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Equilibrium in Multiphase Polydisperse Fuids

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Based on the principle of Gibbs phase equilibrium, three different algorithms are developed for phase equilibrium calculations of polydisperse mixtures. These algorithms are based on (i) the equality of the chemical potentials of components in each phase, (ii) the minimization of the total Gibbs free energy of the system with respect to all the system variables, and (iii) the equilibrium ratios constraint between the phases. All three algorithms demonstrate applicability to mixtures with different mole fraction distribution functions and different equations of state. The results of calculations using the three phase algorithms are compared with the simulated multicomponent hydrocarbon mixture data, and the results are in good agreement.

KEY WORDS: continuous thermodynamics; distribution function; equation of state; Gibbs phase equilibrium; polydisperse mixtures.

1. INTRODUCTION

In conventional Gibbsian thermodynamics for multiphase equilibrium calculations, each component of a mixture is assumed identifiable and its concentration can be determined by ordinary chemical analysis. This assumption is feasible if the system contains only a few components. The species concentrations for highly complex mixtures cannot be determined by ordinary chemical analysis. Examples of such mixtures are petroleum reservoir fluids, vegetable oils, polymer solutions, and the like. In these cases, the assumption of known mole fractions is invalid, and phase prediction using conventional Gibbsian thermodynamics is not feasible.

Another method which is an extension of Gibbsian thermodynamics, generally called continuous thermodynamics, has been used extensively to

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perform phase equilibrium calculations for complex mixtures. Instead of using the mole fractions of components, or of pseudocomponents (a method for lumping components, e.g., Ref. 1), a continuous distribution function is used for describing the composition distributions.

A number of earlier efforts in the direction of continuous thermodynamics are known. To introduce continuous distribution functions to complex mixtures such as reservoir fluids, some investigators have presented a number of theories which can be applied within this framework of thermodynamics and statistical mechanics (e.g., Refs. 2–5). Studies based on the concept of continuous thermodynamics have been presented by another group of investigators for petroleum distillations and polymer separations (e.g., Refs. 6–11). All the contributions mentioned above have been restricted to specific models (Raoult's law). The chemical potentials of real fluids are not based necessarily on the ideal-solution model. Therefore, these studies cannot be applied to the general problem of continuous thermodynamics.

In recent years, a number of advances in the direction of phase equilibrium calculations of nonideal continuous mixtures have been made. A continuous distribution has been applied to equations of state: Gualtieri et al. [12] to the van der Waals equation of state and Briano [13] to the Redlich-Kwong equation of state. Kehlen et al. [14] have reviewed the concept of continuous thermodynamics in generating general thermodynamic property relations for such properties as chemical potential, entropy, enthalpy, and Gibbs free energy of continuous mixtures. More recently, Cotterman and Prausnitz [15] have applied the continuous Soave equation of state to the Gualtieri [12] technique for phase equilibria.

Previously [16], two techniques have been presented based on the minimization of the Gibbs free energy and an equilibrium k-value technique. The work presented here is a new technique for equating the chemical potentials using a field distribution function. The results for the three techniques are compared to the pseudocomponents method using several feed composition distributions and, in each case, using the van der Waals and Peng–Robinson equations of state.

2. THEORY OF CONTINUOUS MIXTURE PHASE EQUILIBRIA

For a polydisperse mixture having a large number of components, compositions may be replaced with a composition distribution function $F(I, I_0, \eta)$ whose independent variable I is some measurable property. This property should characterize each species within the whole range of a polydisperse mixture such as molecular weight or boiling point with initial value of I_0 and variance of η.

The composition distribution function $F(I, I_0, \eta)$ is normalized over the entire range of I such that

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

where I is the molecular weight of species I.

Various investigators have proposed several distribution functions for the composition distribution functions of continuous mixtures. These functions are reported in Table I. For example, a normal distribution function has been adopted by Ratzsch and Kehlen [17] and also by Hoffman [8] for polymers and reservoir fluids. The Schulz [18] distribution function has been used by Gualtieri et al. [12] for their fundamental studies on continuous mixtures. And the gamma distribution function has been selected by Cotterman and Prausnitz [15] for petroleum reservoir fluids. To choose a certain continuous distribution function, some general knowledge about compositions of the many-component mixtures under consideration is necessary. For example, the exponential-decay distribution function [19] can be applied for the gas-condensate reservoir fluids, while the so-called "gamma" distribution function [19] may be applied for heavier petroleum fluids.

In the case of continuous mixtures, an extensive thermodynamic property, such as the compressibility factor Z, may be considered as a function of temperature T, pressure P, and the extensive continuous distribution function $N(I)$:[2]

$$Z = Z[T, P, N(I)] \tag{1}$$

where $N(I)$ is the amount of component I and I is an independent variable such as molecular weight or boiling point. In Eq. (1), $N(I)$ can be expressed with respect to the intensive continuous distribution function $F(I)$ such that

$$N(I) = NF(I)$$

where N is the total number of moles of the mixtures. A similar relation corresponding to the above equation in the discrete case is

$$N_i = Nx_i$$

where x_i is the mole fraction of component i.

From the expression of the compressibility factor, one can derive other thermodynamic properties such as the chemical potential for such a

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[2] Definitions of symbols are given under Nomenclature (below).

Table I. Several Single-Variable Distributions

Distribution	Mean	Variance	Application
Normal, $1/(2\pi\eta)^{1/2} \exp[-(I-I_0)^2/2\eta]$	I_0	η	Petroleum, polymer
Gamma, $1/[\eta^{\alpha}\Gamma(\eta)](I-I_0)^{\alpha-1} \exp[-(I-I_0)/\eta]$	$\alpha\eta$	I_0^2/η	Heavy petroleum, polymer
Schulz, $1/[I\Gamma(\eta)\}(I\eta/I_0)^{\eta} \exp(-I\eta/I_0)$	I_0	$I_0^2/\eta^{1/2}$	Heavy petroleum, polymer
Exponential, $1/\eta \exp[-(I-I_0)/\eta]$	$I_0+\eta$	η	Gas condensate
Weibull, $\alpha\eta(I-I_0)^{\eta-1} \exp[-\alpha(I-I_0)^{\eta}]$	$\alpha^{-1/\eta}\Gamma(1+1/\alpha)$	$\alpha^{-2/\eta}[\Gamma(1+2/\eta)$ $-[\Gamma(1+1/\eta)]^2]$	Petroleum, polymer
Tung, $\eta/I_0(I/I_0)^{\eta-1} \exp[-(I/I_0)^{\eta}]$	$I_0\Gamma(1+1/\eta)$	$I_0^2[\Gamma(1+2/\eta)$ $-\Gamma(1+1/\eta)]^2$	Polymer, colloids

mixture. For example, an expression for the chemical potential of a fraction in a continuous mixture is generally needed for phase equilibrium calculations (e.g., Refs. 12, 13, 15) and can be derived as the following form.

$$\mu(I) = \mu^0(I) + \int_V^\infty \{[dP/dNF(I)]_{T,v,I} - RT/v\}\, dv$$
$$- RT \ln\{v/[RTNF(I)]\} + RT \tag{2}$$

or

$$\mu(I) = \mu^0(I) + \phi[v, T, F(I)] - RT \ln\{v/[NF(I)]\} \tag{3}$$

where

$$\phi[v, T, F(I)] = \int_V^\infty \{[dP/dNF(I)]_{T,v,I} - RT/v\}\, dv + RT + RT \ln RT$$

where $\mu^0(I)$ is the chemical potential of the continuous reference state at temperature T. With regard to the above equation, they have assumed that there is only one family of continuous mixtures in the system.

Classical thermodynamics for multiphase equilibrium calculations usually requires equating the temperatures and pressures between phases and the chemical potentials of components between phases. For vapor–liquid equilibrium of a continuous mixture, this means the following conditions must be satisfied:

$$T = T^L = T^V \tag{4}$$

$$P = P^L[v_L, T, F_L(I)] = P^V[v_V, T, F_V(\mathrm{I})] \tag{5}$$

$$\mu^L(I) = \mu^V(I), \qquad I \in (0, \infty) \tag{6}$$

Since the distribution function variable I changes from some initial value I_0 to very large values, Eq. (6) is representative of a multitude of equations.

To show the difference between discrete and continuous vapor–liquid equilibrium concepts, Table II illustrates comparative balance equations of a continuous mixture and a discrete mixture. Using Eq. (3), we can rewrite the phase equilibrium conditions for a one-family continuous mixture.

$$P = P^L[T, v_L, F_L(I_{0L}, \eta_L, I)] = P^V[T, v_V, F_V(I_{0V}, \eta_V, I)] \tag{7}$$

$$\phi^L[T, v_L, F_L(I_{0L}, \eta_L, I)] - RT \ln\{v_L/[NF_L(I_{0L}, \eta_L, I)]\}$$
$$= \phi^V(T, v_V, F_V(I_{0V}, \eta_V, I))$$
$$- RT \ln\{v_V/[NF_V(I_{0V}, \eta_V, I)]\}, \qquad I \in (0, \infty) \tag{8}$$

It is necessary to use an equation of state to calculate pressure and the chemical potentials in the equilibrium liquid and vapor phases. Generally,

Table II. Comparison of the Balance Equations of a Continuous Mixture and a Discrete Mixture

	Continuous mixture	Discrete mixture
Total material balance	$n_f = n_L + n_V$	$n_f = n_L + n_V$
Component material balance	$n_f F_f(I) = n_L F_L(I) + n_V F_V(I)$ $F_f(I) = F_L F_L(I) + F_V F_V(I)$	$n_f z_i = n_L x_i + n_V y_i$ $z_i = F_L x_i + F_V y_i$
Normalization conditions	$\int_I F_f(I)\, dI = 1$ $\int_I F_L(I)\, dI = 1$ $\int_I F_V(I)\, dI = 1$	$\sum_i z_i = 1$ $\sum_i x_i = 1$ $\sum_i y_i = 1$
Average molecular weight	$M_f = \int_I F_f(I)\, I dI$ $M_L = \int_I F_L(I)\, I dI$ $M_V = \int_I F_V(I)\, I dI$	$M_f = \sum_i z_i M_i$ $M_L = \sum_i x_i M_i$ $M_V = \sum_i y_i M_i$

it is impossible to solve Eqs. (7) and (8) simultaneously for the liquid and vapor continuous mixtures in equilibrium.

To extend the application of continuous thermodynamics to practical cases such as reservoir fluids, polymer solutions, and vegetable oils, we have developed three computational algorithms for the phase behavior predictions of continuous mixtures with wide ranges of molecular weight distribution.

2.1. Equality of the Chemical Potentials Algorithm

Since it is impossible to solve Eqs. (7) and (8) simultaneously, we may assume that the first n derivatives of the chemical potential exist. As a result, Eqs. (7) and (8) can be replaced by the following set of equations as presented by Du and Mansoori [20]:

$$P = P^L[T, v_L, F_L(I_{0L}, \eta_L, I)] = P^V[T, v_V, F_V(I_{0V}, \eta_V, I)] \tag{9}$$

$$\mu^L[T, v_L, F_L(I_{0L}, \eta_L, I)] = \mu^V[T, v_V, F_V(I_{0V}, \eta_V, I)] \tag{10}$$

$$\partial\mu^L[T, v_L, F_L(I_{0L}, \eta_L, I)]/\partial I = \partial\mu^V[T, v_V, F_V(I_{0V}, \eta_V, I)]/\partial I \tag{11}$$

$$\cdots$$

$$\cdots$$

$$\cdots$$

$$\partial^n\mu^L[T, v_L, F_L(I_{0L}, \eta_L, I)]/\partial I^n = \partial^n\mu^V(T, v_V, F_V(I_{0V}, \eta_V, I))/\partial I^n \tag{12}$$

The phase rule developed by Du and Mansoori [21] states that the following degrees of freedom are required for r separate fractions (or families).

$$f = r + 1 \tag{13}$$

For $r = 1$ there are two degrees of freedom. There are seven variables which include the initial values I_{0V} and I_{0L}, and $f = 2$ is required, therefore, the number of equilibrium relations required is five. We now assume that there exists a field distribution function,

$$F_x(I) = F_x(I, \eta_x, I_{0x}) \tag{14}$$

such that the following four equations can effectively represent the n equations given by Eqs. (9)–(12).

$$\int_I \mu^L(I)\, F_x(I)\, dI = \int_I \mu^V(I)\, F_x(I)\, dI \tag{15}$$

$$\int_I [\partial\mu^L(I)/\partial I]\, F_x(I)\, dI = \int_I [\partial\mu^V(I)/\partial I]\, F_x(I)\, dI \tag{16}$$

$$\int_I [\partial^2\mu^L(I)/\partial I^2]\, F_x(I)\, dI = \int_I [\partial^2\mu^V(I)/\partial I^2]\, F_x(I)\, dI \tag{17}$$

$$\int_I [\partial^3\mu^L(I)/\partial I^3]\, F_x(I)\, dI = \int_I [\partial^3\mu^V(I)/\partial I^3]\, F_x(I)\, dI \tag{18}$$

The equality of pressures, Eq. (7), together with Eqs. (15)–(18) will constitute five equations needed for vapor–liquid equilibrium calculation of a one-family continuous mixture. The functional form and parameters of the field distribution function $F_x(I, \eta_x, I_{0x})$ will depend on the nature of the system under consideration. In some instances, it may be chosen to be identical to the distribution function of the feed.

2.2. Minimization of the Gibbs Free Energy and Equilibrium *k*-Value Techniques

For a system in equilibrium (constant T and P), for any differential "virtual displacement" occurring in the system, a general equilibrium criterion should be imposed on the system such that the total Gibbs free energy is minimal,

$$(dG)_{T,P} = 0 \tag{19}$$

To restrict our consideration only to vapor–liquid equilibrium, we have derived a continuous expression for the total Gibbs free energy [16].

$$G = G_{\mathrm{L}} + G_{\mathrm{V}} \tag{20}$$

The equilibrium criterion, Eq. (9), is imposed on the system. Then all of the first derivatives of the total Gibbs free energy G with respect to each variable, such as variance or initial value, will equal zero, and thus, G is minimized at constant T and P. The equality of the pressures and the following four relations give the five relations required by the phase rule. The technique developed uses the following criteria [16].

$$(\partial G/\partial \eta_{\mathrm{L}})_{T,P,\eta_{\mathrm{V}},I_{\mathrm{OL}},I_{\mathrm{OV}}} = 0 \tag{21}$$

$$(\partial G/\partial \eta_{\mathrm{V}})_{T,P,\eta_{\mathrm{L}},I_{\mathrm{OL}},I_{\mathrm{OV}}} = 0 \tag{22}$$

$$(\partial G/\partial I_{0\mathrm{L}})_{T,P,\eta_{\mathrm{V}},\eta_{\mathrm{L}},I_{\mathrm{OV}}} = 0 \tag{23}$$

$$(\partial G/\partial I_{0\mathrm{V}})_{T,P,\eta_{\mathrm{V}},\eta_{\mathrm{L}},I_{\mathrm{OL}}} = 0 \tag{24}$$

The equilibrium k-value technique uses continuous expressions for the fugacity coefficients [16]. The fugacities of each ith component are equated between the phases at equilibrium.

$$f_{ia} = f_{ib} = \cdots = f_{ip} \qquad (i = 1, 2...n) \tag{25}$$

where p and n are the number of phases and components respectively. For a two-phase system the fugacities are equated for each component.

$$\begin{aligned} &\Psi^{\mathrm{L}}[T, v_{\mathrm{L}}, F_{\mathrm{L}}(I_{0\mathrm{L}}, \eta_{\mathrm{L}}, I)]\, F_{\mathrm{L}}(I, I_{0\mathrm{L}}, \eta_{\mathrm{L}}) \\ &\quad = \Psi^{\mathrm{V}}[T, v_{\mathrm{V}}, F_{\mathrm{V}}(I_{0\mathrm{V}}, \eta_{\mathrm{V}}, I)]\, F_{\mathrm{V}}(I, I_{0\mathrm{V}}, \eta_{\mathrm{V}}) \end{aligned} \tag{26}$$

The equilibrium ratio $K(I)$, which is the ratio of two fugacity coefficients of component I, has been defined as follows.

$$K(I) = \Psi^{\mathrm{L}}[T, v_{\mathrm{L}}, F_{\mathrm{L}}(I_{0\mathrm{L}}, \eta_{\mathrm{L}}, I)]/\Psi^{\mathrm{V}}[T, v_{\mathrm{V}}, F_{\mathrm{V}}(I_{0\mathrm{V}}, \eta_{\mathrm{V}}, I)] \tag{27}$$

Mass balances are applied and the following zeroth and first moments of the equations must be solved simultaneously over the range of continuous components [16].

$$\int_I F_{\mathrm{f}}(I, I_{0\mathrm{f}}, \eta_{\mathrm{f}})/\{1 + F_{\mathrm{V}}[K(I) - 1]\}\, dI = 1 \tag{28}$$

$$\int_I F_{\mathrm{f}}(I, I_{0\mathrm{f}}, \eta_{\mathrm{f}})\, K(I)/\{1 + F_{\mathrm{V}}[K(I) - 1]\}\, dI = 1 \tag{29}$$

$$\int_I F_L(I, I_{0L}, \eta_L)\{1 + F_V[K(I) - 1]\}\, I dI = \int_I F_f(I, I_{0f}, \eta_f)\, I\, dI \tag{30}$$

$$\int_I F_L(I, I_{0L}, \eta_L)\{1 + F_V[K(I) - 1]\}\, I/K(I)\, dI = \int_I F_f(I, I_{0f}, \eta_f)\, I\, dI \tag{31}$$

The equality of the pressures, Eq. (7), together with Eqs. (28)–(31) will constitute a system of five equations consistent with the phase rule.

3. A SIMPLE EXAMPLE: PHASE EQUILIBRIUM CALCULATIONS BASED ON THE VAN DER WAALS EQUATION OF STATE

To illustrate the utility of the proposed continuous mixture phase equilibrium algorithms, we present here a simple example in which the van der Waals equation of state is used for mixtures.

$$P = RT/(v - b) - a/v^2 \tag{32}$$

$$a = \sum_i \sum_j x_i x_j (a_{ii} a_{jj})^{1/2} = \left[\sum_i x_i a_{ii}^{1/2}\right]^2 \tag{33}$$

$$b = \sum_i x_i b_i \tag{34}$$

and, for example, the distribution function, the exponential-decay distribution function which can exactly describe the composition of gas-condensate reservoir fluids, is used.

$$F(I) = (1/\eta) \exp[-(I - I_0)/\eta] \tag{35}$$

In order to extend the van der Waals equation of state to continuous mixtures, Eqs. (33) and (34) for a and b must be replaced with the following two expressions, respectively.

$$a = \left\{\int_I F(I)[a(I)]^{1/2}\, dI\right\}^2 \tag{36}$$

$$b = \int_I F(I)\, b(I)\, dI \tag{37}$$

Since a_i and b_i can be fitted to pure-component physical property data, when we apply the above equations for a homologous series of hydrocarbon compounds, $[a(I)]^{1/2}$ and $b(I)$ will be polynomials relating the molecular weight of hydrocarbon compounds. For the family of paraffins, Figs. 1 and 2 indicate that $[a(I)]^{1/2}$ and $b(I)$ can be accurately correlated to the following third-order polynomials, respectively.

$$[a(I)]^{1/2} = a_0 + a_1 I + a_2 I^2 + a_3 I^3 \tag{38}$$

$$b(I) = b_0 + b_1 I + b_2 I^2 + b_3 I^3 \tag{39}$$

By introducing Eqs. (38), (39), and (35) into Eqs. (36) and (37), the following expressions for a and b are derived.

$$a = [a_0 + a_1(I_0 + \eta) + a_2(I_0^2 + 2I_0\eta + 2\eta^2) + a_3(I_0^3 + 3I_0^2\eta + 6I_0\eta^2 + 6\eta^3)]^2 \tag{40}$$

$$b = b_0 + b_1(I_0 + \eta) + b_2(I_0^2 + 2I_0\eta + 2\eta^2) + b_3(I_0^3 + 3I_0^2\eta + 6I_0\eta^2 + 6\eta^3) \tag{41}$$

In what follows, the equations, based on the proposed algorithms and the continuous van der Waals equation of state listed above, have been derived, respectively.

For the present example, since $I_{0f} = I_{0L} = I_{0V}$ = molecular weight of methane, we need only three equations to perform vapor–liquid equilibrium calculation of a one-family continuous mixture. As a result, the following equations need to be solved simultaneously.

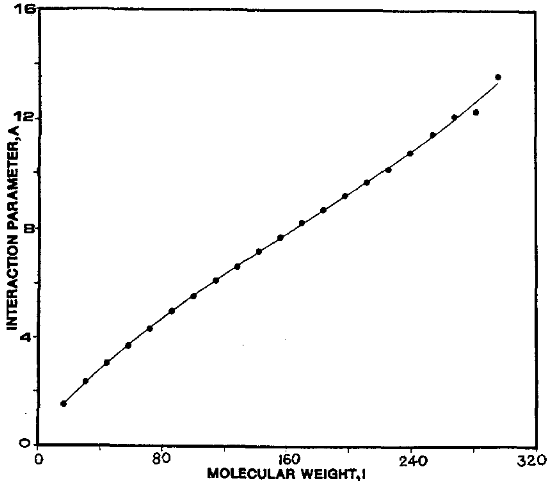

Fig. 1. Parameter $a_i^{1/2}$ of the van der Waals equation of state versus the molecular weight of paraffins. The dots are the calculated data, while the solid line is the fitted curve defined by Eq. (38).

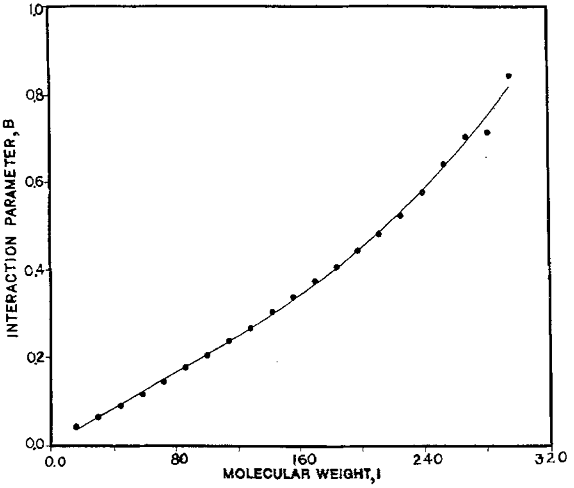

Fig. 2. Parameter b_i of the van der Waals equation of state versus the molecular weight of paraffins. The dots are the calculated data, while the solid line is the fitted curve defined by Eq. (39).

In all three methods the equality of the pressures is an equilibrium criterion.

$$P = RT/(v_L - b_L) - a_L/v_L^2 = RT/(v_V - b_V) - a_V/v_V^2 \tag{42}$$

(i) In order to use the equality of chemical potentials algorithm, we need to derive expressions for the chemical potentials in the continuous mixtures. Equation (32) is substituted into Eq. (2) with the following result.

$$\mu(I) = D_0 + D_1 I + D_2 I^2 + D_3 I^3 \tag{43}$$

where

$$D_0 = -\ln(v - b) + b_0/(v - b) - 2a_0 Q(I, h)/(RTv) - \ln(\eta) + I_0/\eta \tag{44}$$

$$D_1 = b_1/(v - b) - 2a_1 Q(I, h)/(RTv) - 1/\eta \tag{45}$$

$$D_2 = b_2/(v - b) - 2a_2 Q(I, h)/(RTv) \tag{46}$$

$$D_3 = b_3/(v - b) - 2a_3 Q(I, h)/(RTv) \tag{47}$$

$$Q(I, \eta) = 2[a(I)]^{1/2}\,[a_0 + a_1(I_0 + \eta) + a_2(I_0^2 + 2I_0\eta + 2\eta^2) + a_3(I_0^3 + 3I_0^2\eta + 6I_0\eta^2 + 6\eta^3)] \tag{48}$$

According to Eqs. (43)–(47), D_0, D_1, D_2, and D_3 are all functions of the temperature, volume, and distribution variance η. To perform vapor–liquid equilibrium calculations we need to substitute Eq. (43) into Eqs. (15)–(18). For the present example, $n = 3$. But since $I_0 = I_{0L} = I_{0V} = I_{0f}$ (the molecular weight of methane), we need to consider only the zeroth and first derivatives of the chemical potential. As a result, we need to solve the following set of four equations:

$$P = RT/(v_L - b_L) - a_L/v_L^2 = RT/(v_V - b_V) - a_V/v_V^2 \tag{42}$$

$$\begin{aligned} &D_{0L} - D_{0V} + (D_{1L} - D_{1V})(I_{0x} + \eta_x) + (D_{2L} - D_{2V})(I_{0x}^2 + 2I_{0x}\eta_x + 2\eta_x^2) \\ &\quad + (D_{3L} - D_{3V})(I_{0x}^3 + 3I_{0x}^2\eta_x + 6I_{0x}\eta_x^2 + 6\eta_x^3) = 0 \end{aligned} \tag{49}$$

$$D_{1L} - D_{1V} + 2(D_{2L} - D_{2V})(I_{0x} + \eta_x) + 3(D_{3L} - D_{3V})(I_{0x}^2 + 2I_{0x}\eta_x + 2\eta_x^2) = 0 \tag{50}$$

The simultaneous solutions of the above four equations, using a trial value of $\eta_f = 15.0$ and a proper choice of $\eta_x = 397.51$ are plotted as a P–T diagram in Fig. 3. In Fig. 3, the P–T diagram using the present algorithm is compared with the results of Gualtieri et al. [12]. In their model, linearity of parameters a and b of the van der Waals equation of state with

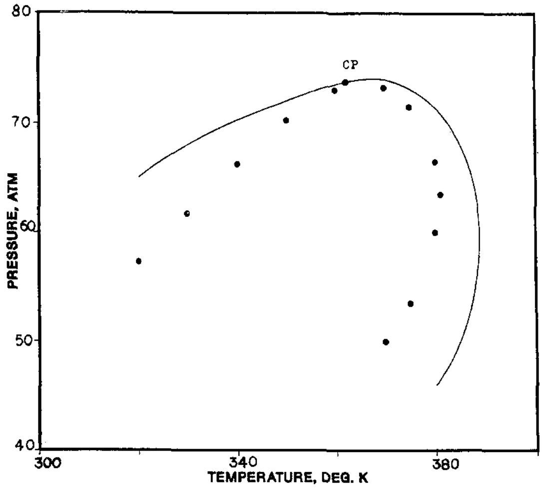

Fig. 3. The P–T diagram using the continuous van der Waals equation of state with $\eta_f = 15.0$. The dots are results taken from Gualtieri et al. [12]. The smooth line is from the identical results using the three phase algorithms, equality of the chemical potentials with $\eta_x = 397.51$, minimization of the Gibbs free energy, and equilibrium k-value algorithms.

respect to molecular weight is assumed. According to Fig. 3, such an assumption will produce a result which is far from the phase diagram of the continuous mixture.

(ii) For the minimization of the Gibbs free energy technique, the simultaneous solutions for a trial value of $\eta_f = 15.0$ are plotted as a P–T diagram. A P–T diagram identical to that in Fig. 3 is produced.

(iii) The equilibrium ratio algorithm for phase equilibrium calculations of continuous mixtures has been applied to a feed described by $\eta_f = 15.0$. A P–T diagram identical to those in the other two algorithms (also Fig. 3) is produced.

Application of the proposed algorithms for the van der Waals equation of state is a simple example of continuous mixture phase equilibrium calculations. In what follows we introduce the proposed algorithms for a Peng–Robinson equation of state which is extensively used for many practical phase behavior calculations.

4. PHASE EQUILIBRIUM CALCULATION BASED ON THE CONTINUOUS PENG–ROBINSON EQUATION OF STATE

The Peng–Robinson equation of state for mixtures,

$$P = RT/(v-b) - a(T)/[v(v+b) + b(v-b)] \tag{51}$$

$$a(T) = \sum_i \sum_j x_i x_j (a_{ii} a_{jj})^{1/2} = \left[\sum_i x_i a_{ii}^{1/2}\right]^2 \tag{52}$$

$$b = \sum_i x_i b_i \tag{53}$$

where

$$a_{ii}(T) = a(T_{ci})[1 + k_i(1 - \mathrm{T}_{ri}^{1/2})]^2 \tag{54}$$

$$a(T_{ci}) = 0.45724 R^2 T_{ci}^2 / P_{ci} \tag{55}$$

$$b_i = 0.0778 R T_{ci} / P_{ci} \tag{56}$$

$$k = 0.37464 + 1.54226\omega - 0.26992\omega^2 \tag{57}$$

has received widespread acceptance in phase behavior calculation of varieties of fluid mixtures. In order to extend this equation of state to continuous mixtures, we write Eq. (54) in the following form:

$$[a(T)]^{1/2} = a_1 - a_2 T^{1/2} \tag{58}$$

$$a_1 = \sum_i x_i a_{i1}; \qquad a^2 = \sum_i x_i a_{i2} \tag{59}$$

and

$$a_{i1} = [a(T_{ci})]^{1/2}(1 + k_i) \tag{60}$$

$$a_{i2} = [a(T_{ci})/T_{ci}]^{1/2} k_i \tag{61}$$

Graphical representations of a_{i1}, a_{i2}, and b_i for homologous series of paraffinic hydrocarbons (starting with methane) versus molecular weight are shown in Figs. 4–6. We have been able to represent $a_1(I)$, $a^2(I)$, and $b(I)$ of paraffins by the following third-order polynomials with respect to molecular weight I:

$$a_1(I) = a_{10} + a_{11}I + a_{12}I^2 + a_{13}I^3 \tag{62}$$

$$a_2(I) = a_{20} + a_{21}I + a_{22}I^2 + a_{23}I^3 \tag{63}$$

$$b(I) = b_0 + b_1 I + b_2 I^2 + b_3 I^3 \tag{64}$$

We can derive continuous mixture expressions for parameters a_1, a_2, and b of the Peng–Robinson equation of state. The exponential-decay distribution function is used along with a procedure similar to the previous van der Waals equation of state with the following expressions.

$$a_1 = a_{10} + a_{11}(I_0 + \eta) + a_{12}(I_0^2 + 2I_0\eta + 2\eta^2) + a_{13}(I_0^3 + 3I_0^2\eta + 6I_0\eta^2 + 6\eta^3) \tag{65}$$

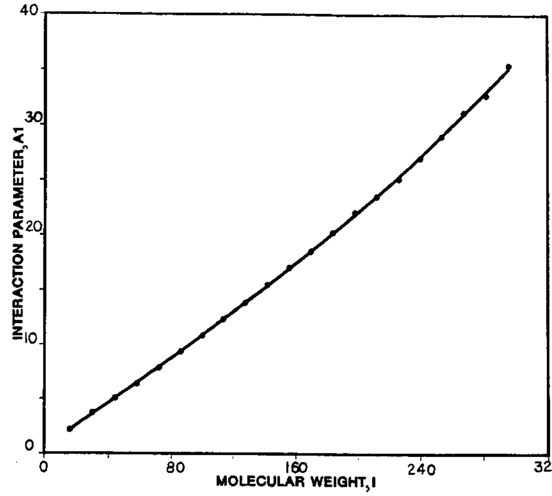

Fig. 4. Parameter a_{i1} as defined by Eq. (60) of the Peng–Robinson equation of state versus the molecular weight of normal paraffins. The dots are the calculated data, while the solid line is the fitted curve defined by Eq. (62).

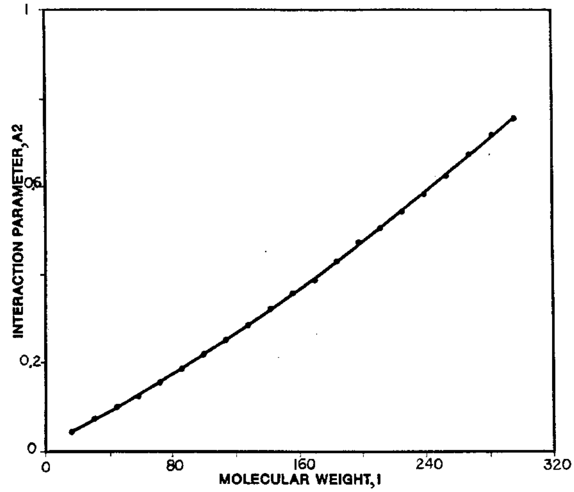

Fig. 5. Parameter a_{i2} as defined by Eq. (61) of the Peng–Robinson equation of state versus the molecular weight of normal paraffins. The dots are the calculated data, while the solid line is the fitted curve defined by Eq. (63).

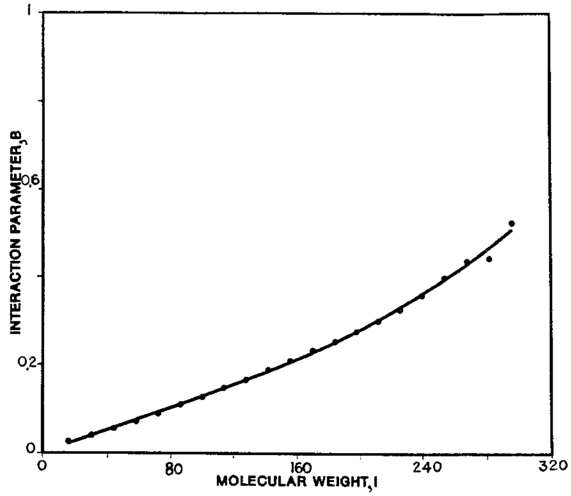

Fig. 6. Parameter b_i as defined by Eq. (56) of the Peng–Robinson equation of state versus the molecular weight of normal paraffins. The dots are the calculated data, while the solid line is the fitted curve defined by Eq. (64).

$$a_2 = a_{20} + a_{21}(I_0 + \eta) + a_{22}(I_0^2 + 2I_0\eta + 2\eta^2) + a_{23}(I_0^3 + 3I_0^2\eta + 6I_0\eta^2 + 6\eta^3) \tag{66}$$

$$b = b_0 + b_1(I_0 + \eta) + b_2(I_0^2 + 2I_0\eta + 2\eta^2) + b_3(I_0^3 + 3I_0^2\eta + 6I_0\eta^2 + 6\eta^3) \tag{67}$$

Using the continuous mixture Peng–Robinson equation of state, the required equations, based on the proposed algorithms for a one-family continuous mixture, have been derived. The derivation follows.

(i) In order to utilize the equality of the chemical potentials algorithm for phase equilibrium calculations of continuous mixtures, the expression of the chemical potential of component I is derived in the following form:

$$\mu(I) = D_0 + D_1 I + D_2 I^2 + D_3 I^3 \tag{68}$$

where

$$D_0 = -RT\ln(v - b) + C_1 b_0 + C_2(a_{10} + a_{20}T^{1/2}) - RT\ln\eta + RTI^0/\eta \tag{69}$$

$$D_1 = C_1 b_1 + C_2(a_{11} - a_{21}T^{1/2}) - RT/\eta \tag{70}$$

$$D_2 = C_1 b_2 + C_2(a_{12} - a_{22}T^{1/2}) \tag{71}$$

$$D_3 = C_1 b_3 + C_2(a_{13} - a_{23}T^{1/2}) \tag{72}$$

and

$$\begin{aligned} C_1 &= RT/(v - b) - av/[b(v^2 + 2vb - b^2)] \\ &\quad - a/(2.828b^2)\ln[(v - 0.414b)/(v + 2.414b)] \end{aligned}$$

$$C_2 = Q(h)/(1.414b)\ln[(v - 0.414b)/(v + 2.414b)]$$

$$\begin{aligned} Q(h) &= a_{10} + a_{11}(I_0 + \eta) + a_{12}(I_0^2 + 2I_0\eta + 2\eta^2) \\ &\quad + a_{13}(I_0^3 + 3I_0^2\eta + 6I_0\eta^2 + 6\eta^3) - [a_{20} + a_{21}(I_0 + \eta) \\ &\quad + a_{22}(I_0^2 + 2I_0\eta + 2\eta^2) + a_{23}(I_0^3 + 3I_0^2\eta + 6I_0\eta^2 + 6\eta^3)]\, T^{1/2} \end{aligned}$$

To perform vapor–liquid equilibrium calculations we need to substitute Eq. (68) into Eqs. (15)–(18). In this example, $n = 3$. But, since $I_{0x} = I_{0L} = I_{0V} = I_{0f}$ (molecular weight of methane), we need to consider only the zeroth and first derivatives of the chemical potential in the equilibrium criteria. As a result, we need to solve the following set of four equations.

$$\begin{aligned} P &= RT/(v_L - b_L) - (a_{1L} - a_{2L}T^{1/2})^2/[v_L(v_L + b_L) + b_L(v_L - b_L)] \\ &= RT/(v_V - b_V) - (a_{1V} - a_{2V}T^{1/2})^2/[v_V(v_V + b_V) + b_V(v_V - b_V)] \end{aligned} \tag{76}$$

$$(D_{0L}-D_{0V})+(D_{1L}-D_{1V})(I_0+\eta_x)+(D_{2L}-D_{2V})(I_0^2+2I_0\eta_x+2\eta_x^2 \\ +(D_{3L}-D_{3V})(I_0^3+3I_0^2\eta_x+6I_0\eta_x^2+6\eta_x^3)=0 \tag{77}$$

$$(D_{1L}-D_{1V})+2(D_{2L}-D_{2V})(I_0+\eta_x)+3(D_{3L}-D_{3V})(I_0^2+2I_0\eta_x+2\eta_x^2)=0 \tag{78}$$

It should be noted that Eqs. (77) and (78) are similar to Eqs. (49) and (50) which were derived for the van der Waals equation of state. By using Eqs. (76)–(78), the *P–T* diagrams of three different hypothetical continuous mixtures are calculated and are shown in Figs. 7–9, respectively. Also reported in these figures are the *P–T* diagrams of the same fluid mixtures assumed to contain 6, 10, and 20 pseudocomponents, respectively. According to Figs. 7–9, the proposed continuous mixture model can effectively represent the phase behavior of a many-component mixture.

(ii) Application of the Gibbs minimization technique to the Peng–Robinson equation of state has been used to produce the *P–T* diagrams of three different hypothetical gas–condensate reservoir fluids with $\eta_f = 5.72$, 9.05, and 25.0 shown in Figs. 10–12, respectively. Also shown in these figures are the *P–T* diagrams of the same reservoir fluids assumed to contain 6, 10, and 20 components, respectively. Figures 10–12 show that the proposed algorithm can predict the phase behavior of a many-component mixture effectively.

(iii) The equilibrium ratio algorithm has been used along with the Peng–Robinson equation of state to produce the *P–T* diagrams of three different hypothetical continuous mixtures with $\eta_f = 5.72$, 9.05, and 25.0 calculated by using a similar procedure and argument as in the case of the continuous van der Waals model. They are shown in Figs. 13–15, respectively. Also reported in these figures are the *P–T* diagrams of the same fluid mixtures assumed to contain 6, 10, and 20 components, respectively. According to Figs. 13–15, the proposed algorithm can present the phase behavior prediction of a continuous mixture effectively.

The *P–T* diagrams produced using three different algorithms which are reported in this paper are generated by doing dew-/bubble-point calculations. The coexisting component mole fractions, equilibrium ratios, and liquid volume percentages (with respect to the total volume of the system) resulting from flash calculations are compared with experimental data [22]. The flash calculations performed by using the proposed continuous mixture algorithms are in good agreement with experimental data, which are reported in previous publications [16, 20, 21].

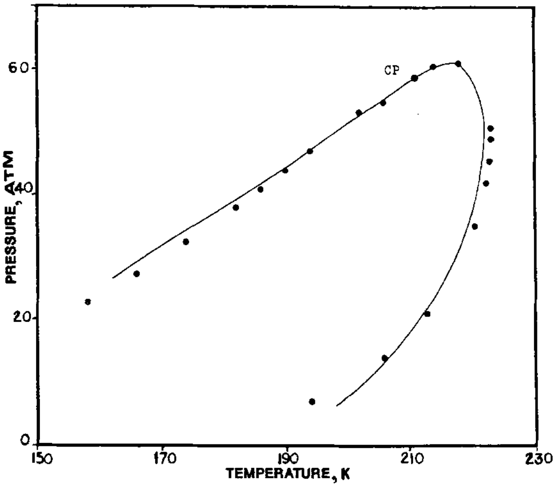

Fig. 7. The P–T diagram using the continuous Peng–Robinson equation of state with $\eta_f = 5.72$. The dots are from using the pseudocomponents method for the six components chosen. The smooth line results from using the equality of the chemical potentials phase algorithm with $\eta_x = 9.7225$.

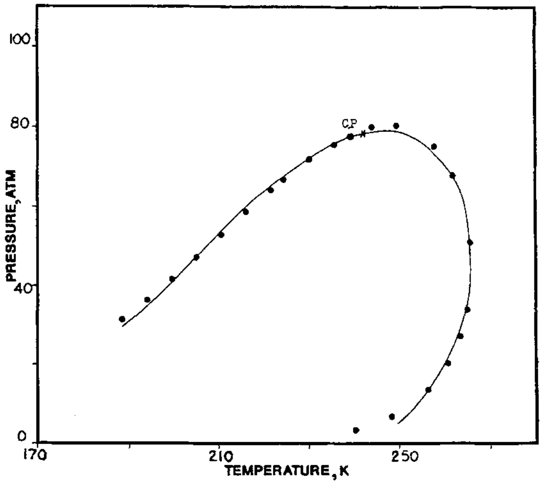

Fig. 8. The P–T diagram using the continuous Peng–Robinson equation of state with $\eta_f = 9.05$. The dots are from using the pseudocomponents method for the 10 components chosen. The smooth line results from using the equality of the chemical potentials phase algorithm with $\eta_x = 365.82$.

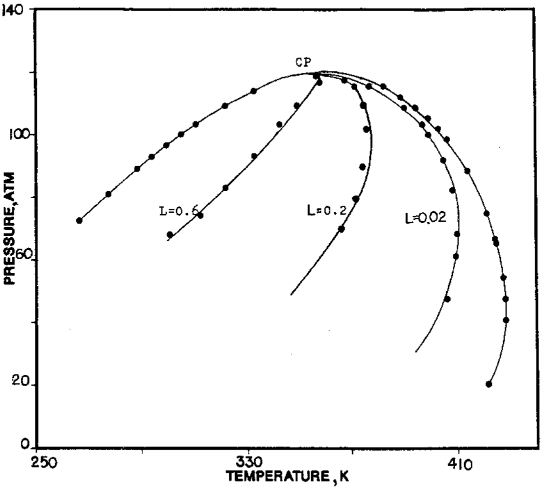

Fig. 9. The *P–T* diagram using the continuous Peng–Robinson equation of state with $\eta_f = 25.0$. The dots are from using the pseudocomponents method for the 10 components chosen. The smooth line results from using the equality of the chemical potentials phase algorithm $\eta_x = 59.527$.

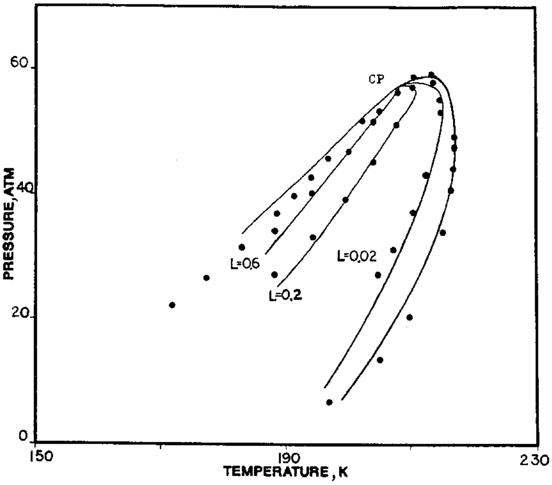

Fig. 10. The *P–T* diagram using the continuous Peng–Robinson equation of state with $\eta_f = 5.72$. The dots are from using the pseudocomponents method for the six components chosen. The smooth line results from using the minimization of the Gibbs free energy phase algorithm.

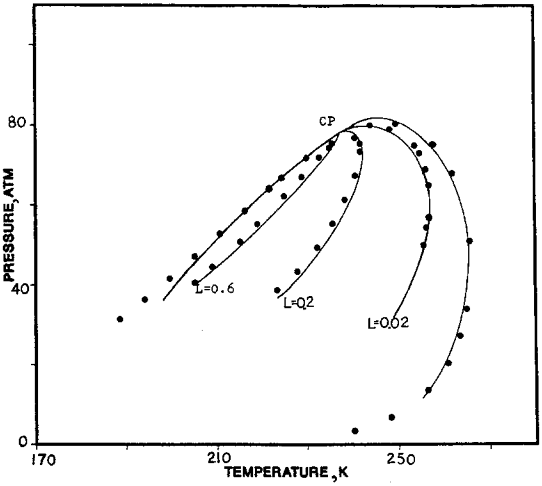

Fig. 11. The P–T diagram using the continuous Peng–Robinson equation of state with $\eta_f = 9.05$. The dots are from using the pseudocomponents method for the 10 components chosen. The smooth line results from using the minimization of the Gibbs free energy phase algorithm.

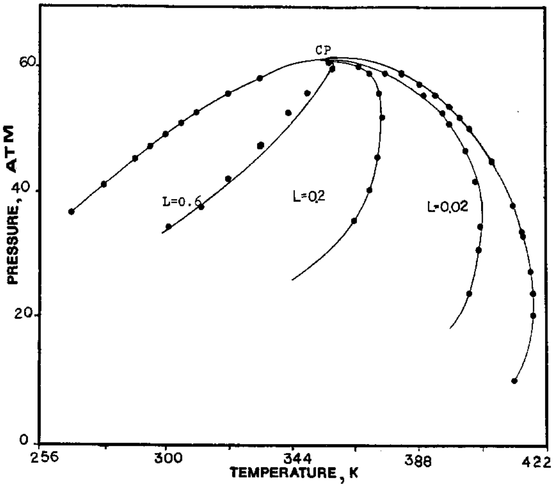

Fig. 12. The P–T diagram using the continuous Peng–Robinson equation of state with $\eta_f = 25.0$. The dots are from using the pseudocomponents method for the 20 components chosen. The smooth line results from using the minimization of the Gibbs free energy phase algorithm.

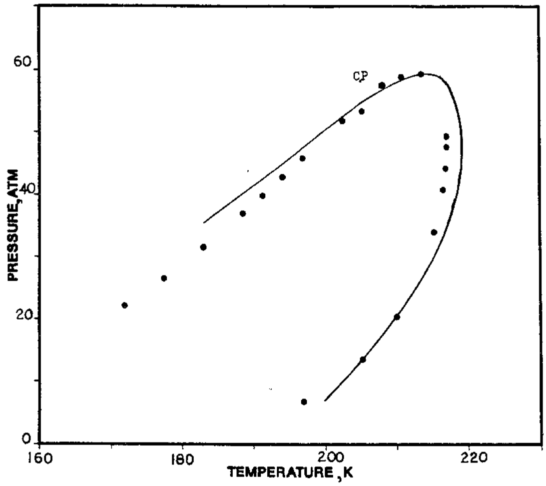

Fig. 13. The P–T diagram using the continuous Peng–Robinson equation of state with $\eta_f = 5.72$. The dots are from using the pseudocomponents method for the six components chosen. The smooth line results from using the equilibrium k-value phase algorithm.

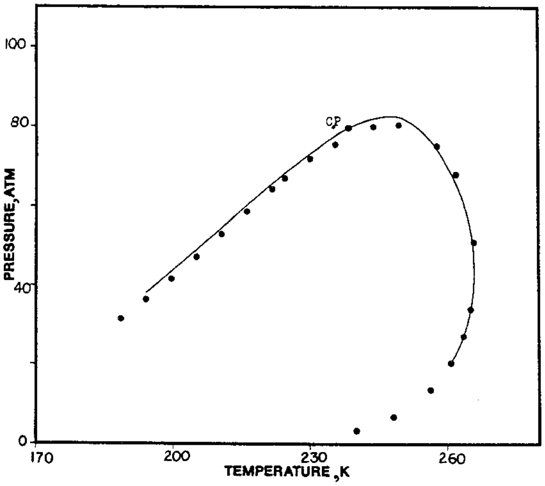

Fig. 14. The P–T diagram using the continuous Peng–Robinson equation of state with $\eta_f = 9.05$. The dots are from using the pseudocomponents method for the 10 components chosen. The smooth line results from using the equilibrium k-value phase algorithm.

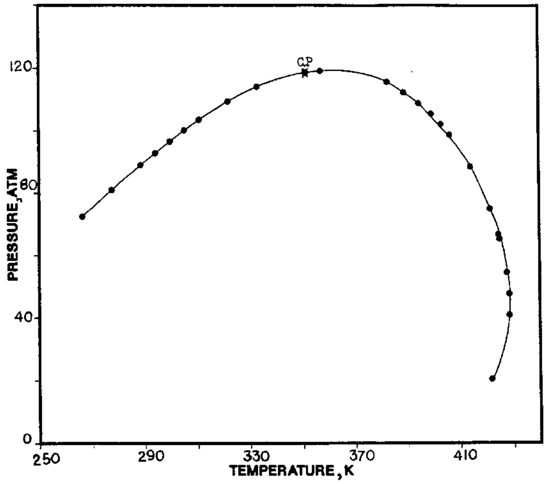

Fig. 15. The P–T diagram using the continuous Peng–Robinson equation of state with $\eta_f = 25.0$. The dots are from using the pseudocomponents method for the 20 components chosen. The smooth line results from using the equilibrium k-value phase algorithm.

5. CONCLUSIONS

Accurate prediction of polydisperse fluid phase behavior using a pseudocomponent method requires the choice of a large number of pseudocomponents. As a result of this large number, excessive computer time is needed. A new technique, the equality of the chemical potentials phase algorithm, and two other techniques we have previously developed use analytical expressions for chemical potentials, fugacity coefficients, and Gibbs minimization equations and are also in forms which are applicable to gas condensate systems. These proposed continuous mixture techniques can reduce the required computer time significantly, while they retain accurate predictions. The computational time needed for these proposed schemes is roughly equivalent to the time required for a binary vapor–liquid mixture. This can be expected because, instead of a multitude of equations, using a pseudocomponent technique a finite number of equations is required to be solved for phase equilibrium problems of continuous mixtures.

These proposed continuous mixture techniques are applicable to varieties of reservoir fluids, equations of state, and mixing rules. In the present report, the application for some hypothetical gas condensate systems using two representive equations of state, the van der Waals and the Peng–Robinson equations, is demonstrated.

For purpose of comparing the three algorithms with the discrete component algorithms, the unlike binary interaction parameters have been omitted. For a realistic fluid, continuous expressions for these interactions should be included. All three methods require the simultaneous solution of one order of magnitude fewer equations than the comparable 20-pseudocomponent case. These proposed algorithms are important means for greatly reducing computational time.

ACKNOWLEDGMENT

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NOMENCLATURE

a, b	Interaction parameter in the equation of state
CP	Critical point
$F(I)$	Density distribution function
f	Fugacity
G	Gibbs free energy
I	Distributed variable
I_0	Initial value of density distribution function
$K(I)$	Equilibrium ratio of component I
P	Pressure (atm)
R	Gas constant
T	Temperature (K)
v	Molar volume
Z	Compressibility factor

Greek Letters

h	Variance of density distribution function
μ	Chemical potential
F_V	Moles vapor per moles in system
Y	Fugacity coefficient

Subscripts and Superscripts

i, j	Component identifiers
f	Feed stream
L	Liquid phase
V	Vapor phase

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