEED
COMP RATE

1 90.979996
2 0.010000
3 3.000000
4 3.000000
5 3.000000
6 0.010000

REBOILER DUTY IN FR = 3.656000E+05
REBOILER DUTY IN STRIPPER = 2.077000E+06

IDEAL GAS ENTHALPIES AT -40 C

COMPONENT NO	ENTHALPY, CAL/GM MOLE
1	3513.05
2	521.93
3	-773.62
4	-194.51
5	-1199.32
6	-249.94

ITERATION NO. = 7

STAGE	T, C	L	V	L/V	H LIQ	H VAPOR	P, ATM
1	-20.36	1431.42	66.38	21.56	387.84	2919.76	22.00
2	-20.52	1406.12	147.80	9.51	395.08	2952.96	22.00
3	-30.67	97.25	22.50	4.32	185.00	2248.36	20.00
4	-21.53	1493.09	119.75	12.47	373.87	3153.59	20.00
5	-20.03	1383.62	109.46	12.64	405.85	3310.21	20.00
6	-39.58	103.09	3.75	27.49	7.91	1692.58	18.00
7	-23.56	697.86	106.84	6.53	331.10	3288.42	18.00
8	-22.60	2058.58	701.61	2.93	351.37	3394.54	18.00
9	-22.49	1379.87	678.71	2.03	353.74	3406.87	18.00

STAGE	COMPONENT						SUM
	1	2	3	4	5	6	
1	X= 9.9419E-01	2.6325E-05	1.9856E-03	1.8662E-03	1.8303E-03	6.5787E-06	0.99991
	Y= 8.8638E-01	7.4800E-05	3.6060E-02	3.8447E-02	3.9037E-02	5.5345E-05	1.00005
	K= 8.9156E-01	2.8414E+00	1.8161E+01	2.0601E+01	2.1329E+01	8.4127E+00	
2	X= 9.9454E-01	2.8479E-05	1.9514E-03	1.7160E-03	1.6573E-03	9.7270E-06	0.99990
	Y= 8.9400E-01	8.1106E-05	3.5357E-02	3.5304E-02	3.5229E-02	8.1774E-05	1.00005
	K= 8.9890E-01	2.8479E+00	1.8119E+01	2.0574E+01	2.1257E+01	8.4069E+00	
3	X= 9.8856E-01	6.7115E-05	4.4305E-03	3.7046E-03	3.2863E-03	3.0208E-05	1.00007
	Y= 7.3277E-01	1.9327E-04	9.4532E-02	8.7069E-02	8.5187E-02	2.8203E-04	1.00004
	K= 7.4126E-01	2.8797E+00	2.1337E+01	2.3503E+01	2.5922E+01	9.3362E+00	
4	X= 9.9718E-01	2.9741E-05	1.0633E-03	8.4927E-04	7.8849E-04	8.4593E-06	0.99992
	Y= 9.4049E-01	9.0825E-05	2.1364E-02	1.9371E-02	1.8678E-02	7.7533E-05	1.00007
	K= 9.4315E-01	3.0539E+00	2.0093E+01	2.2810E+01	2.3689E+01	9.1654E+00	
5	X= 9.9880E-01	2.5799E-05	4.4587E-04	3.2803E-04	2.9893E-04	5.2990E-06	0.99990
	Y= 9.7669E-01	7.9582E-05	8.3691E-03	7.4393E-03	6.9781E-03	4.8416E-05	1.00010
	K= 9.7787E-01	3.0847E+00	1.9892E+01	2.2679E+01	2.3344E+01	9.1368E+00	
6	X= 9.8542E-01	3.8869E-04	6.4188E-03	4.4583E-03	3.4427E-03	1.6044E-04	1.00029
	Y= 6.0702E-01	1.1618E-03	1.6171E-01	1.1950E-01	1.0906E-01	1.6812E-03	1.00013
	K= 6.1601E-01	2.9891E+00	2.5193E+01	2.6803E+01	3.1678E+01	1.0478E+01	
7	X= 9.9886E-01	1.2662E-04	5.2413E-04	3.3167E-04	2.6560E-04	2.1147E-05	1.00013
	Y= 9.7214E-01	4.1583E-04	1.1870E-02	8.4963E-03	7.1499E-03	2.1382E-04	1.00028
	K= 9.7324E-01	3.2842E+00	2.2647E+01	2.5616E+01	2.6920E+01	1.0111E+01	
8	X= 9.9978E-01	3.9987E-05	6.1574E-05	3.7938E-05	3.1763E-05	2.9753E-06	0.99996
	Y= 9.9677E-01	1.3215E-04	1.3857E-03	9.6861E-04	8.4710E-04	3.0020E-05	1.00013
	K= 9.9698E-01	3.3048E+00	2.2504E+01	2.5531E+01	2.6669E+01	1.0090E+01	
9	X= 9.9986E-01	2.2712E-05	7.6167E-06	4.1762E-06	3.3601E-06	7.4456E-07	0.99990
	Y= 9.9463E-01	7.5112E-05	1.7128E-04	1.0658E-04	8.9513E-05	7.5108E-06	1.00007
	K= 9.9976E-01	3.3072E+00	2.2488E+01	2.5521E+01	2.6640E+01	1.0088E+01	

DES= 2.1849E+02 DMS= 4.6677E-04

HEAT LOAD ON FR COND = -3.090239E+05

HEAT LOAD ON FINAL CONDENSER = -3.440447E+05

HEAT LOAD ON MAIN CONDENSER = -1.800000E+06

D.F. = 2.72

C.F. KP = 16.81

C.F. LG = 6.12

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