



Chemical Engineering Communications 1987, vol 54, pp. 139-148

Photocopying permitted by license only
© 1987 Gordon and Breach Science Publishers S.A.
Printed in the United States of America

PHASE EQUILIBRIUM OF MULTICOMPONENT MIXTURES: CONTINUOUS MIXTURE GIBBS FREE ENERGY MINIMIZATION AND PHASE RULE

P.C. DU and G.A. MANSOORI†

*Department of Chemical Engineering
University of Illinois
(Box 4348) Chicago, Ill. 60680
U.S.A.*

(Received July 25, 1986; in final form January 12, 1987)

A phase equilibrium computational algorithm based on the minimization of the total Gibbs free energy of the multicomponent continuous system is introduced and the phase rule for a multi-family and multi-phase continuous mixture is formulated. Utilizing this technique it is now possible to perform phase equilibrium computations for mixtures containing both continuous component families and discrete components. Illustrative and comparative examples are introduced by using a continuous mixture equation of state, mixing rules, and combining rules. Comparisons of the experimental phase equilibrium data of a realistic gas-condensate system with the calculated results indicate excellent agreement between the two. The computational time required for the proposed algorithm is substantially reduced from the conventional pseudocomponent techniques.

KEYWORDS Continuous mixture Phase equilibrium Phase rule
Gibbs free energy minimization Equation of state Mixing rule

1. INTRODUCTION

The fundamental basis of the classical thermodynamics for multicomponent phase behavior prediction is generally based on the assumption of well defined compositions for all components expressed in mole fractions. Some complex mixtures, such as petroleum fluids, vegetable oils, and polymer solutions contain a great number of similar chemical species. In such cases description of these complex mixtures by component mole fractions is difficult. Therefore, instead of using mole fractions, an alternative method, which is generally called "continuous thermodynamics", is proposed. In this method, a distribution function is introduced to describe the composition of these complex mixtures consisting of a great number of components.

Since DeDoner (1931), who as a pioneer, outlined the thermodynamics of mixtures consisting of many components and phases in which an infinite number of reactions would take place, many workers have made contributions in the field of continuous systems: Dickinson (1980) applied continuous thermodynamics

† To whom correspondence concerning this article should be addressed.

within the conformal solution theory. Blum and Stell (1979) introduced a diameter distribution to characterize a hard-sphere polydisperse mixture. Some other studies, which applied the concept of thermodynamics of continuous mixtures in polymer solutions, have been reported in earlier years [e.g. Scott (1949); Koningsveld (1969); Flory and Abe (1978)]. Also, concerning petroleum distillation, some flash calculation schemes which were restricted to a simple model, such as Raoult's law, have been reported for continuous mixtures [e.g. Bowman (1949); Hoffman (1968); Taylor and Edmister (1971)].

In recent years, some significant contributions towards potential applications (e.g. Gualtieri *et al.* (1982); Briano (1983); Kehlen, Ratzach and Bergmann (1985); Cotterman and Prausnitz (1985) based on continuous thermodynamics have been reported for continuous mixtures or semicontinuous mixtures. However, due to the lack of a general algorithm for phase equilibrium calculations of continuous mixtures in the past, a number of simplifying assumptions were made, which are only valid for a mixture with a narrow molecular weight distribution.

In order to predict the phase behavior of a continuous mixture with a wide range of molecular weight distribution we have developed three different computational algorithms by which one can perform flash calculation of fully continuous mixtures [Du and Mansoori (1986a, b, c)]. In the present report we utilize one of the three algorithms (minimization of the total Gibbs free energy of the continuous mixture) in order to demonstrate its utility in realistic phase equilibrium calculations. We also report the phase rule for a multi-family multi-phase continuous system.

In part II the basic theory of phase equilibrium of continuous mixtures is presented. In part III the concept of the minimization of Gibbs free energy for phase equilibrium of continuous mixtures is introduced. In part V the proposed algorithm is used for phase equilibrium calculations using the Peng–Robinson equation of state and comparisons are made between the continuous mixture calculations and a realistic multicomponent system.

II. THEORY OF PHASE EQUILIBRIUM OF CONTINUOUS MIXTURES

For a mixture with a large number of components all in one family (such as paraffins, aromatics, etc.), composition may be replaced with a composition distribution function $F(I, I_0, \eta)$ whose independent variable I is some measurable property (such as molecular weight, boiling point, or density) with mean value of I_0 and variance of η . The composition distribution function $F(I, I_0, \eta)$ is normalized such that

$$\int_I F(I) dI = 1$$

over the entire range of I . In order to perform phase equilibrium calculation for a continuous mixture according to the classical thermodynamics of multicomponent

multiphase system it is necessary to equate temperatures, pressures, and chemical potentials of components in every phase. Thus, for the vapor–liquid equilibrium this means that the following conditions must be satisfied:

$$T = T^L = T^V \quad (1)$$

$$P = P^L(T, v_L, I_{0L}, \eta_L) = P^V(T, v_V, I_{0V}, \eta_V) \quad (2)$$

$$\mu^L(I, T, v_L, I_{0L}, \eta_L) = \mu^V(I, T, v_V, I_{0V}, \eta_V) \quad I \in (1 \Rightarrow \infty) \quad (3)$$

However, considering the fact that Eq. (3) is representative of a multitude of equations it is generally impossible to solve Eqs. (1)–(3) simultaneously for the liquid and vapor continuous mixtures in equilibrium. To resolve this problem we have developed three different computational algorithms (Du and Mansoori, 1986a, b, c) one of which is based on the minimization of the total Gibbs free energy of the continuous systems.

III. DIRECT MINIMIZATION OF THE GIBBS FREE ENERGY OF CONTINUOUS SYSTEMS

According to thermodynamics for a system at the equilibrium state, differential virtual variations can occur in the system properties at constant T and P without increasing the total Gibbs free energy of the system from its minimum condition. Thus, a general criterion for a system to be at equilibrium is

$$(\delta G)_{T,P} = 0 \quad (4)$$

To demonstrate the application of this criterion for continuous mixture phase equilibrium calculations, we restrict consideration only to vapor–liquid equilibrium. In such a case, the total Gibbs free energy of the system is

$$G = G_L + G_V \quad (5)$$

Generally, the Gibbs free energy of a one-family continuous mixture can be presented by the following expression:

$$G = \int_v^\infty [P - NRT/v] dv - NRT \int_I F(I) \ln\{v/[NF(I)RT]\} dI + PV + G^0 \quad (6)$$

Where N is the number of moles and G^0 is the Gibbs free energy of the continuous reference state at temperature T . Thus the total Gibbs free energy, G , is a function of temperature, volume, mean values and variances in liquid and vapor phases. Since the system is in phase equilibrium, the equilibrium criterion, Eq. (4), is imposed on the system. Thus, all of the first derivatives of the total Gibbs free energy, G , with respect to the system variables (variances and mean values) will be equal to zero.

$$(\partial G / \partial \eta_L)_{T,P,\eta_V,I_{0L},I_{0V}} = 0 \quad (7)$$

$$(\partial G / \partial \eta_V)_{T,P,\eta_L,I_{0L},I_{0V}} = 0 \quad (8)$$

$$(\partial G / \partial I_{0L})_{T,P,\eta_L,\eta_V,I_{0V}} = 0 \quad (9)$$

$$(\partial G / \partial I_{0V})_{T,P,\eta_L,\eta_V,I_{0L}} = 0 \quad (10)$$

To perform flash calculations for a one-family continuous mixture, Eqs. (7)–(10) and Eq. (2) will form a set of 5 nonlinear equations which must be solved simultaneously. In order to generalize the theory of phase equilibrium presented here to a multi-family and multi-phase continuous system we will formulate the phase rule for such a system.

IV. THE PHASE RULE OF FULLY CONTINUOUS MIXTURES

(i). In a one-phase continuous mixture system consisting of r groups (or families such as paraffins, naphthenes or aromatics) of continuous compounds group-compositions may be specified by defining $(r - 1)$ “group mole fractions”, ξ_i , where $\sum^r \xi_i = 1$. Thus the total number of compositions to be specified for the system is $(r - 1)$. There exist also two variables, variance η and mean value I_0 , for each group to be characterized. Then the number of variables to be specified is $r - 1 + 2r = 3r - 1$. There are two more variables which have to be considered (temperature and pressure) so that the total number of independent variables (degrees of freedom) in a one-phase continuous mixture system is

$$f = (3r - 1) + 2 = 3r + 1 \quad (11)$$

(ii). Consider now a multifamily–multiphase system that consists of p homogeneous phases and r groups of continuous compounds at a constant pressure and temperature. This system is at thermal and mechanical equilibrium but not at chemical equilibrium. For a phase that contains r groups of continuous mixtures, its group composition may be specified by defining $(r - 1)$ “group mole fractions”, ξ_i^p , where $\sum^r \xi_i^p = 1$. Thus the total number of concentrations to be specified for the whole system is $(r - 1)p$. There exist also two variables, variance η and mean value I_0 , for each group to be characterized. Then the number of variables to be specified is $(r - 1)p + 2rp = (3r - 1)p$. In general, there are $(p - 1)$ phase fractions and two variables which have to be considered for temperature and pressure so that the total number of independent variables (degrees of freedom) in the whole multifamily–multiphase continuous system is

$$f = 3rp + 1 \quad (12)$$

This equation will reduce to Eq. (11) when $p = 1$.

(iii). Next let us consider a multifamily–multiphase system in thermal, mechanical and chemical equilibrium, the number of relationships which must be satisfied as a result of equilibrium between the phases must be subtracted from Eq. (12) in order to find the number of independent variables in this system. Such relationships exist due to the fact that the total Gibbs free energy of the multifamily–multiphase system must be minimum at equilibrium with respect to the “equilibrium variables” of the system. For a system consisting of r families of

continuous mixtures and p phases, there are $2rp$ equilibrium variables resulting from the total number of variances, η 's, and mean values, I_0 's, in the system. Also we need to define $(p-1)r$ equilibrium relationships for calculating family concentrations. As a result, the total number of equilibrium relationships for this system in equilibrium are

$$2rp + (p-1)r = 3rp - r. \quad (13)$$

Thus the number of independent variables (degrees of freedom) in a multifamily-multiphase continuous system at equilibrium is:

$$f = (3rp + 1) - (3rp - r) = r + 1 \quad (14)$$

This equation is the phase rule for specifying the number of degrees of freedom in a multifamily-multiphase continuous system at equilibrium.

V. COMPARISON OF CALCULATED AND EXPERIMENTAL RESULTS FOR A REALISTIC SYSTEM USING AN EQUATION OF STATE

As an example, in what follows we introduce the proposed algorithm for the Peng–Robinson equation of state and we perform VLE calculations for a gas-condensate system. the Peng–Robinson equation of state for mixtures

$$P = RT/(V - b) - a(T)/[v(v + b) + b(v - b)] \quad (15)$$

$$a(T) = \sum_i \sum_j x_i x_j (a_{ii} a_{jj})^{1/2} = [\sum x_i a_{ii}^{1/2}]^2 \quad (16)$$

$$b = \sum x_i b_i \quad (17)$$

$$a_{ii}(T) = a(T_{ci}) [1 + \kappa_i (1 - T_{ii}^{1/2})]^2 \quad (18)$$

$$a(T_{ci}) = 0.45724 R^2 T_{ci}^2 / P_{ci} \quad (19)$$

$$b_i = 0.0778 R T_{ci} / P_{ci} \quad (20)$$

$$\kappa_i = 0.37464 + 1.54226 \omega - 0.26992 \omega^2, \quad (21)$$

joined with the exponential-decay distribution function [Du and Mansoori, 1986],

$$F(I) = (1/\eta) \exp[-(I - I_0)/\eta] \quad (22)$$

which is suitable for gas-condensate reservoir fluids, is used to perform flash calculations for gas-condensate mixtures. In order to extend this equation of state to continuous mixtures, we rewrite Eq. (18) in the following form:

$$[a(T)]^{1/2} = a_1 - a_2 T^{1/2} \quad (23)$$

where

$$a_1 = \sum_i x_i a_{i1}; \quad a_1 = \int_I F(I) a_1(I) dI \quad (24)$$

$$a_2 = \sum_i x_i a_{i2}; \quad a_2 = \int_I F(I) a_2(I) dI \quad (25)$$

and

$$a_{i1} = [a(T_{ci})]^{1/2} (1 + \kappa_i) \quad (26)$$

$$a_{i2} = [a(T_{ci})/T_{ci}]^{1/2} \kappa_i \quad (27)$$

Graphical representation of a_{i1} , a_{i2} , and b_i for paraffinic hydrocarbons versus molecular weight are shown [Du and Mansoori (1986b)] to obey third order polynomials in the following forms:

$$a_1(I) = a_{10} + a_{11}I + a_{12}I^2 + a_{13}I^3, \quad (28)$$

$$a_2(I) = a_{20} + a_{21}I + a_{22}I^2 + a_{23}I^3, \quad (29)$$

$$b(I) = b_0 + b_1I + b_2I^2 + b_3I^3, \quad (30)$$

where:

$$\begin{aligned} a_{10} &= 0.4771, & a_{11} &= 0.1055, & a_{12} &= 0.4066 \times 10^{-4}, \\ a_{13} &= 0.2700 \times 10^{-6}, & a_{20} &= 0.0157, & a_{21} &= 0.1747 \times 10^{-2}, \\ a_{22} &= 0.2960 \times 10^{-5}, & a_{23} &= 0.1318 \times 10^{-8}, & b_0 &= 0.9351 \times 10^{-4}, \\ b_1 &= 0.1410 \times 10^{-2}, & b_2 &= -0.2337 \times 10^{-5}, & b_3 &= 0.1147 \times 10^{-7}. \end{aligned}$$

By replacing the exponential-decay distribution function, Eq. (22), into Eqs. (24) and (25), we can derive analytic expressions for parameters a_1 , a_2 , and b of the Peng–Robinson equation of state. In order to utilize the present algorithm for VLE calculations of continuous mixtures, we need to derive an analytic expression for the Gibbs free energy. By replacing Eq. (15) into Eq. (6), the total Gibbs free energy of the system will be in the following form:

$$G = (\eta_f - \eta_v)/(\eta_L - \eta_v)g_L + (\eta_L - \eta_f)/(\eta_L - \eta_v)g_V \quad (31)$$

where

$$\begin{aligned} g_L &= -RT \ln(v_L - b_L) + a_L/(2.828b_L) \ln[(v_L - 0.414b_L)/(v_L + 2.414b_L)] \\ &\quad - RT \ln \eta_L + v_L RT/(v_L - b_L) - a_L v_L/[v_L(v_L + b_L) + b_L(v_L - b_L)] \quad (32) \end{aligned}$$

The expression for g_V will be the same as for g_L when subscript L is replaced with V in Eq. (31). To perform VLE flash calculations, we need to substitute Eq. (31) into Eqs. (7)–(10). But, since for gas–condensates $I_{of} = I_{oL} = I_{oV} =$ (the molecular weight of methane), Eq. (9) and Eq. (10) will vanish.

To illustrate the application of the proposed algorithm to realistic many-component mixtures, the flash-calculation results determined by utilizing the

minimization of the total Gibbs free energy algorithm will be compared with an experimental gas condensate data set. Hoffmann *et al.* (1953) have presented the equilibrium condensate phase analyses (Figure 1), and flash yields at different temperatures (Figure 2) for a gas–condensate system. In their work, methane to pentane are identified and the hydrocarbon fractions heavier than pentane are divided arbitrarily with mid-boiling points roughly equivalent to those of the respective normal paraffin hydrocarbons. In our calculations, we treat this gas condensate mixture as a discrete mixture of methane (with a mole fraction of 0.9135) and a continuous fraction of other hydrocarbons. The continuous fraction

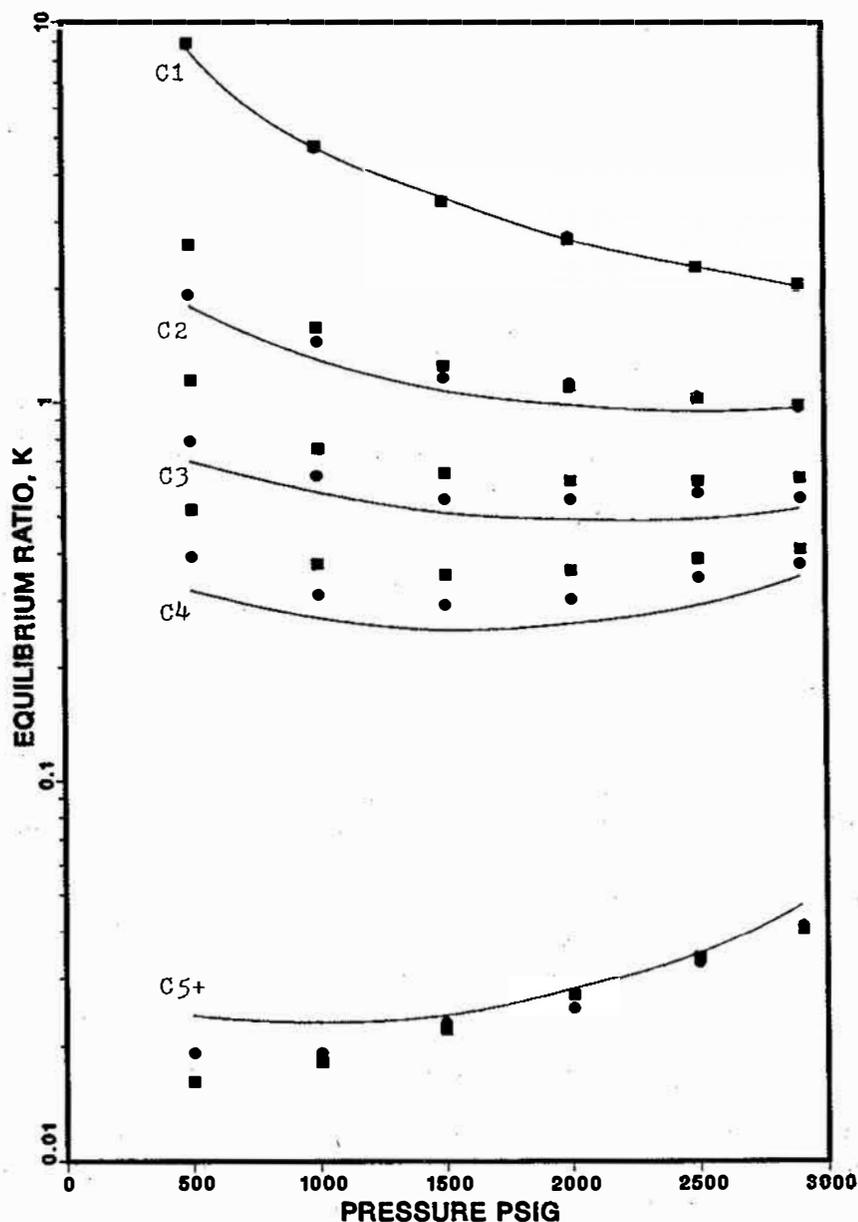


FIGURE 1 Component mole fraction equilibrium ratio, K -value, of a gas condensate fluid [Hoffmann *et al.* (1953)] at 201°F. Squares are the results by using a pseudocomponent method [Katz and Firoozabadi (1978)], circles are the experimental data, and the lines are the results by using the minimization of Gibbs free energy algorithm.

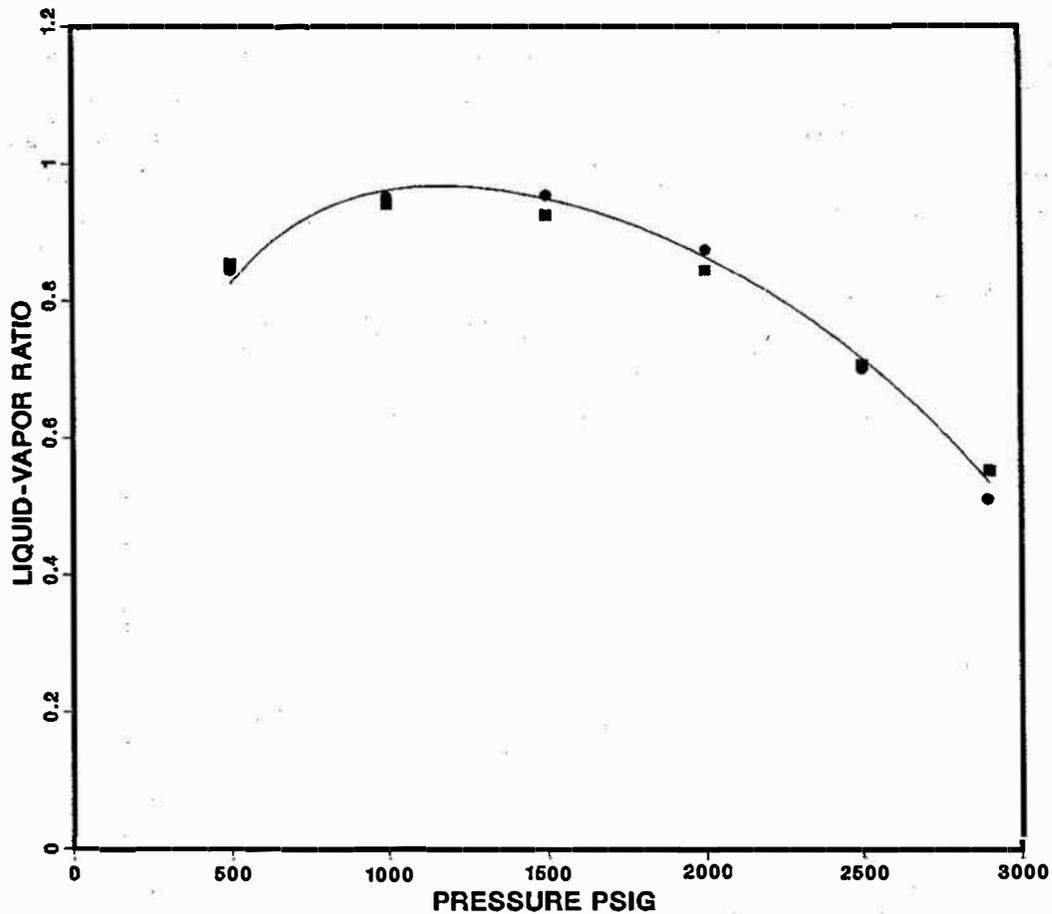


FIGURE 2 Liquid-vapor volume ratio of the gas condensate fluid of Figure 1 at 201°F. Squares are the results by using a pseudocomponent method [Katz and Firoozabadi (1978)], circles are the experimental data, and the line is the result by using the minimization of Gibbs free energy algorithm.

is described by an exponential-decay distribution function (starting from the molecular weight of ethane, with a variance of $\eta = 22.3$). The Peng-Robinson equation of state is used to perform flash calculations for this gas condensate system.

The binary interaction parameters, k_{ij} , is set equal to zero for all binary pairs except for methane-heavier (C_7^+ fraction), ethane-heavier, and propane-heavier fractions. The k_{ij} correlation proposed by Katz and Firoozabadi (1978), for the methane- C_7^+ fraction, in terms of the heavier fraction specific gravity is given by

$$k_{1,i} = 0.129(SG)_i - 0.055855, \quad (33)$$

where $(SG)_i$ is the specific gravity at 60°F of the heavier component. Based on the experimental data reported by Hoffmann *et al.* (1953), an expression for the heavy component specific gravity as a linear function of the molecular weight has been determined. This expression is substituted into Eq. (33) resulting in $k_{1,i}$ for methane-heavier fractions as a linear function of molecular weight:

$$k_{1,i} = -0.0579 + 0.4411 \times 10^{-4}I. \quad (34)$$

For binary interaction parameters of ethane-heavier and propane-heavier fractions, the value of $k_{i,j} = 0.01$ [Katz and Firoozabadi (1978)] is used in our calculations.

The proposed minimization of the total Gibbs free energy algorithm is applied to perform flash calculations for different pressures at the same temperature of 201°F. The compositions and liquid yields are calculated and they are shown to be in agreement with the experimental data. Figures (1) and (2) report the calculated and experimental equilibrium ratios K_i for each component and liquid yields, respectively. Calculations using the pseudocomponent method are also reported in these figures. As these two figures illustrate flash calculations based on the proposed technique are as accurate as those using conventional pseudocomponent techniques.

Calculations also indicate that the proposed technique can reduce the required computer time significantly while it retains the accuracy of the predictions. The proposed continuous mixture technique is applicable to varieties of multicomponent mixtures, equations of state, and mixing rules.

ACKNOWLEDGMENT

The authors would like to thank Miss Ellen Antoniadis for her helpful comments and review of the manuscript. This research is supported by the Chemical Sciences Division, Office of Basic Energy Sciences of the U.S. Department of Energy, Grant DE-FG02-84ER13229.

NOMENCLATURE

a, b	equation of state parameters
F	density distribution function
G	Gibbs free energy
I	distributed variable of component I
P	absolute pressure
R	universal gas constant
T	temperature, K
v	molar volume
Z	compressibility factor

Greek Letters

μ	chemical potential
η	variance of density distribution function

Superscripts and Subscripts

0	mean value of density distribution function
f	feed stream
i, j	component identifiers
L	liquid phase
V	vapor phase

REFERENCES

- Blum, L., and Stell, G., "Polydisperse System. I. Scattering function for polydisperse fluids of hard or permeable spheres", *J. Chem. Phys.* **71**, 42 (1979).
- Bowman, J.R., "Distillation of an Indefinite Number of Components", *Ind. Eng. Chem.*, **41**, 2004 (1949).
- Briano, J.G., "Classical and Statistical Thermodynamics of Continuous Mixtures", Ph.D. Thesis, University of Pennsylvania (1983).
- Cotterman, R.L., and Prausnitz, J.M., "Flash Calculation for Continuous or Semicontinuous Mixtures Using an Equation of State", *Ind. Eng. Chem. Process Des. Dev.*, **24**, 434 (1985).
- DeDoner, Th., "*L'Affinite (second partie)*". Gauthier-Villars, Paris, (1931).
- Dickinson, E., "Statistical Thermodynamics of Fluid Phase Equilibrium in a Conformal Polydisperse System", *J. Chem. Soc. Faraday II*, **76**, 1458 (1980).
- Du, P.C., and Mansoori, G.A., "Phase Equilibrium Computational Algorithms of Continuous Mixtures", *Fluid Phase Equilibria*, **30**, pp. 57-64, (1986a).
- Du, P.C., and Mansoori, G.A., "A Continuous Mixture Computational Algorithm for Reservoir Fluids Phase Behavior", SPE Paper #15082, Proceedings of the 1986 California Regional Meeting of SPE, Society of Petroleum Engineers, Richardson, Tx, (1986b).
- Du, P.C., and Mansoori, G.A., "Continuous Mixture Computational Algorithm of Reservoir Fluid Phase Behavior Applicable for Compositional Reservoir Simulation", SPE Paper #15953, Proceedings of the 1986 Eastern Regional Meeting of SPE, Society of Petroleum Engineers, Richardson, Tx, (1986c).
- Edmister, W.C., "Improved Integral Technique for Petroleum Distillation Calculations", *Ind. Eng. Chem.*, **47**, 1685 (1955).
- Flory, P.J., and Abe, A., "Statistical Thermodynamics of Mixtures of Rodlike Particles", *Macromolecules*, **11**, 1119 (1978).
- Gualtieri, J.A., Kinacid, J.M., and Morrison, G., "Phase Equilibria in Polydisperse Fluids", *J. Chem. Phys.*, **77**, 521 (1982).
- Hoffman, E.J., "Flash Calculations for Petroleum Fractions", *Chem. Eng. Sci.*, **23**, 957 (1968).
- Hoffmann, A.E., Crump, J.S., and Hocott, C.R., "Equilibrium Constants for a Gas-Condensate System", *Pet. Trans., AIME*, **198**, 1 (1953).
- Katz, D.L., and Firoozabadi, A., "Predicting Phase Behavior of Condensate/Crude-Oil Systems Using Methane Interaction Coefficients", *J. Pet. Tech.*, **228**, 1649 (Nov. 1978).
- Kehlen, H., Ratzach, M.T., and Bergmann, J., "Continuous Thermodynamics of Multicomponent Systems", *AIChE J.*, **31**, 1136 (1985).
- Koningsveld, R., "Phase Relationships and Fractionation in Multicomponent Polymer Solutions", *Pure Appl. Chem.*, **20**, 271 (1969).
- Scott, R.L., "The Thermodynamics of High-polymer Solutions", *J. Chem. Phys.*, **17**, 268 (1949).
- Taylor, D.L., and Edmister, W.C., "Solutions for Distillation Processes Treating Petroleum Fractions", *AIChE J.* **17**, 1324 (1971).