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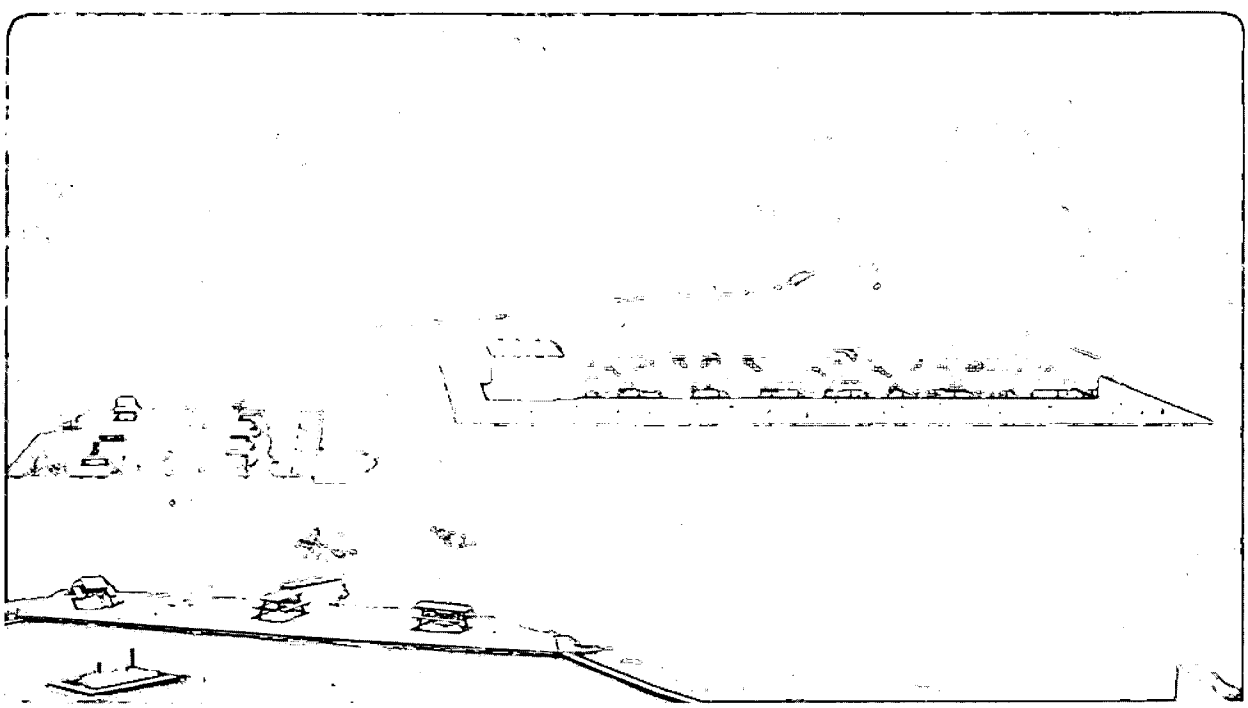

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Three-Phase Flash Calculations for Multicomponent Systems

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Abstract A three-phase flash algorithm (Nelson, 1987) has been incorporated into a program for calculating high-pressure phase equilibria (Dohrn, Brunner, 1989a). The method presented here includes the à priori determination of the number of phases present and the solution of the flash equations once the number of phases has been determined. Although an extension to more than three coexisting phases is possible, the method given here is restricted to multicomponent systems with a maximum of three phases in equilibrium. To illustrate the method, phase-equilibrium calculations are shown for the ternary systems Hexadecane-Water-Hydrogen and Toluene-Water-Hydrogen at elevated pressures and temperatures.

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INTRODUCTION

The multiple-phase flash problem can be solved by using either of two techniques. The traditional flash algorithm is based on the thermodynamic condition of equal fugacities for each component in each phase. By assuming the number of phases present at equilibrium and estimating the initial values for the distribution coefficients, the material balances are solved for the phase fractions. The resulting phase compositions then provide better values for updating the distribution coefficients, using an equation of state. Convergence has to be achieved for the phase compositions (or distribution coefficients).

Alternatively, flash algorithms may be based on a Gibbs-energy minimization as proposed, for example, by Gautam and Seider (1979) and Michelsen (1982). The Gibbs energy is at its minimum when all flash equations are satisfied. Although minimization methods are superior to the fugacity-matching methods whenever chemical reactions have to be considered, they appear not to be competitive for normal physical equilibrium calculations (Ohanomah and Thompson, 1984).

The flash algorithm discussed in this paper is based on the fugacity-matching method. To avoid unnecessary computations for three-phase equilibria when only one phase or two phases exist, the search for a two-phase solution is only performed when all single-phase tests failed; the three-phase flash is started only when there is no solution to two-phase equilibria.

THE ISOTHERMAL-ISOBARIC FLASH

Four types of equations are required to describe the three-phase flash completely; they are

Phase equilibrium :

$$K_i^{I} = \frac{y_i}{x_i^{I}} = \frac{\phi_{iL}^{I}}{\phi_{iV}} \qquad K_i^{II} = \frac{y_i}{x_i^{II}} = \frac{\phi_{iL}^{II}}{\phi_{iV}} \qquad (i=1,2,...,C) \tag{1}$$

Component material balance :

$$F z_i = V y_i + L^{I} x_i^{I} + L^{II} x_i^{II} \qquad (i=1,2,...,C) \tag{2}$$

Total material balance (summing up eq, (2) over all components):

$$F = V + L^{I} + L^{II} \tag{3}$$

Stoichiometric :

$$\sum_{i=1}^{K} y_i = \sum_{i=1}^{K} x_i^{I} = \sum_{i=1}^{K} x_i^{II} = 1 \tag{4}$$

All symbols are defined at the end.

Using eq. (1), eq. (2) can be solved for the mole fractions of the vapor phase, liquid-phase I and liquid-phase II :

$$y_i = \frac{z_i F K_i^{I} K_i^{II}}{V K_i^{I} K_i^{II} + L^{I} K_i^{II} + L^{II} K_i^{I}} \qquad (i=1,2,...,C) \qquad (5)$$

$$x_i^{I} = \frac{z_i F K_i^{II}}{V K_i^{I} K_i^{II} + L^{I} K_i^{II} + L^{II} K_i^{I}} \qquad (i=1,2,...,C) \qquad (6)$$

$$x_i^{II} = \frac{z_i F K_i^{I}}{V K_i^{I} K_i^{II} + L^{I} K_i^{II} + L^{II} K_i^{I}} \qquad (i=1,2,...,C) \qquad (7)$$

Summing eq. (5) to (7) over all components and using eq. (3) and (4), equations (8) to (10) follow after rearranging :

$$P_1(\Psi^{I}, \Psi^{II}) = \sum_{i=1}^{K} y_i - 1$$

$$= \sum_{i=1}^{K} \frac{z_i K_i^{I} K_i^{II}}{K_i^{I} K_i^{II} + \Psi^{I} K_i^{II} (1 - K_i^{I}) + \Psi^{II} K_i^{I} (1 - K_i^{II})} - 1 = 0 \quad (8)$$

$$P_2(\Psi^{I}, \Psi^{II}) = \sum_{i=1}^{K} x_i^{I} - 1$$

$$= \sum_{i=1}^{K} \frac{z_i K_i^{II}}{K_i^{I} K_i^{II} + \Psi^{I} K_i^{II} (1 - K_i^{I}) + \Psi^{II} K_i^{I} (1 - K_i^{II})} - 1 = 0 \quad (9)$$

$$P_3(\Psi^{I}, \Psi^{II}) = \sum_{i=1}^{K} x_i^{II} - 1$$

$$= \sum_{i=1}^{K} \frac{z_i K_i^{I}}{K_i^{I} K_i^{II} + \Psi^{I} K_i^{II} (1 - K_i^{I}) + \Psi^{II} K_i^{I} (1 - K_i^{II})} - 1 = 0 \quad (10)$$

where the phase fractions Ψ^{I} and Ψ^{II} are defined by

$$\Psi^{I} = \frac{L^{I}}{F} \tag{11}$$

$$\Psi^{II} = \frac{L^{II}}{F} \tag{12}$$

Equations (8) to (10) are the objective functions which must be satisfied simultaneously for the three-phase flash. Two problems arise when using these objective functions. First, only two of them can be independent because there are only two independent variables, Ψ^{I} and Ψ^{II}. Also, all three functions have a superfluous root at one of the vertices of the triangular domain of interest. This behavior causes difficulties when a gradient-based root-finding technique is applied. Depending on the starting value for the phase fraction Ψ^{I} or Ψ^{II}, either root will be reached.

More suitable for numerical solution are the two independent functions derived from eq. (8) to (10) :

$$\begin{aligned} Q_1(\Psi^{I}, \Psi^{II}) &= \sum_{i=1}^{K} x_i^{I} - \sum_{i=1}^{K} y_i \\ &= P_2(\Psi^{I}, \Psi^{II}) - P_1(\Psi^{I}, \Psi^{II}) \\ &= \sum_{i=1}^{K} \frac{z_i K_i^{II}(1-K_i^{I})}{K_i^{I} K_i^{II} + \Psi^{I} K_i^{II}(1-K_i^{I}) + \Psi^{II} K_i^{I}(1-K_i^{II})} = 0 \end{aligned} \tag{13}$$

$$\begin{aligned} Q_2(\Psi^{I}, \Psi^{II}) &= \sum_{i=1}^{K} x_i^{II} - \sum_{i=1}^{K} y_i \\ &= P_3(\Psi^{I}, \Psi^{II}) - P_1(\Psi^{I}, \Psi^{II}) \end{aligned}$$

$$= \sum_{i=1}^{K} \frac{z_i K_i^{I}(1-K_i^{II})}{K_i^{I} K_i^{II} + \Psi^{I} K_i^{II} (1 - K_i^{I}) + \Psi^{II} K_i^{I} (1 - K_i^{II})} = 0 \qquad (14)$$

The values of Q_1, and Q_2 at the vertices of the triangular domain are shown in Table 1. Figure 1 depicts the Q-functions for normal three-phase behavior.

Q_1 is normally positive at (0,0) and negative at (1,0). Q_1 changes sign somewhere along the Ψ^{I}-axis. The same is true for Q_2 along the Ψ^{II}-axis and for Q_1-Q_2 along the diagonal. The solution of the three-phase flash (the equilibrium point for all three phases), lies in the triangular domain where both Q-functions intersect and equal zero. If no such point exists within the domain, a vapor-liquid 1 system can exist, if the Q_1-function equals zero along the Ψ^{I}-axis. For the presence of a vapor-liquid 2 system, Q_2 equals zero along the Ψ^{II}-axis. Q_1-Q_2 equals zero along the diagonal, if a liquid 1-liquid 2 system exists. Under certain conditions, no root can be found along the axis or the diagonal; in that event, only a single phase exists.

Since the single-phase tests do not require iterating calculations, they precede the two-phase flash calculations. To check for single-phase behavior, it is only necessary to evaluate the Q-functions and the difference Q_1-Q_2 at the vertices of the triangular domain (Table 1).

The tests can be presented by

a) single vapor phase :

$$\sum_{i=1}^{K} \frac{z_i}{K_i^{I}} < 1 \qquad \text{and} \qquad \sum_{i=1}^{K} \frac{z_i}{K_i^{II}} < 1$$

b) single liquid-phase 1 :

$$\sum_{i=1}^{K} z_i K_i^{I} < 1 \qquad \text{and} \qquad \sum_{i=1}^{K} z_i \frac{K_i^{II}}{K_i^{I}} < 1$$

c) single liquid-phase 2 :

$$\sum_{i=1}^{K} z_i K_i^{II} < 1 \qquad \text{and} \qquad \sum_{i=1}^{K} z_i \frac{K_i^{I}}{K_i^{II}} < 1$$

As indicated above, the solution of the flash equations for the two-phase flash is a point on either the Ψ-axis or the diagonal. Again, criteria for three different systems can be represented by

a) vapor phase and liquid-phase 1 :

$$\sum_{i=1}^{K} \frac{z_i}{K_i^{I}} > 1 \qquad \text{and} \qquad \sum_{i=1}^{K} z_i K_i^{I} > 1$$

with $Q_2\left(\Psi^{I}, 0\right) < 0$ at the point $Q_1\left(\Psi^{I}, 0\right) = 0$

b) vapor phase and liquid-phase 2 :

$$\sum_{i=1}^{K} \frac{z_i}{K_i^{II}} > 1 \qquad \text{and} \qquad \sum_{i=1}^{K} z_i K_i^{II} > 1$$

with $Q_1\left(0, \Psi^{II}\right) < 0$ at the point $Q_2\left(0, \Psi^{II}\right) = 0$

c) liquid-phase 1 and liquid-phase 2 :

$$\sum_{i=1}^{K} z_i \frac{K_i^{I}}{K_i^{II}} > 1 \qquad \text{and} \qquad \sum_{i=1}^{K} z_i \frac{K_i^{II}}{K_i^{I}} > 1$$

with $Q_1\left(\Psi^{I}, 1-\Psi^{I}\right) > 0$ $\left[\text{or} \quad Q_2\left(\Psi^{I}, 1-\Psi^{I}\right) > 0\right]$

at the point $Q_1\left(\Psi^{I}, 1-\Psi^{I}\right) - Q_2\left(\Psi^{I}, 1-\Psi^{I}\right) = 0$

For finding the roots of the Q-functions, the Newton-Raphson procedure can be used :

a) $$Q_1(\Psi^{I}, 0) = 0 \tag{15}$$

$$\left(\Psi^{I}\right)_{M+1} = \left(\Psi^{I}\right)_{M} - \frac{\left[Q_1\left(\Psi^{I}, 0\right)\right]_M}{\left[\dfrac{dQ_1\left(\Psi^{I}, 0\right)}{d\Psi^{I}}\right]_M} \tag{16}$$

with $$\frac{dQ_1\left(\Psi^{I}, 0\right)}{d\Psi^{I}} = \sum_{i=1}^{K} \frac{-z_i\left(K_i^{II}\right)^2\left(1-K_i^{I}\right)^2}{\left(K_i^{I} K_i^{II} + \Psi^{I} K_i^{II}\left(1-K_i^{I}\right)\right)^2} \tag{17}$$

b) $$Q_1(0, \Psi^{II}) = 0 \tag{18}$$

$$\left(\Psi^{II}\right)_{M+1} = \left(\Psi^{II}\right)_{M} - \frac{\left[Q_2\left(0, \Psi^{II}\right)\right]_M}{\left[\dfrac{dQ_2\left(0, \Psi^{II}\right)}{d\Psi^{II}}\right]_M} \tag{19}$$

$$\text{with} \quad \frac{dQ_2\left(0, \Psi^{II}\right)}{d\Psi^{II}} = \sum_{i=1}^{K} \frac{-z_i\left(K_i^{I}\right)^2\left(1-K_i^{II}\right)^2}{\left(K_i^{I}K_i^{II} + \Psi^{II}K_i^{I}(1-K_i^{II})\right)^2} \tag{20}$$

c) $$Q_1(\Psi^I, 1-\Psi^I) - Q_2(\Psi^I, 1-\Psi^I) = 0 \tag{21}$$

$$\left(\Psi^{I}\right)_{M+1} = \left(\Psi^{I}\right)_{M} - \frac{\left[Q_1\left(\Psi^{I}, 1-\Psi^{I}\right) - Q_2\left(\Psi^{I}, 1-\Psi^{I}\right)\right]_M}{\left[\dfrac{d\left(Q_1 - Q_2\right)}{d\Psi^{I}}\right]_M} \tag{22}$$

$$\text{with} \quad \frac{d\left(Q_1 - Q_2\right)}{d\Psi^{I}} = \sum_{i=1}^{K} \frac{-z_i\left(K_i^{II} - K_i^{I}\right)^2}{\left(K_i^{I} - \Psi^{I}(K_i^{I} - K_i^{II})\right)^2} \tag{23}$$

Only if none of the above single-phase tests or two-phase flashes lead to the solution, is a three-phase flash performed. The criteria are :

$$Q_1\left(\Psi^{I}, \Psi^{II}\right) = 0 \tag{13}$$

$$Q_2\left(\Psi^{I}, \Psi^{II}\right) = 0 \tag{14}$$

The solution of eq. (13) and (14) is iteratively determined by applying the Newton-Raphson procedure :

$$\begin{pmatrix} \Psi^{I} \\ \Psi^{II} \end{pmatrix}_{M+1} = \begin{pmatrix} \Psi^{I} \\ \Psi^{II} \end{pmatrix}_{M} - \frac{\begin{pmatrix} Q_1 \\ Q_2 \end{pmatrix}_M}{\left[d\begin{pmatrix} Q_1 \\ Q_2 \end{pmatrix} / d\begin{pmatrix} \Psi^{I} \\ \Psi^{II} \end{pmatrix} \right]_M} \tag{24}$$

$$= \begin{pmatrix} \Psi^{I} \\ \Psi^{II} \end{pmatrix}_{M} - \left[d\begin{pmatrix} Q_1 \\ Q_2 \end{pmatrix} / d\begin{pmatrix} \Psi^{I} \\ \Psi^{II} \end{pmatrix} \right]_M^{-1} \begin{pmatrix} Q_1 \\ Q_2 \end{pmatrix}_M \tag{25}$$

with $$\left[\frac{d\begin{pmatrix} Q_1 \\ Q_2 \end{pmatrix}}{d\begin{pmatrix} \Psi^{I} \\ \Psi^{II} \end{pmatrix}} \right]_M^{-1} = \left[\begin{matrix} \left(\frac{dQ_1}{d\Psi^{I}}\right) & \left(\frac{dQ_1}{d\Psi^{II}}\right) \\ \left(\frac{dQ_2}{d\Psi^{I}}\right) & \left(\frac{dQ_2}{d\Psi^{II}}\right) \end{matrix} \right]_M^{-1}$$

$$= \frac{1}{D} \left[\begin{matrix} \left(\frac{dQ_2}{d\Psi^{II}}\right) & \left(-\frac{dQ_1}{d\Psi^{II}}\right) \\ \left(-\frac{dQ_2}{d\Psi^{I}}\right) & \left(\frac{dQ_1}{d\Psi^{I}}\right) \end{matrix} \right]_M \tag{26}$$

with D as the determinant of the Jacobian Matrix :

$$D = \frac{dQ_1}{d\Psi^{I}} \frac{dQ_2}{d\Psi^{II}} - \frac{dQ_1}{d\Psi^{II}} \frac{dQ_2}{d\Psi^{I}} \tag{27}$$

and the derivatives :

$$\frac{dQ_1}{d\Psi^{I}} = \sum_{i=1}^{K} \frac{-z_i \left(K_i^{II}\right)^2 \left(1-K_i^{I}\right)^2}{\left(K_i^{I} K_i^{II} + \Psi^{I} K_i^{II} (1 - K_i^{I}) + \Psi^{II} K_i^{I} (1 - K_i^{II})\right)^2} \tag{28}$$

$$\frac{dQ_1}{d\Psi^{II}} = \frac{dQ_2}{d\Psi^{I}} = \sum_{i=1}^{K} \frac{-z_i K_i^{I} K_i^{II} \left(1-K_i^{I}\right)\left(1-K_i^{II}\right)}{\left(K_i^{I} K_i^{II} + \Psi^{I} K_i^{II} (1 - K_i^{I}) + \Psi^{II} K_i^{I} (1 - K_i^{II})\right)^2} \tag{29}$$

$$\frac{dQ_2}{d\Psi^{II}} = \sum_{i=1}^{K} \frac{-z_i \left(K_i^{I}\right)^2 \left(1-K_i^{II}\right)^2}{\left(K_i^{I} K_i^{II} + \Psi^{I} K_i^{II} (1 - K_i^{I}) + \Psi^{II} K_i^{I} (1 - K_i^{II})\right)^2} \tag{30}$$

PROGRAM DESCRIPTION

Based on the algorithm described above, a subroutine for flash calculations has been written and adjusted to an existing program for high-pressure phase-equilibrium calculations. The flash subroutine is linked to the main program and to the subroutine in which the distribution coefficients are evaluated, based on some selected equation of state.

For the entire calculation procedure, two sets of distribution coefficients (K_i^{I} and K_i^{II}) are required, even if fewer than three phases are present. Figure 2 presents a schematic of the flash subroutine.

With given pressure P, temperature T and feed composition z_i, as well as first estimates for the mole fractions of all three phases (x_i^{I}, x_i^{II} and y_i) and the phase fractions (Ψ^{I}, Ψ^{II}), the equation of state used provides updated initial values for the two sets of distribution coefficients.

The first step is to check for single-phase behavior. This step is easily achieved since no iterating calculations are performed.

In the preceding two-phase flash, it is necessary to determine the root of the Q-functions or the difference of both $Q_1 - Q_2$ along the axis or the diagonal using the Newton-Raphson procedure. At least one of the two-phase flashes will lead to the solution of the appropriate Q-function but at most for one of these flashes will all criteria be satisfied. Once the root is found with constant sets of distribution coefficients and the criteria mentioned earlier are all met, the mole fractions of the three phases are recalculated using eqs. (5) to (7). For the nonexisting phase, the mole fractions will sum up to less than unity and should be normalized. With these improved estimates for the phase compositions, new sets of distribution coefficients are calculated using the equation of state. The two-phase flash continues with a new search for the root of the Q-function until all distribution coefficients converge within tolerance.

If all two-phase flashes fail, the three-phase flash has to be performed by iteratively and simultaneously searching for the roots of Q_1 and Q_2. Similar to the two-phase flashes, the solution of the Q-functions will lead to better estimates for the phase compositions of all three phases calculated by eqs. (5) to (7); thereafter, new distribution coefficients can be determined. The flash problem is solved when distribution coefficients converge within tolerance.

For a two-phase flash, we use initial values of 0.5, for phase fractions Ψ^{I} and Ψ^{II}. If a three-phase flash must be performed, a good starting point (Ψ^{I}, Ψ^{II}) is found from the two-phase flash which solved the Q-function without solving the flash problem.

Finding initial values for the mole fractions is simple if experimental data are available for all phases. If the existence of a second liquid phase is

in question, suitable starting values for the composition of this phase are obtained by assuming that one component is in excess.. The mole fraction of this component is arbitrarily set to 0.998 at the beginning of the iterating procedure.

EXAMPLES

Using the method described above, we have calculated phase equilibria for the ternary systems Hexadecane-Water-Hydrogen at 200° C and 200 bar and Toluene-Water-Hydrogen at 200° C and 100 bar using experimental data from Dohrn (1986) and Liebold (1988). The first example was calculated using the Redlich-Kwong-Hederer equation of state (Hederer et al., 1976); the second example used the Peng-Robinson equation of state with modified parameters (Dohrn and Brunner, 1989).

Table 2 shows the pure-component parameters for the equations of state. Figures 3 and 4 illustrate the experimental and calculated phase-equilibrium data. Interaction parameters Θ_{ij} were fitted to the experimental data of the ternary system.

In both examples the calculation procedure consists of two sections. In the first section, the flash calculations were performed using the experimental data for the phase compositions as starting values. Where only two experimental phases were present, the composition of the third phase was estimated as described above to start the flash calculation procedure. In the second section, the calculation procedure started at the binary boundary of the triangular diagram by using the calculated mole fractions of the last flash as starting values for the next flash. After each successful flash, the feed composition is changed in such a way that the feed point moves on a straight line toward the upper vertex of the ternary

diagram. If the composition point of the feed reaches the three-phase region, the three-phase flash is entered. After this flash is completed, the calculation procedure continues at either boundary of the three-phase region to cover all possible miscibility gaps in the system.

CONCLUSIONS

The flash algorithm described in this paper can be used to calculate phase-equilibria for multicomponent systems with two or three coexisting phases at equilibrium. It has been installed into a program for calculating high-pressure phase-equilibria with a selected equation of state. In ternary systems containing Water, Hydrogen and Hexadecane or Toluene at elevated pressures and temperatures, the two- and three-phase regions are correctly predicted using either one of two cubic equations of state. Where no experimental data were given, the composition of the second liquid phase had to be estimated. For all calculations performed, this was easily done by initially assuming, that this phase contains one component in excess.

Program listings and tapes are available upon request.

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NOMENCLATURE

a = parameter of the RKH equation of state

a_c = parameter of the PR equation of state (modified parameters)

b = parameter of the RKH and PR (modified) equation of state

C = number of components

D = determinant of the Jacobian Matrix, equations (25)

F = total moles of feed to the flash

K_i^I = vapor/liquid distribution coefficient for component i and liquid phase I

K_i^{II} = vapor/liquid distribution coefficient for component i and liquid phase II

L^I = moles of liquid in phase 1

L^{II} = moles of liquid in phase 2

P = pressure

P_i = objective functions defined by equations (8) to (10)

Q_i = objective functions defined by equations (13) and (14)

T = temperature

V = moles of vapor phase

x_o = parameter pf the PR equation of state (modified parameter)

x_i^I = mole fraction of component i in liquid phase 1

x_i^{II} = mole fraction of component i in liquid phase 2

y_i = mole fraction of component i in the vapor phase

z_i = mole fraction of component i in the feed

α = parameter of the RKH equation of state

ϕ_{iL}^I = fugacity coefficient of component i in liquid phase 1

ϕ_{iL}^{II} = fugacity coefficient of component i in liquid phase 2

ϕ_{iV} = fugacity coefficient of component i in the vapor phase

Ψ^{I} = phase fraction of liquid phase 1

Ψ^{II} = liquid 2 phase fraction

Θ_{ij} = interaction parameter for the binary system containing components i and j

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CAPTIONS

Fig. 1 : Objective functions Q_1, Q_2 and Q_1 - Q_2 for normal three-phase behavior : ———— Q_1 function; - - - - - - - Q_2 function; ····· Q_1 - Q_2 function.

Fig. 2 : Schematic of the program for three-phase flash calculations

Fig. 3 : Ternary phase diagram for the system Hexadecane(1)-Water(2)-Hydrogen(3) at 200 °C and 200 bar. • experimental phase composition and ····· experimental tie lines (Dohrn, 1986); ———— calculated binodal curve and tie lines (Redlich-Kwong-Hederer EOS); interaction parameters : Θ (1,2) = 0.2756, Θ (1 ,3) = 0.2249, Θ (2,3) = 0.4201.

Fig. 4 : Ternary phase diagram for the system Toluene(1)-Water(2)-Hydrogen(3) at 200 °C and 100 bar. • experimental phase composition and ····· experimental tie lines (Liebold, 1988); ———— calculated binodal curve and tie lines (Peng-Robinson EOS with modified parameters (Dohrn, Brunner, 1989)). interaction parameters : Θ (1,2) = 0.2500, Θ (1 ,3) = 0.9500, Θ (2,3) = 0.6000.

Table 1 : Values of Q_1 , Q_2 and $Q_1 - Q_2$ at the vertices of the triangular domain

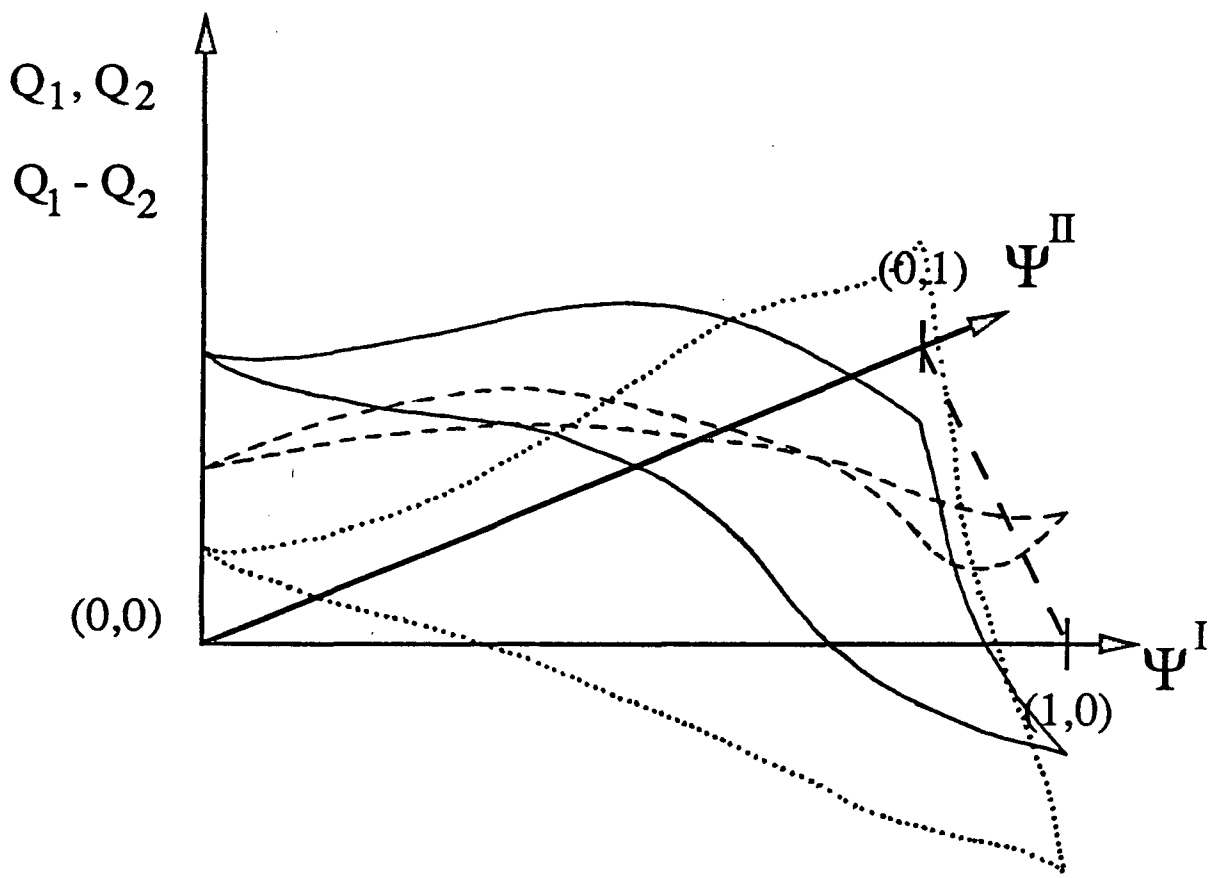
Ψ^I	Ψ^{II}	$Q_1(\Psi^I, \Psi^{II})$	$Q_2(\Psi^I, \Psi^{II})$	$Q_1 - Q_2$
0	0	$\sum_{i=1}^{K} \frac{z_i}{K_i^I} - 1$	$\sum_{i=1}^{K} \frac{z_i}{K_i^{II}} - 1$	$\sum_{i=1}^{K} \frac{z_i}{K_i^I} - \sum_{i=1}^{K} \frac{z_i}{K_i^{II}}$
1	0	$1 - \sum_{i=1}^{K} z_i K_i^I$	$\sum_{i=1}^{K} z_i \frac{K_i^I}{K_i^{II}} - \sum_{i=1}^{K} z_i K_i^I$	$1 - \sum_{i=1}^{K} z_i \frac{K_i^I}{K_i^{II}}$
0	1	$\sum_{i=1}^{K} z_i \frac{K_i^{II}}{K_i^I} - \sum_{i=1}^{K} z_i K_i^{II}$	$1 - \sum_{i=1}^{K} z_i K_i^{II}$	$\sum_{i=1}^{K} z_i \frac{K_i^{II}}{K_i^I} - 1$

Table 2 : Pure-component parameters

Component	RKH EOS			PR EOS (modified parameters)		
	α [-]	a [bar m^6/kmole^2 K^{α}]	b [m^3/kmole]	a_c [bar m^6/kmole^2 K]	x_o [-]	b [m^3/kmole]
Toluene	671.50	-0.51570	0.09199	19.350	0.55997	0.09057
Hexadecane	41,261.3	-0.92199	0.27492	97.531	0.86464	0.26897
Hydrogen	0.30	-0.01049	0.01772	0.274 *	1.58355 *	0.01682 *
Water	114.60	-0.47909	0.01607	6.064 *	0.93742 *	0.01917 *

* calculated from the PR EOS

Figure 1



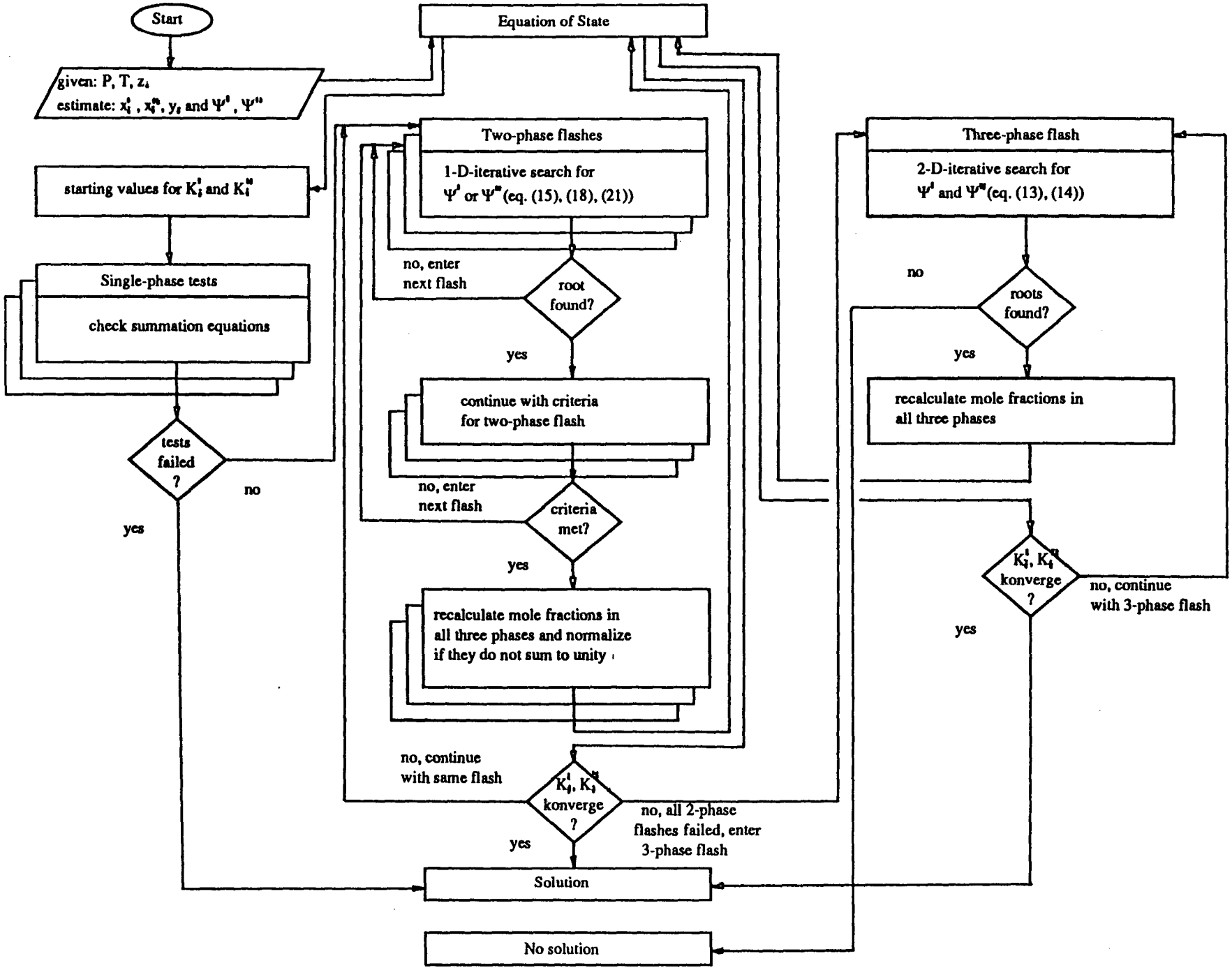

Start
given: P, T, z_i
estimate: x_i^I, x_i^{III}, y_i and Ψ^I, Ψ^{III}
starting values for K_i^I and K_i^{III}
Single-phase tests
check summation equations
tests failed ?
no
yes
Equation of State
Two-phase flashes
1-D-iterative search for
Ψ^I or Ψ^{III} (eq. (15), (18), (21))
no, enter next flash
root found?
yes
continue with criteria for two-phase flash
no, enter next flash
criteria met?
yes
recalculate mole fractions in all three phases and normalize if they do not sum to unity
no, continue with same flash
K_i^I, K_i^{III} konverge ?
yes
no, all 2-phase flashes failed, enter 3-phase flash
Three-phase flash
2-D-iterative search for
Ψ^I and Ψ^{III} (eq. (13), (14))
no
roots found?
yes
recalculate mole fractions in all three phases
K_i^I, K_i^{III} konverge ?
no, continue with 3-phase flash
yes
Solution
No solution

Figure 2

Figure 3

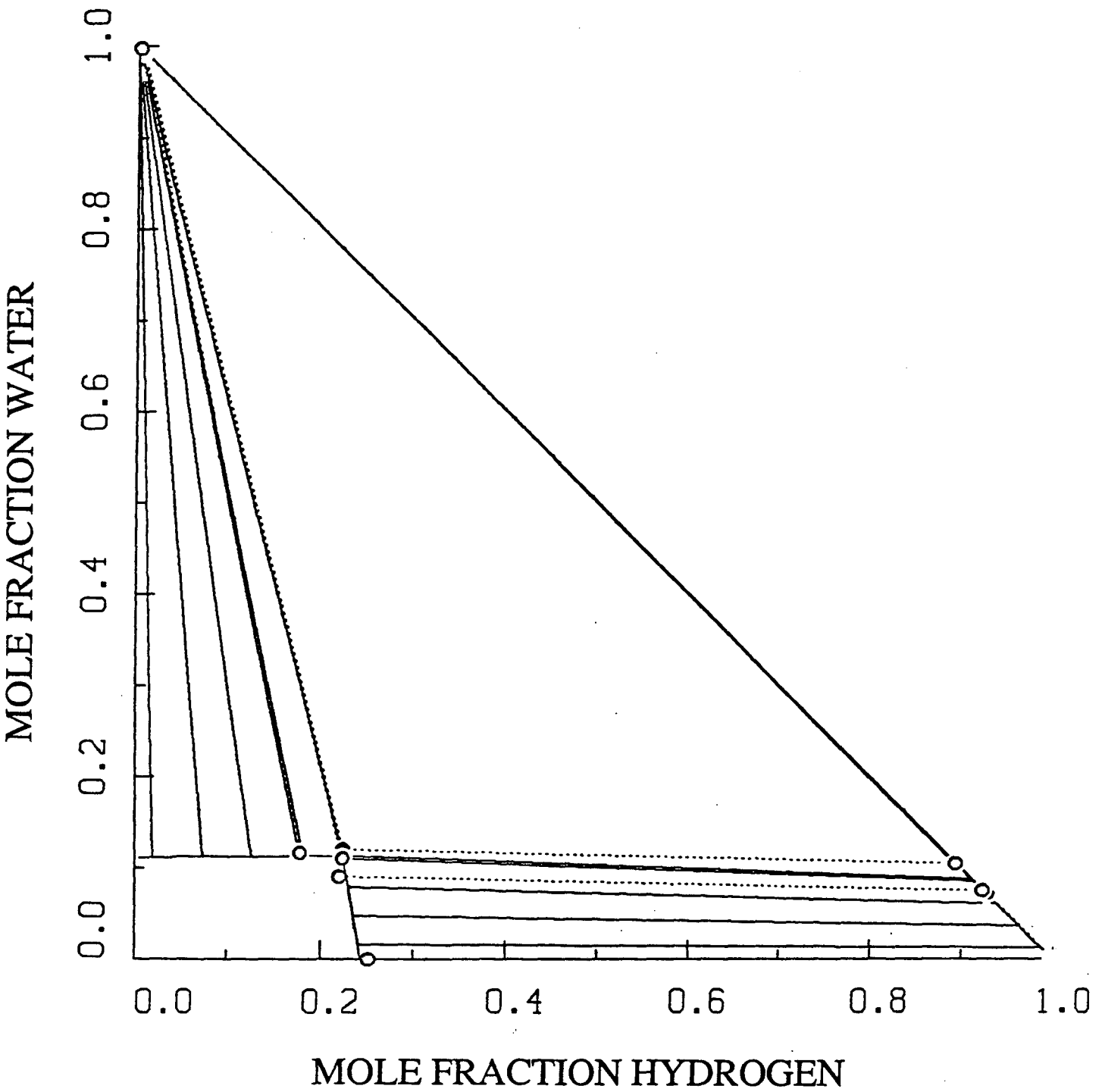
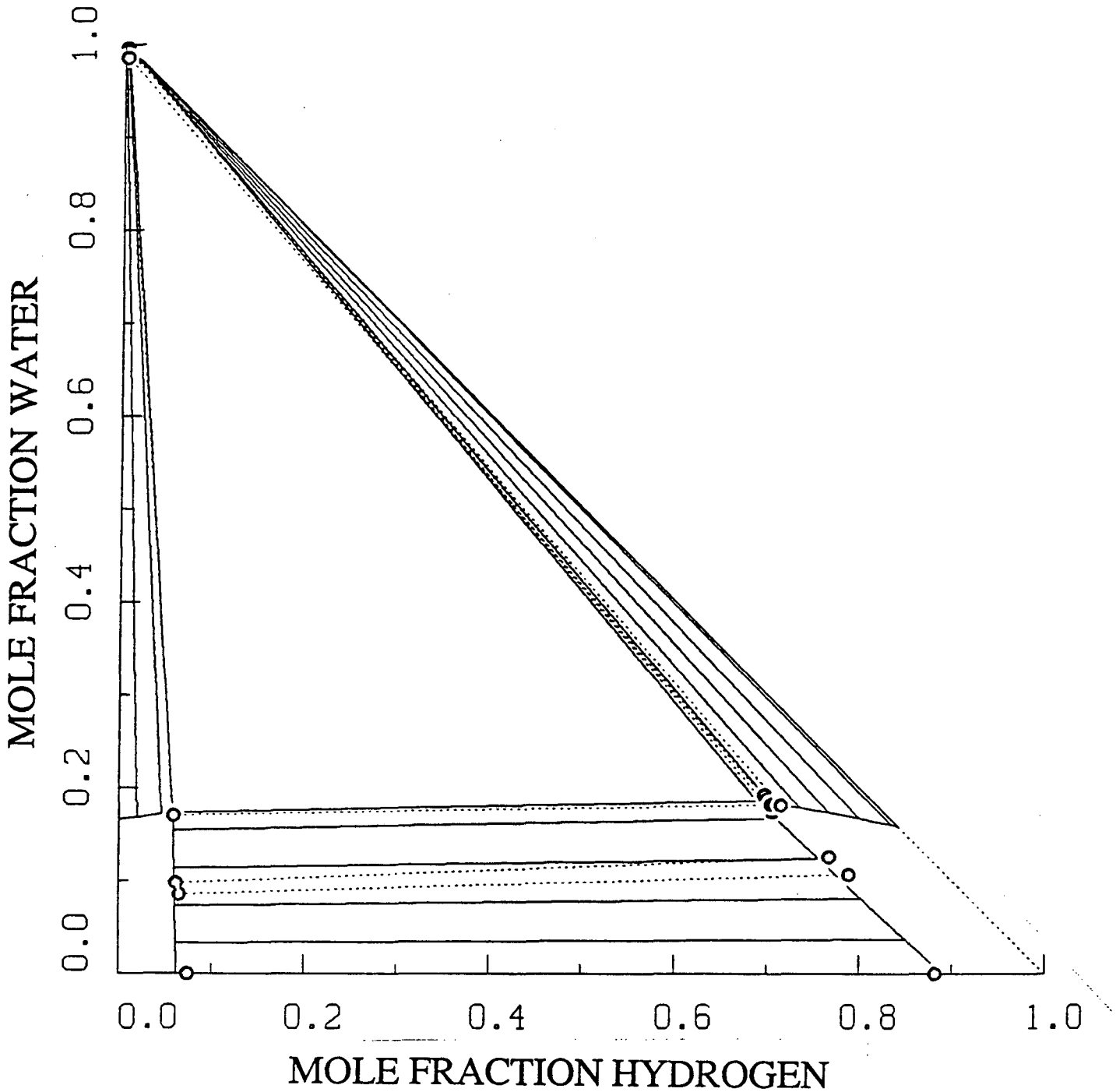

MOLE FRACTION WATER
1.0
0.8
0.6
0.4
0.2
0.0
0.0
0.2
0.4
0.6
0.8
1.0
MOLE FRACTION HYDROGEN

Figure 4


MOLE FRACTION WATER
0.0
0.2
0.4
0.6
0.8
1.0
MOLE FRACTION HYDROGEN
0.0
0.2
0.4
0.6
0.8
1.0

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