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### **A Model-Free Method for Calculating Vapor-Liquid Equilibria for Multicomponent Systems from Total-Pressure or Boiling-Point Data**

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**A MODEL-FREE METHOD FOR CALCULATING VAPOR-  
LIQUID EQUILIBRIA FOR MULTICOMPONENT SYSTEMS  
FROM TOTAL-PRESSURE OR BOILING-POINT DATA**

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**ABSTRACT**

A curved-surface spline function is used to describe the reduced excess Gibbs energy for multicomponent liquid mixtures in a model-free thermodynamic method for calculating vapor compositions from experimental temperatures, pressures and liquid compositions. A Newton-Raphson iteration procedure modified by Broyden is used for solving the method's nonlinear equations. The method is illustrated with calculations for a variety of binaries, ternaries and two quaternaries; these calculations indicate that this new method is both stable and reliable. Calculated vapor compositions are in good agreement with experiment. The method converges rapidly and has no special requirements for selecting initial guesses. The method may be used for either isothermal or isobaric data.

## INTRODUCTION

For measuring vapor-liquid equilibria in mixtures at constant temperature and at low or moderate pressures, two methods are commonly used. In the first method, the quantities measured are liquid composition  $x$ , vapor composition  $y$ , and total pressure  $P$  all at fixed temperature  $T$ . In the second method, only  $x$  and  $P$  are measured; from these isothermal measurements, vapor compositions  $y$  are calculated using the Gibbs-Duhem equation. The relative advantages and disadvantages of these two methods have been discussed extensively in the literature; see, for example, Van Ness (1982) and Abbott (1986). The main advantage of the second method is that experimental difficulties in measuring  $y$  are avoided entirely because  $y$  is not measured. The main advantage of the first method is that the experimental data can be tested for thermodynamic consistency ( see, for example, Prausnitz et al, 1986); such a test is not possible for the second method because the calculation of  $y$  from isothermal  $P-x$  data assumes thermodynamic consistency.

A variation of the second method is to obtain  $T-x$  data of constant total pressure. In this case,  $y$  is also calculated using the Gibbs-Duhem equation.

While application of the second method has been extensive, almost all attention has been restricted to binary systems. This work concerns application to multicomponent systems. We refer to the second method as the isothermal  $P-x$  method or the isobaric  $T-x$  method.

The simplest and most popular isothermal  $P-x$  method is that proposed by Barker (1953) which uses an arbitrary model for the molar excess Gibbs energy  $g^E$  and then obtains the constants in that model from the isothermal  $P-x$  data. Alternatively, Barker's method can also be used for isobaric  $T-x$  data. Barker's method for binary mixtures is easily extended to multicomponent mixtures, as shown, for example, by Abbott and Van Ness (1975) and by Loehe et al (1981). However, Barker's method has an inherent weakness: to reduce isothermal  $P-x$  data or isobaric  $T-x$  data, the user must choose a model for  $g^E$ . Final results depend on that choice.

To avoid use of a model for  $g^E$ , several authors have suggested procedures for numerical calculations. These procedures fall into two classes: indirect methods yield  $g^E$  (e.g. Mixon et al, 1965) while direct methods integrate the Gibbs-Duhem equation to yield  $y$  (e.g. Boissonnas, 1939; Ho et al, 1961; Van Ness, 1970; Martinez-Ortiz and Manley, 1977,1978; Hu and Ying, 1980). However, these model-free methods are essentially restricted to binary mixtures. Although Mixon et al (1965) and Hu et al (1980) showed examples of calculations for some ternaries, the indicated calculation efficiency was very low; further, serious convergence problems were encountered. Sayegh and Vera (1980) presented an extensive review on model-free methods for binaries.

This work presents a new indirect model-free method for multicomponent systems. The reduced excess Gibbs energy is simulated by a curved-surface spline function. Parameters for the spline function are obtained using a Broyden-revised Newton-Raphson iteration procedure. The method has been successfully tested for a variety of binaries, ternaries and quaternaries.

### Thermodynamic Framework

For a  $K$ -component system in vapor-liquid equilibrium, for each component  $i$  the equality of fugacities gives

$$Py_i \phi_i = f_i^* x_i \gamma_i \quad (1)$$

where  $f_i^*$  is the fugacity of pure liquid  $i$  and  $\phi_i$  is the fugacity coefficient of component  $i$  in the vapor phase, both at system temperature  $T$  and pressure  $P$ . Activity coefficient  $\gamma_i$  can be related to the molar excess Gibbs energy  $g^E$  of the liquid mixture by an equation derived from the Gibbs-Duhem equation:

$$\ln \gamma_i = Q + \left( \frac{\partial Q}{\partial x_i} \right)_{T,P,x[i,K]} - \sum_{j=1}^{K-1} x_j \left( \frac{\partial Q}{\partial x_j} \right)_{T,P,x[j,K]} \quad (2)$$

where  $Q$  is the reduced excess Gibbs energy defined by

$$Q \equiv g^E / RT \quad (3)$$

The total pressure can then be related to  $Q$  and its partial derivatives.

$$P = \sum_{i=1}^K P y_i = \sum_{i=1}^K \frac{f_i^* x_i}{\phi_i} \exp \left[ Q + \left( \frac{\partial Q}{\partial x_i} \right)_{T,P,x[i,K]} - \sum_{j=1}^{K-1} x_j \left( \frac{\partial Q}{\partial x_j} \right)_{T,P,x[j,K]} \right] \quad (4)$$

where subscript  $x[i,K]$  in the partial derivatives indicates that all liquid mole fractions are constant except  $x_i$  and  $x_K$ . The partial derivatives in eq.(1) can be expressed as:

$$\begin{aligned} \left( \frac{\partial Q}{\partial x_i} \right)_{T,P,x[i,K]} &= \left( \frac{\partial Q}{\partial x_i} \right)_{x[i,K]} - \left( \frac{\partial Q}{\partial T} \right)_{P,x} \left( \frac{\partial T}{\partial x_i} \right)_{P,x[i,K]} - \left( \frac{\partial Q}{\partial P} \right)_{T,x} \left( \frac{\partial P}{\partial x_i} \right)_{T,x[i,K]} \\ &= \left( \frac{\partial Q}{\partial x_i} \right)_{x[i,K]} + \frac{h^E}{RT^2} \left( \frac{\partial T}{\partial x_i} \right)_{P,x[i,K]} - \frac{v^E}{RT} \left( \frac{\partial P}{\partial x_i} \right)_{T,x[i,K]} \end{aligned} \quad (5)$$

where  $h^E$  and  $v^E$  are the molar excess enthalpy and the molar excess volume of the liquid mixture, respectively.

We define an objective function  $F$  to express the relative deviation between calculated total pressure  $P_{calc}$  by eq.(4) and its corresponding experimental value  $P_{expt}$ . The mathematical expectation of that function should be zero.

$$\begin{aligned} F &= (P_{calc} - P_{expt}) / P_{expt} \\ &= F(x_i, Q, \partial Q / \partial x_i) = 0 \end{aligned} \quad (6)$$

By solving eq.(6) simultaneously for all data points, we can, in principle, obtain reduced excess Gibbs energies  $Q$  and corresponding partial derivatives  $\partial Q / \partial x_i$ . Activity coefficients  $\gamma_i$  can therefore be calculated by eq.(2). Substituting into eq.(1), we obtain vapor compositions  $y_i$ . Fugacity coefficients  $\phi_i$  in eq.(1) are estimated using an equation of state with vapor compositions obtained from the last iteration.

For all data points, eq.(6) forms a set of nonlinear partial differential equations. For multicomponent systems, the essential requirement of the indirect model-free method is to develop an efficient procedure for solving eq.(6) to obtain  $Q$  as a function of  $x_i$ .

### Curved-Surface Spline Function

For a  $K$ -component system, reduced excess Gibbs energy  $Q$  is a continuous function with  $K-1$  dimensions in a physically meaningful thermodynamic space. When the number of ( $P-x$ ) data points in that space is  $N$ , we can construct a curved-surface spline function  $S(x_1, \dots, x_{K-1})$  fitting all  $N$  lattice points. A powerful method for constructing a spline function was developed by aeronautical engineers Harder and Desmarais (1972). In that

method, the curved-surface spline function is simulated by the deformation of an infinite plate which has no curvature in the absence of any loading. Deformation  $S$  is related to load  $q$  bearing on the plate and to the rigidity of the plate  $D$  by the partial differential equation:

$$D \nabla^4 S = q \quad (7)$$

Eq.(7) gives deformation  $S$  at  $N$  independent lattice points with the boundary condition that the surface becomes flat at points remote from all loads. The curved-surface spline function can be expressed as:

$$S(x_1, \dots, x_{K-1}) = \sum_{n=1}^N [d_n R_n^2 \ln(R_n^2 + e)] + \sum_{i=1}^{K-1} d_{N+i} x_i + d_{N+K} + C \quad (8)$$

where

$$R_n^2 = \sum_{i=1}^{K-1} (x_i - x_{i,n})^2 \quad (9)$$

In eq.(8),  $x_{i,n}$  is  $x_i$  at the  $n$ th lattice point and  $d_n$  are parameters of the spline function subject to the restraints:

$$L_i = \sum_{n=1}^N d_n x_{i,n} = 0, \quad i = 1, \dots, K-1 \quad (10)$$

$$L_K = \sum_{n=1}^N d_n = 0 \quad (11)$$

In eq.(8),  $C$  is a weighting factor related to the quality of the fit. It can be varied from one region to another in the lattice space. When the spline function is required to pass strictly through all experimental points,  $C$  equals zero.

Parameter  $e$  is a small adjustable quantity whose value is chosen according to practical conditions. If the surface is characterized by a sharp curvature,  $e$  is about  $10^{-4} - 10^{-6}$ . If the curvature of the surface is moderate,  $e$  is about  $1 - 10^{-2}$ . We take  $e=0.001$  in all cases. The partial derivative of  $S$  with respect to composition can be written:

$$\left(\frac{\partial S}{\partial x_i}\right)_{x_{[i,K]}} = 2 \sum_{n=1}^N \{ d_n (x_i - x_{i,n}) \left[ \frac{R_n^2}{R_n^2 + e} + \ln(R_n^2 + e) \right] \} + d_{N+i}, \quad (12)$$

### Application of the Curved-Surface Spline Function to the Model-Free Method

From experimental measurements, there are  $N$  independent isothermal total pressures or  $N$  independent isobaric boiling temperatures at different liquid compositions including  $K$  data points for pure components  $\{x_{1,n}, \dots, x_{K-1,n}, T_n, p_n; n = 1 - N\}$ . For those  $N-K$  multicomponent points, we replace the reduced excess Gibbs energy  $Q$  and the corresponding derivatives in eqs.(4) and (6) by the curved-surface spline function and its derivatives, i.e., eqs (8) and (12):

$$Q_{n^+} = S(x_{1,n^+}, \dots, x_{K-1,n^+}) = \sum_{n=1}^N [d_n R_{n,n^+}^2 \ln(R_{n,n^+}^2 + e)] + \sum_{i=1}^{K-1} d_{N+i} x_{i,n^+} + d_{N+K} + C$$

$$n^+ = 1, \dots, N-K \quad (13)$$

where

$$R_{n,n^+}^2 = \sum_{i=1}^{K-1} (x_{i,n^+} - x_{i,n})^2 \quad (14)$$



$$\left(\frac{\partial Q}{\partial x_{i,n^+}}\right)_{x[i,K]} = \left(\frac{\partial S}{\partial x_{i,n^+}}\right)_{x[i,K]} = 2 \sum_{n=1}^N \{ d_n (x_{i,n^+} - x_{i,n}) \left[ \frac{R_{n,n^+}^2}{R_{n,n^+}^2 + e} + \ln(R_{n,n^+}^2 + e) \right] \} + d_{N+i} ,$$

$$n^+ = 1, \dots, N-K \quad , \quad i = 1, \dots, K-1 \quad . \quad (15)$$

Therefore, we have  $N-K$  independent equations for the objective function, eq.(6):

$$F_n = F(x_{1,n}, \dots, x_{K-1,n}, d_1, \dots, d_{N+K}) = 0$$

$$n = 1, \dots, N-K \quad (16)$$

where  $d_1, \dots, d_{N+K}$  are  $N+K$  unknown parameters of the curved-surface spline function for the reduced excess Gibbs energy  $Q$ . For every pure component,  $Q$  equals zero. We then have additional  $K$  equations of the form

$$F_{N-K+i} = Q(x_i=1) = 0 \quad , \quad i = 1, \dots, K \quad . \quad (17)$$

In addition, we have another  $K$  restraint equations for  $d_n$ , eqs.(10) and (11):  $L_i = 0, i = 1, \dots, K$ . Now we have  $N+K$  independent equations in total, eqs.(10),(11),(16) and (17). We can solve for  $N+K$  parameters of the curved-surface spline function for the reduced excess Gibbs energy  $Q$ . After calculating activity coefficients by eq.(2), vapor compositions can then be obtained using eq(1).

### Computation Procedures

Eqs.(10),(11),(16) and (17) can be rewritten in an abbreviated vector form:

$$Y(X) = 0 \quad (18)$$

where  $X$  and  $Y$  are vectors.

$$X = \{ d_1, \dots, d_{N+K} \}^T \quad (19)$$

$$Y = \{ F_1, \dots, F_{N-K}, \dots, F_N, L_1, \dots, L_K \}^T \quad (20)$$

Here superscript  $T$  means "transpose".

Various numerical methods can be used to solve this set of nonlinear equations, indicated by eq.(18). We use the Newton-Raphson method modified by Broyden. Details are given elsewhere (Holland, 1981). Elementary iteration procedures are as follows:

$$\Delta X^k = - (J^k)^{-1} Y(X^k) \quad (21)$$

$$X^{k+1} = X^k + \Delta X^k \quad (22)$$

Where  $J$  is the Jacobian matrix. The essential of the Broyden modification is to establish a recurrence relation between  $J$ 's of two successive iterations:

$$(J^k)^{-1} = (J^{k-1})^{-1} + \Delta (J^{k-1})^{-1} \quad (23)$$

Because the inverse matrix of  $J$  at the  $k$ th iteration can be obtained from that at the preceding  $k-1$ th iteration by eq.(24), the computing time for estimating a Jacobian and its inverse matrix can be greatly reduced.

### ILLUSTRATIONS

## 1. Binaries

Before applying the preceding method, it is necessary to smooth experimental isothermal  $P-x$  data or isobaric  $T-x$  data. Such data are first fit by some analytical function, for instance, a polynomial, from which values of total pressures or boiling temperatures can be interpolated. For isothermal binaries, we use

$$P = x_1 P_1^* + x_2 P_2^* + x_1 x_2 W_{12} \quad (24)$$

For isobaric binaries, we use

$$T = x_1 T_1^* + x_2 T_2^* + x_1 x_2 W_{12} \quad (25)$$

where  $P_i^*$  and  $T_i^*$  are vapor pressure and boiling temperature of pure component  $i$ , respectively;  $i = 1, 2$ .

$$W_{12} = \sum_{k=1} J_k (x_1 - x_2)^{k-1} \quad (26)$$

Here  $J_k$  are parameters of the polynomial.

Vapor-phase nonideality is taken into account through fugacity coefficients in eq.(4) estimated by the Peng-Robinson equation of state. Vapor compositions needed in these calculations are taken from the last iteration; for the first iteration, all  $y$ 's are set equal to liquid compositions. Initial values for  $d_i$  in eq.(19) are 0.001.  $C$  in eq.(8) or (13) is set equal to zero because experimental data have been smoothed. Parameter  $e$  in eq.(8) is 0.001.

Tables 1 and 2 show two examples for calculations using the indirect model-free method in this work. The first example, the chloroform(1)/ethanol(2) binary at 55°C, is isothermal; the second example, the benzene(1)/2-propanol(2) binary at 101.325kPa, is isobaric. For both systems, calculated vapor compositions are in good agreement with experiment. Average deviations are 0.0016 and 0.0052, respectively.

We do not use experimental excess volumes for isothermal data or experimental excess enthalpies for isobaric data. Although we allow for these excess quantities, as indicated in eq.(5), neglecting them has no significant effect on the results. However, when we use the direct method for isobaric data (Hu and Ying, 1980), setting excess enthalpies equal to zero, the standard deviation is tripled, as shown in Table 2. The direct method is more sensitive to  $h^E$  because the fundamental equation in the direct method contains  $dy / dx$ , which is a higher-order differential equation than eq.(4) in the indirect method of this work.

Table 3 shows average deviations for calculations of vapor compositions by the present method for 21 binaries. Results are good.

## 2. Ternaries

For ternaries, polynomials are again used to correlate experimental  $T$ ,  $P$  and  $x$  data. For isothermal ternaries, we use

$$P = x_1 P_1^* + x_2 P_2^* + x_3 P_3^* + x_1 x_2 W_{12} + x_1 x_3 W_{13} + x_2 x_3 W_{23} \\ + x_1 x_2 x_3 (A_0 + B_0 x_1 + C_0 x_2 + D_0 x_1 x_2 + E_0 x_1 x_3 + F_0 x_2 x_3 + G_0 x_1 x_2 x_3) \quad (27)$$

For isobaric ternaries, we use

$$T = x_1 T_1^* + x_2 T_2^* + x_3 T_3^* + x_1 x_2 W_{12} + x_1 x_3 W_{13} + x_2 x_3 W_{23} \\ + x_1 x_2 x_3 (A_0 + B_0 x_1 + C_0 x_2 + D_0 x_1 x_2 + E_0 x_1 x_3 + F_0 x_2 x_3 + G_0 x_1 x_2 x_3) \quad (28)$$

where  $W_{ij}$  (see eq.27) is a polynomial obtained from binary  $i-j$  data and  $A_0, B_0, C_0, D_0, E_0, F_0$  and  $G_0$  are ternary parameters.

For simplicity, because the total pressure  $s$  are low, we neglected vapor-phase nonidealities in our calculations for ternaries. Excess properties  $v^E$  or  $h^E$  are also not used as in calculations for binaries. In eq.(9), parameter  $e$  is 0.001 in all cases.

Tables 4 and 5 show two ternary examples. The first, methanol(1)/methyl acetate(2)/ethyl acetate(3) is isothermal at 40°C. The second, acetone(1)/chloroform(2)/benzene(3) is isobaric at 101.325kPa. Both show good agreement with experimental vapor compositions. Average deviations for calculated vapor compositions are 0.0136 and 0.0065 for  $y_1$ , 0.0144 and 0.0063 for  $y_2$ , 0.0043 and 0.0057 for  $y_3$ , respectively. Tables 6 and 7 show more examples; all show satisfactory results. For systems that are nearly ideal, (e.g. dichloromethane/chloroform/carbon tetrachloride, and 1,3,5- 1,2,4- and 1,2,3-trimethyl benzenes), the number of iterations is very low; a few iterations can reach convergence. However, as nonideality increases, more iterations are needed.

Figures 1 and 2 show the reduced excess Gibbs energy  $Q$  as a function of composition. In Figure 1, for the dichloromethane(1)/chloroform(2)/carbon tetrachloride(3) ternary,  $Q$  is everywhere positive. In Figure 2, for the acetone(1)/chloroform(2)/ethanol(3) ternary,  $Q$  is positive for the binaries chloroform/ethanol and acetone/ethanol with a minimum-boiling azeotrope for chloroform-ethanol. However, for the acetone/chloroform binary,  $Q$  is negative with a maximum-boiling azeotrope. A saddle-shape  $Q$  surface describes the ternary. As shown in Table 7, for such a complicated case, only 9 iterations are required for convergence. Average deviations for  $y_1, y_2$  and  $y_3$  are 0.0103, 0.0080 and 0.0088 respectively, for 36 ternary data points.

### 3. Quaternaries

The method presented here can also be applied to systems containing four components. To illustrate, neglecting vapor-phase nonidealities, Table 8 shows results for the system cyclohexane(1)/benzene(2)/2-propanol(3)/2-butanone(4) at 101.325kPa. With 36 iterations, convergence was obtained for 58 quaternary data points. Average deviations of vapor compositions are 0.0134, 0.0134, 0.0133 and 0.0095 for  $y_1, y_2, y_3$  and  $y_4$ , respectively. Table 9 shows results for another example, the ethanol(1)/chloroform(2)/acetone(3)/n-hexane(4) quaternary at 55°C. With 25 iterations, convergence was obtained for 84 quaternary data points. Average deviations of vapor compositions are 0.0144, 0.0145, 0.0288 and 0.0201 for  $y_1, y_2, y_3$  and  $y_4$ , respectively.

### CONCLUSION

The power of thermodynamics follows from its rigorous general relations between a system's different properties. Therefore it is sometimes possible to avoid a difficult experimental measurement because the quantity that cannot easily be measured can be calculated from other quantities that, perhaps, are measured more easily. In the work discussed here, the rigorous general relation is the Gibbs-Duhem equation; using either isothermal  $P-x$  data or isobaric  $T-x$  data, this equation permits us to calculate vapor composition  $y$  which is often difficult to obtain accurately with standard experimental methods.

The work presented here provides a robust and accurate numerical method for performing the necessary calculations to obtain  $y$ . The method does not require assumption of a particular

model for  $g^E$  nor does it require any experimental data for  $v^E$  and  $h^E$  that appear in the Gibbs-Duhem equation. Finally, the method described here permits the user to correct for vapor-phase nonidealities in any way he wishes.

The method presented here is not restricted to binaries. Illustrative results are shown for a variety of binary and ternary systems and for a few quaternary systems where experimental data are rare.

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#### List of Symbols

$A_0, B_0, C_0, D_0, E_0, F_0, G_0$  parameters for polynomials in eqs.(27) and (28)

$C_k$  parameter in spline functions, eqs(8) and (13)

$d_i$  parameters in spline functions, eqs(8) and (13)

$D$  the rigidity of a plate

$e$  parameter in spline functions, eqs(8) and (13)

$f$  fugacity

$F$  functions of  $x_j$  and  $d_i$

$g$  molar Gibbs energy

$G$  Gibbs energy

$h$  molar enthalpy

$J_k$  coefficients of polynomial in eq.(26)

$J$  Jacobian matrix

$K$  number of components

$L$  restraint equations for  $d_i$

$N$  number of lattice points or data points

$P$  pressure

$q$  load on the plate

$Q$  reduced excess Gibbs energy

$R$  gas constant

$R_n$  function defined by eqs.(9) and (14)

$S$  spline function

$t$  temperature in Celsius

$T$  temperature

$v$  molar volume

$V$  volume

W	polynomial defined by eq.(26)
x	liquid-phase mole fraction
X	parameter matrix for spline function
y	vapor-phase mole fraction
Y	function matrix
$\gamma$	activity coefficient
$\phi$	fugacity coefficient

### Subscripts

calc	calculated value
expt	experimental value
<i>i, j</i>	component
<i>k, n</i>	ordinal number

### Superscripts

*	pure component
E	excess property

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### Figure Captions

Figure 1.  $Q$  surface for the isothermal dichloromethane(1)/chloroform(2)/carbon tetrachloride(3) ternary

Figure 2.  $Q$  surface for the isobaric acetone(1)/chloroform(2)/ethanol(3) ternary

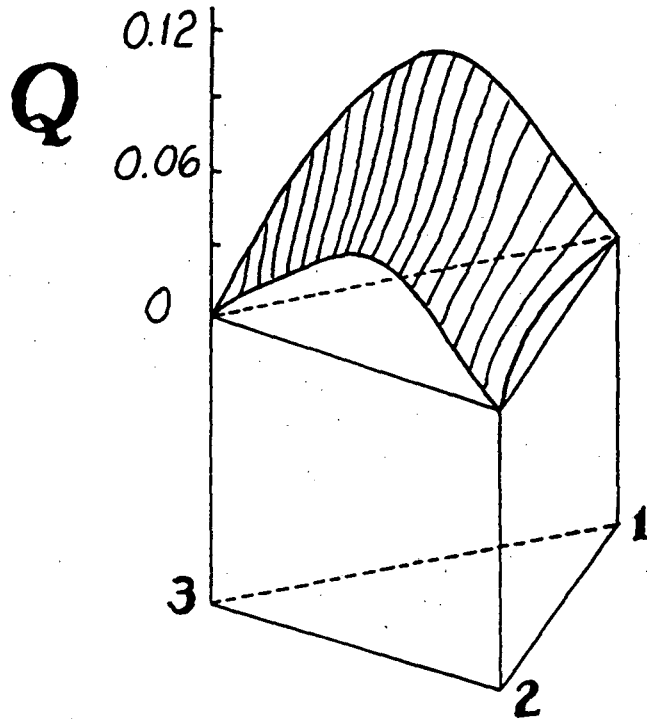


Figure 1

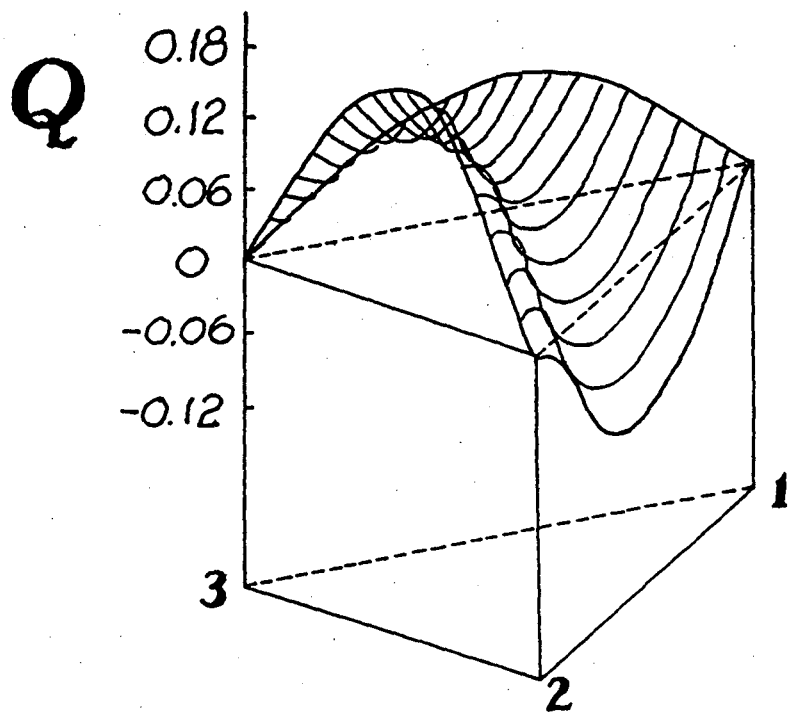


Figure 2



Table 1. Test of this work for the binary  
chloroform(1)/ethanol(2), 55°C

$x_1$	$p/\text{kPa}$	$y_{1,expt}$	$y_{1,calc}$
0.00	37.31	0.0000	0.0000
0.01	38.38	0.0372	0.0372
0.02	39.44	0.0726	0.0725
0.05	42.75	0.1694	0.1702
0.10	48.57	0.3054	0.3089
0.20	60.26	0.4988	0.5032
0.30	69.48	0.6108	0.6130
0.40	76.08	0.6774	0.6804
0.50	80.69	0.7252	0.7274
0.60	83.83	0.7598	0.7631
0.70	85.81	0.7914	0.7941
0.80	86.96	0.8264	0.8269
0.90	86.77	0.8774	0.8783
0.95	85.62	0.9226	0.9205
0.98	83.99	0.9634	0.9614
0.99	83.20	0.9800	0.9801
1.00	82.37	1.0000	1.0000

$$\Delta y_1 = 0.0016$$

Data source: Scatchard, G., Raymond, C. L., Gillmann, H. H., JACS., 60 1275 (1938).

Table 2. Test of this work for the binary  
benzene(1)/2-propanol(2), 101.325kPa

$x_1$	$t / C$	$y_{1,expt}$	$y_{1,calc} (a)$	$y_{1,calc} (b)$	$y_{1,calc} (c)$
0.000	82.2	0.0000	0.0000	0.0000	0.0000
0.084	78.5	0.2080	0.2059	0.2052	0.2071
0.126	77.1	0.2760	0.2776	0.2754	0.2786
0.153	76.3	0.3160	0.3175	0.3151	0.3191
0.199	75.3	0.3710	0.3758	0.3718	0.3768
0.240	74.4	0.4100	0.4611	0.4572	0.4635
0.291	73.6	0.4510	0.4611	0.4572	0.4635
0.357	73.0	0.4930	0.5005	0.4954	0.5020
0.440	72.4	0.5350	0.5372	0.5358	0.5419
0.492	72.3	0.5580	0.5581	0.5578	0.5641
0.556	72.2	0.5830	0.5901	0.5884	0.5946
0.624	72.0	0.6120	0.6301	0.6272	0.5799
0.685	72.1	0.6380	0.6327	0.6518	0.5901
0.762	72.4	0.6730	0.6653	0.6793	0.6178
0.836	73.0	0.7170	0.7120	0.7148	0.6921
0.887	73.8	0.7600	0.7509	0.7573	0.7394
0.936	75.5	0.8250	0.8173	0.8218	0.8084
0.972	77.5	0.9010	0.9016	0.9046	0.8984
1.000	80.1	1.0000	1.0000	1.0000	1.0000

$$\Delta y_1(a) = 0.0052, \Delta y_1(b) = 0.0058, \Delta y_1(c) = 0.0181$$

- (a) this work, (b) direct method (Hu and Ying, 1980),  
(c) direct method,  $h^E=0$  (Hu and Ying, 1980)

Data source: Nagata, I., Can. J. Chem. Eng., 42 82 (1964).

Table 3. Test of this work for binaries

System (1)-(2)	$p/\text{kPa}$	$t/^\circ\text{C}$	$\Delta y_1$	Data Source
cyclohexane/n-heptane	101.325		0.0008	a
cyclohexane/toluene	101.325		0.0019	a
diethyl amine/ethyl acetate		24.83	0.0003	b
		74.94	0.0006	b
		124.88	0.0017	b
dichloromethane/chlorobenzene		24.88	0.0001	c
		74.82	0.0003	c
		124.95	0.0014	c
dichloromethane/benzene		25.00	0.0001	c
		74.85	0.0006	c
diethyl ether/acetonitrile		24.99	0.0007	d
		65.01	0.0013	d
		115.02	0.0031	d
diethyl ether/acetone		24.91	0.0007	d
		65.04	0.0011	d
		115.15	0.0024	d
diethyl ether/methanol		25.01	0.0009	d
		65.02	0.0016	d
		115.00	0.0034	d
chloroform/ethanol		55.00	0.0016	e
benzene/2-propanol	101.325		0.0052	f

a: Black, C., IEC., 51 211 (1959).

b: Srivastova, R. et al, J. Chem. Eng. Data, 31 94 (1986).

c: Srivastova, R. et al, J. Chem. Eng. Data, 30 313 (1985).

d: Srivastova, R. et al, J. Chem. Eng. Data, 31 89 (1986).

e: Scatchard, G. et al., JACS., 60 1275 (1938).

f: Nagata, I., Can. J. Chem., 42 82 (1964).

Table 4. Test of this work for the ternary  
methanol(1)/methyl acetate(2)/ethyl acetate(3), 40°C

$x_1$	$x_2$	$p/\text{kPa}$	$y_{1, \text{expt}}$	$y_{1, \text{calc}}$	$y_{2, \text{expt}}$	$y_{2, \text{calc}}$
0.1000	0.8000	54.97	0.1470	0.1480	0.7920	0.7862
0.2000	0.7000	56.65	0.2490	0.2475	0.6910	0.6908
0.1000	0.7000	52.95	0.1520	0.1459	0.7260	0.7279
0.3000	0.6000	57.07	0.3140	0.3143	0.6260	0.6237
0.2000	0.6000	54.44	0.2520	0.2500	0.6300	0.6281
0.1000	0.6000	50.90	0.1550	0.1483	0.6630	0.6636
0.4000	0.5000	56.63	0.3640	0.3611	0.5720	0.5738
0.3000	0.5000	54.66	0.3220	0.3196	0.5570	0.5562
0.2000	0.5000	52.20	0.2590	0.2580	0.5640	0.5610
0.1000	0.5000	48.73	0.1590	0.1520	0.5970	0.6020
0.5000	0.4000	55.63	0.4070	0.3992	0.5220	0.5309
0.4000	0.4000	53.96	0.3780	0.3692	0.4940	0.4985
0.3000	0.4000	52.15	0.3350	0.3312	0.4830	0.4846
0.2000	0.4000	49.78	0.2690	0.2669	0.4940	0.4942
0.1000	0.4000	46.34	0.1670	0.1594	0.5290	0.5339
0.6000	0.3000	54.06	0.4500	0.4394	0.4680	0.4840
0.5000	0.3000	52.51	0.4290	0.4093	0.4280	0.4454
0.4000	0.3000	51.02	0.3990	0.3848	0.4060	0.4157
0.3000	0.3000	49.36	0.3540	0.3495	0.4010	0.4050
0.2000	0.3000	47.07	0.2860	0.2823	0.4140	0.4175
0.1000	0.3000	43.61	0.1790	0.1707	0.4490	0.4571
0.7000	0.2000	51.44	0.5050	0.4835	0.3950	0.4273
0.6000	0.2000	50.18	0.4840	0.4552	0.3480	0.3799
0.5000	0.2000	48.91	0.4600	0.4273	0.3200	0.3455
0.4000	0.2000	47.67	0.4290	0.4100	0.3050	0.3189
0.3000	0.2000	46.17	0.3830	0.3777	0.3030	0.3097
0.2000	0.2000	43.91	0.3120	0.3064	0.3160	0.3243
0.1000	0.2000	40.38	0.1970	0.1888	0.3510	0.3606
0.8000	0.1000	46.59	0.5890	0.5630	0.2790	0.3266
0.7000	0.1000	46.32	0.5620	0.5166	0.2260	0.2839
0.6000	0.1000	45.58	0.5360	0.4845	0.1990	0.2499
0.5000	0.1000	44.77	0.5090	0.4568	0.1840	0.2269
0.4000	0.1000	43.84	0.4750	0.4415	0.1760	0.2088
0.3000	0.1000	42.46	0.4260	0.4117	0.1780	0.1990
0.2000	0.1000	40.15	0.3510	0.3409	0.1890	0.2069
0.1000	0.1000	36.37	0.2280	0.2157	0.2140	0.2317

$$\Delta y_1 = 0.0136, \quad \Delta y_2 = 0.0144, \quad \Delta y_3 = 0.0043$$

Data source: Gmehling, J. et al, Vapor-Liquid Equilibrium Data  
Collection, DECHEMA, Vol I. 1977-1984.

Table 5. Test of this work for the ternary  
acetone(1)/chloroform(2)/benzene(3), 101.325kPa

$x_1$	$x_2$	$T/^\circ\text{C}$	$y_{1,\text{expt}}$	$y_{1,\text{calc}}$	$y_{2,\text{expt}}$	$y_{2,\text{calc}}$
0.0190	0.0610	77.85	0.0560	0.0450	0.0860	0.0955
0.1640	0.4220	68.95	0.2360	0.2285	0.4660	0.4623
0.0540	0.5220	69.58	0.0740	0.0702	0.6320	0.6269
0.1670	0.3250	69.74	0.2670	0.2598	0.3550	0.3510
0.1740	0.1920	70.42	0.3130	0.3059	0.2020	0.2006
0.0630	0.2920	72.85	0.1200	0.1139	0.3640	0.3582
0.0670	0.8830	62.98	0.0640	0.0502	0.9290	0.9247
0.2000	0.6150	66.29	0.2140	0.2156	0.6620	0.6561
0.0830	0.8510	63.47	0.0610	0.0677	0.9040	0.8969
0.2210	0.5640	66.61	0.2530	0.2536	0.5990	0.5926
0.0920	0.6500	66.92	0.0990	0.0973	0.7400	0.7346
0.0950	0.4870	69.41	0.1320	0.1312	0.5690	0.5642
0.2350	0.3350	68.23	0.3450	0.3400	0.3390	0.3367
0.2410	0.2560	68.46	0.3800	0.3726	0.2500	0.2493
0.1010	0.2780	71.83	0.1890	0.1809	0.3290	0.3217
0.2510	0.0990	68.52	0.4380	0.4296	0.0900	0.0978
0.1100	0.6110	67.35	0.1240	0.1231	0.6940	0.6889
0.1110	0.4080	70.13	0.1720	0.1662	0.4750	0.4699
0.2930	0.4880	66.39	0.3540	0.3400	0.4890	0.5031
0.1240	0.4950	68.79	0.1660	0.1658	0.5640	0.5579
0.3020	0.5110	66.09	0.3540	0.3436	0.5100	0.5207
0.1300	0.1510	71.96	0.2640	0.2531	0.1690	0.1741
0.3130	0.3180	66.80	0.4350	0.4314	0.2950	0.2932
0.1450	0.5740	67.45	0.1700	0.1686	0.6420	0.6363
0.3390	0.5910	65.11	0.3600	0.3628	0.5900	0.5875
0.1640	0.5440	67.99	0.1990	0.1983	0.6000	0.5947
0.3420	0.2150	66.33	0.5030	0.4943	0.1840	0.1832
0.3770	0.4110	65.53	0.4710	0.4727	0.3750	0.3694
0.3840	0.3870	65.45	0.4860	0.4890	0.3470	0.3399
0.4400	0.1440	64.34	0.6160	0.6018	0.1050	0.1104
0.4480	0.2670	64.49	0.5880	0.5792	0.2110	0.2132
0.5780	0.3360	62.73	0.6820	0.6579	0.2550	0.2807
0.6420	0.2890	61.75	0.7470	0.7395	0.2030	0.2130
0.6840	0.0910	60.29	0.8030	0.7872	0.0520	0.0612
0.7680	0.1170	59.33	0.8580	0.8470	0.0660	0.0762
0.8780	0.0530	57.70	0.9290	0.9266	0.0260	0.0334

$$\Delta y_1 = 0.0065, \quad \Delta y_2 = 0.0063, \quad \Delta y_3 = 0.0057$$

Data source: Kojima, K. et al, J. Chem. Eng. Data 36 343 (1991).

Table 6. Ternaries tested

No.	System (1)-(2)-(3)	$p/kPa$	$t/^\circ C$	$N$	Data Source
1	2-propanol/methyl acetate/dichloromethane		25.0	34	a
2	acetone/chloroform/benzene	101.325		36	b
3	n-pentane/methyl acetate/dichloromethane		25.0	32	c
4	dichloromethane/chloroform/carbon tetrachloride		45.0	32	d
5	methyl acetate/2-propanol/benzene	101.325		32	d
6	methyl ethyl ketone/benzene/2-propanol		50.0	19	d
7	methyl ethyl ketone/benzene/2-propanol	101.325		19	d
8	n-hexane/benzene/toluene	101.325		26	d
9	chloroform/methyl ethyl ketone/benzene	101.325		36	d
10	toluene/n-octane/ethyl benzene	101.325		20	d
11	benzene/cyclohexane/methyl ethyl ketone	101.325		32	d
12	tetrachloromethane/benzene/2-propanol	101.325		39	d
13	ethyl acetate/acetone/methyl acetate	101.325		16	d
14	chloroform/acetone/carbon disulfide		25.0	35	d
15	methanol/methyl acetate/ethyl acetate		40.0	36	d
16	acetone/ethyl acetate/ethanol	101.325		59	e
17	acetone/methanol/ethanol	101.325		22	f
18	benzene/n-hexane/cyclohexane	101.325		43	g
19	acetone/chloroform/ethanol	101.325		36	g
20	acetone/methanol/water	101.325		38	g
21	acetone/chloroform/n-hexane	101.325		37	g
22	ethanol/chloroform/n-hexane	101.325		36	g
23	methyl acetate/chloroform/benzene	101.325		45	g
24	ethanol/1-propanol/water	101.325		51	g
25	methanol/ethanol/1-propanol	101.325		45	g
26	methanol/chloroform/acetone		50.0	42	h
27	methanol/chloroform/acetone		40.0	45	h
28	acetonitrile/methyl ethyl ketone/benzene		55.0	25	i
29	acetonitrile/methanol/benzene		55.0	17	i
30	ethanol/acetonitrile/chloroform		40.0	34	j
31	ethanol/benzene/cyclohexane	101.325		53	k
32	2-propanol/chloroform/benzene		50.0	16	l
33	methanol/ethanol/benzene		25.0	24	m
34	acetonitrile/2-propanol/benzene		50.0	23	n
35	n-pentane/ethanol/acetone		99.55	31	o
36	methyl acetate/chloroform/benzene		50.0	39	p
37	1,3,5-/1,2,4-/1,2,3 trimethyl benzene	101.325		24	q
38	benzene/n-hexane/cyclohexane		70.0	21	r

N: number of data points.

a: Acevedo, I. L. et al, J. Chem. Eng. Data, 36 137 (1991).

b: Kojima, K et al, J. Chem. Eng. Data, 36 343 (1991).

c: Acevedo, I. L. et al, Fluid Phase Equilibria, 74 145 (1992).

- d: Gmehling, J. et al, Vapor-Liquid Equilibrium Data Collection, DECHEMA, Vol. I., 1977-1984.
- e: Carta, R. et al, J. Chem. Eng. Data, 29 463 (1984).
- f: Amer, H. H. et al, IEC., 48 142 (1956).
- g: Kojima, K. et al, Prediction of VLE by ASOG Method, Elsevier, Amsterdam, 1979.
- h: Goral, M. et al, Fluid Phase Equilibria, 23 89 (1985).
- i: Ohta, T et al, J. Chem. Eng. Data, 28 398 (1983).
- j: Nagata, I., J. Chem. Eng. Data, 33 286 (1988).
- k: Arce, A. et al, J. Chem. Eng. Data, 32 247 (1987).
- l: Nagata, I., J. Chem. Eng. Data, 30 80 (1985).
- m: Nagata, I., J. Chem. Eng. Data, 30 201 (1985).
- n: Nagata, I., J. Chem. Eng. Data, 30 363 (1985).
- o: Campell, S. W. et al, J. Chem. Eng. Data, 32 454 (1987).
- p: Nagata, I. et al, J. Chem. Eng. Japan, 3 161 (1970).
- q: Guo, N. et al, Chem. Eng. China, (4) 27 (1983).
- r: Susalev, M. P. et al, Russian J. Phys. Chem., 37 1739 (1963).

Table 7. Test of this work for ternaries

No.	$\Delta y_1$	$\Delta y_2$	$\Delta y_3$	NI
1	0.0133	0.0358	0.0319	9
2	0.0065	0.0063	0.0057	6
3	0.0367	0.0233	0.0470	42
4	0.0093	0.0065	0.0056	4
5	0.0147	0.0165	0.0123	14
6	0.0193	0.0133	0.0153	9
7	0.0102	0.0159	0.0126	9
8	0.0059	0.0112	0.0096	10
9	0.0217	0.0195	0.0147	8
10	0.0120	0.0113	0.0112	14
11	0.0129	0.0161	0.0158	15
12	0.0235	0.0270	0.0267	30
13	0.0391	0.0189	0.0275	3
14	0.0119	0.0424	0.0451	13
15	0.0136	0.0144	0.0043	16
16	0.0346	0.0245	0.0352	22
17	0.0122	0.0127	0.0080	9
18	0.0112	0.0097	0.0106	11
19	0.0103	0.0080	0.0088	9
20	0.0149	0.0183	0.0084	12
21	0.0133	0.0086	0.0157	20
22	0.0329	0.0354	0.0397	25
23	0.0095	0.0106	0.0068	6
24	0.0168	0.0159	0.0228	32
25	0.0305	0.0271	0.0182	6
26	0.0097	0.0094	0.0046	52
27	0.0086	0.0089	0.0044	26
28	0.0061	0.0071	0.0062	6
29	0.0189	0.0190	0.0233	12
30	0.0121	0.0079	0.0107	28
31	0.0255	0.0180	0.0188	19
32	0.0149	0.0231	0.0147	10
33	0.0372	0.0093	0.0416	18
34	0.0225	0.0194	0.0173	12
35	0.0206	0.0142	0.0174	24
36	0.0046	0.0041	0.0043	10
37	0.0097	0.0093	0.0088	2
38	0.0068	0.0053	0.0052	11

NI: number of iterations.



Table 8. Test of this work for the quaternary  
cyclohexane(1)/benzene(2)/2-propanol(3)/2-butanone(4), 101.325kPa

$x_1$	$x_2$	$x_3$	$T/^\circ\text{C}$	$y_{1,expt}$	$y_{1,calc}$	$y_{2,expt}$	$y_{2,calc}$	$y_{3,expt}$	$y_{3,calc}$
0.0200	0.8580	0.0060	78.40	0.0280	0.0296	0.8390	0.8226	0.0150	0.0168
0.0270	0.8410	0.0140	77.80	0.0410	0.0386	0.8020	0.7951	0.0380	0.0376
0.0410	0.8020	0.0380	76.40	0.0530	0.0543	0.7500	0.7308	0.0900	0.0938
0.0530	0.7500	0.0900	74.20	0.0710	0.0659	0.6600	0.6455	0.1800	0.1889
0.0510	0.6790	0.1480	73.10	0.0660	0.0665	0.5920	0.5836	0.2410	0.2456
0.1120	0.4990	0.3160	71.00	0.1510	0.1466	0.4610	0.4780	0.3340	0.3237
0.1860	0.4210	0.3520	70.20	0.2350	0.2291	0.3900	0.3923	0.3430	0.3477
0.0180	0.9560	0.0050	79.20	0.0250	0.0254	0.9380	0.9359	0.0170	0.0148
0.0250	0.9380	0.0170	77.90	0.0360	0.0412	0.8820	0.8753	0.0610	0.0584
0.0810	0.8360	0.0050	77.80	0.1040	0.1052	0.8020	0.7962	0.0110	0.0136
0.1460	0.7180	0.0070	76.80	0.1810	0.1905	0.6570	0.6479	0.0140	0.0192
0.2150	0.5830	0.0550	73.20	0.2530	0.2460	0.4710	0.4888	0.1340	0.1190
0.2750	0.3540	0.2580	70.10	0.3010	0.2999	0.3130	0.2907	0.2910	0.3176
0.0350	0.5460	0.0270	76.70	0.0480	0.0552	0.5260	0.5177	0.0420	0.0518
0.0480	0.5260	0.0420	75.90	0.0710	0.0785	0.4990	0.4818	0.0710	0.0791
0.0710	0.4990	0.0710	74.90	0.0970	0.1075	0.4760	0.4671	0.1070	0.1110
0.0930	0.4580	0.1340	74.00	0.1620	0.1292	0.4310	0.4457	0.1420	0.1691
0.2560	0.2650	0.2810	70.10	0.3280	0.3277	0.2230	0.2268	0.2860	0.2865
0.3400	0.2250	0.2970	69.50	0.3850	0.3762	0.1950	0.2059	0.3020	0.3007
0.0060	0.0750	0.0470	78.80	0.0140	0.0118	0.1300	0.0882	0.0260	0.0592
0.0140	0.1300	0.0260	78.20	0.0260	0.0265	0.1820	0.1586	0.0350	0.0333
0.0460	0.1560	0.1180	75.80	0.0900	0.0846	0.1570	0.1731	0.1430	0.1528
0.1270	0.1810	0.1500	73.40	0.2080	0.2010	0.1700	0.1702	0.1720	0.1803
0.2750	0.1680	0.1840	70.60	0.3560	0.3480	0.1360	0.1429	0.2020	0.2074
0.3500	0.1350	0.1990	69.90	0.3970	0.3869	0.1160	0.1077	0.2190	0.2378
0.0050	0.0160	0.2370	77.50	0.0150	0.0110	0.0190	0.0207	0.2620	0.2690
0.0430	0.0640	0.3020	75.10	0.1040	0.0984	0.0720	0.0821	0.2970	0.3041
0.1300	0.0720	0.2900	72.50	0.2280	0.2241	0.0680	0.0827	0.2640	0.2756
0.3060	0.0840	0.2480	70.10	0.3900	0.4358	0.0760	0.0938	0.2310	0.1916
0.3760	0.0830	0.2280	69.50	0.4300	0.4562	0.0700	0.0872	0.2310	0.2064
0.0080	0.3640	0.3850	73.70	0.0170	0.0138	0.3940	0.3772	0.3850	0.4081
0.0430	0.4790	0.3840	71.90	0.0700	0.0619	0.4910	0.5013	0.3680	0.3761
0.0990	0.4760	0.3670	71.00	0.1380	0.1339	0.4610	0.4795	0.3610	0.3471
0.2360	0.3840	0.3570	69.80	0.2670	0.2741	0.3550	0.3539	0.3580	0.3538
0.0750	0.1820	0.2130	73.90	0.1460	0.1274	0.1800	0.1837	0.2340	0.2429
0.1460	0.1800	0.2320	72.40	0.2300	0.2225	0.1660	0.1666	0.2370	0.2502
0.7470	0.0760	0.0100	72.50	0.6030	0.6022	0.0720	0.1132	0.0440	0.0262
0.5480	0.0530	0.0900	70.00	0.5210	0.5365	0.0410	0.0491	0.1380	0.1248
0.5080	0.0200	0.1640	69.40	0.5060	0.6120	0.0300	0.0194	0.1840	0.1359
0.4950	0.0200	0.1670	69.60	0.4910	0.5967	0.0160	0.0197	0.1980	0.1424
0.4660	0.5100	0.0010	76.50	0.4580	0.4925	0.4870	0.4752	0.0120	0.0027
0.4290	0.3870	0.0200	73.80	0.4200	0.4475	0.3440	0.3213	0.0400	0.0434
0.4060	0.2040	0.1700	70.40	0.4110	0.3894	0.1740	0.1430	0.2190	0.2692
0.4360	0.1310	0.2520	69.20	0.4470	0.4435	0.1150	0.1052	0.2720	0.2924

0.4670	0.1160	0.2670	69.10	0.4790	0.4675	0.0950	0.1064	0.2850	0.2915
0.7210	0.1130	0.1250	70.10	0.5890	0.5548	0.0960	0.1439	0.2590	0.2437
0.6070	0.0910	0.2480	69.20	0.5310	0.5197	0.0870	0.1082	0.3130	0.3103
0.5080	0.0770	0.3420	69.10	0.5160	0.5161	0.0770	0.0993	0.3290	0.3115
0.4670	0.2550	0.2070	69.60	0.4580	0.4489	0.2110	0.1914	0.2690	0.3023
0.0040	0.0050	0.9170	80.20	0.0160	0.0131	0.0340	0.0161	0.8450	0.8332
0.0140	0.0340	0.8490	78.10	0.0520	0.0373	0.0770	0.0851	0.7360	0.7238
0.0380	0.0710	0.7410	75.90	0.1060	0.0844	0.1310	0.1391	0.5980	0.5961
0.1650	0.1910	0.4820	70.90	0.2700	0.2483	0.2190	0.2265	0.3780	0.3839
0.2740	0.2050	0.3860	70.00	0.3530	0.3450	0.2010	0.2217	0.3330	0.3201
0.3820	0.1780	0.3340	69.20	0.4120	0.4391	0.1610	0.1792	0.3330	0.2897
0.0280	0.4270	0.4700	72.10	0.0490	0.0448	0.4790	0.4774	0.4140	0.4202
0.0560	0.4940	0.4000	71.30	0.0840	0.0783	0.5040	0.5101	0.3760	0.3794
0.1540	0.2480	0.5000	70.70	0.2460	0.2392	0.2740	0.2790	0.3960	0.3957

$$\Delta y_1 = 0.0133, \Delta y_2 = 0.0134, \Delta y_3 = 0.0133, \Delta y_4 = 0.0095$$

Number of iterations: 36

Data source: Gmehling, J. et al, Vapor-Liquid Equilibrium Data Collection,

Vol. I, DECHEMA, 1977-1984.

Table 9. Test of this work for quaternaries

No.	$p$ /kPa	$t$ /°C	N	$\Delta y_1$	$\Delta y_2$	$\Delta y_3$	$\Delta y_4$	NI
1	101.325		58	0.0134	0.0134	0.0133	0.0095	36
2		55.0	84	0.0144	0.0145	0.0288	0.0201	25

1: cyclohexane(1)/benzene(2)/2-propanol(3)/butanone(4)

2: ethanol(1)/chloroform(2)/acetone(3)/n-hexane(4)

N: number of data points,

NI: number of iterations,

Data source: Gmehling, J. et al, Vapor-Liquid Equilibrium

Data Collection, Vol. I, DECHEMA, 1977-1984.

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