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# $C_7^+$ Fraction Characterization

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EDITED BY

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## INTRODUCTION

The literature concerned with what is known as "Thermodynamics" is growing rapidly. Thermodynamics-related papers appear in periodicals of many different disciplines such as biology, biological engineering, chemical engineering, chemistry, geology, mechanical engineering, metallurgical engineering, meteorology, petroleum engineering, physics, etc. However, there is a growing need for an interdisciplinary forum on thermodynamics.

The Advances in Thermodynamics Series is designed in order to develop a linkage among the thermodynamicists working in different disciplines and to foster and promote interdisciplinary thermodynamics education and research. Every volume of the series is intended to address a specific thermodynamics topic of scientific and/or technological importance and authored by one or more investigators.

In this series we hope to promote discussions and exchange of ideas on theoretical and experimental developments in reversible and irreversible thermodynamics and statistical mechanics which will include prediction, measurement, and simulation of thermodynamic properties, phase transitions, equations of change, and equations of state of solids, fluids, and mixtures of scientific and industrial interest.

The first volume in this series is devoted to the subject of  $C_{7+}$  fraction characterization which is of major importance in thermodynamics of complex fluid mixtures appearing in fossil fuel industries. Such industries include gas condensate recovery and treatment, petroleum recovery and refining, oil shale retorting, tar sand utilization, and coal liquefaction and gasification industries.  $C_{7+}$  fraction refers to the multitude of hydrocarbons, and other organic compounds, which usually exist in fossil fuels with more than seven carbon atoms in their structure. Experience of many practicing engineers and investigators indicate that an inaccurate characterization of such compounds in complex fossil fuel mixtures causes significant economic burden on the design of the industrial processes for treatment of those fluids. The papers appearing in this volume are contributions of a dozen of leading research groups from around the world who have been involved with this problem and who have contributed to the advances of our knowledge in this area of thermodynamics.

# Multicomponent Fractions Characterization: Principles and Theories

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## ABSTRACT

The historical and scientific background for  $C_{7+}$  fraction characterization techniques is presented. It is shown that there exist two different routes for  $C_{7+}$  fraction characterization of multicomponent hydrocarbon mixtures: They include: (i) the pseudocomponent approach; (ii) and the continuous mixture approach. Discussions are made about the relative merits of the two techniques. The contents of the papers on  $C_{7+}$  fraction characterization, appearing in the later parts of this volume, are briefly analyzed and reviewed.

## INTRODUCTION

Many of the fluids which are encountered within chemical, food, pharmaceutical and fuel industries consist of mixtures whose chemical analysis are not accurately measurable and the components comprising such fluids are not well characterized. Examples of such fluids are petroleum reservoir fluids, distillates produced in the oil refineries, coal derived liquids resulting from coal liquefaction or conversion processes, vegetable oils, and polymer melts and solutions (Bowman 1949, Edmister 1984, Koningsveld 1969, Reid, et al. 1977, Stalkup 1983). The chemical analysis of such mixtures cannot be uniquely represented by a series of discrete values of concentrations

(such as mole fractions, weight fractions, or volume fractions). While the principle of thermodynamic principals of multicomponent systems are well established (Kreglewski 1984, Reid, et al. 1977) its extension for property calculation and phase equilibrium prediction of such industrially important mixtures has been an elusive problem for practicing engineers. Consequently resolution of this problem has been of considerable interest to both researchers and practicing engineers.

Severity of this problem in the fields of petroleum production, transportation, and processing has taken a new dimension due to its immediate economic impact on such operations. There are increased amounts of low quality synthetic liquid fuels and heavy petroleum fluids being either processed or considered for processing in today's industry. Processing of such complex mixtures involves removal of their solid contaminants, separation of the heavy ends from the lighter species, and cracking of the heavy ends (Kawanaka et al. 1988, Stalkup 1983). These complex fluids are either results of enhanced oil recovery and coal conversion technologies, or they are naturally occurring. The knowledge about their thermodynamic properties is required for the design and operation of plants which extract or treat them. Because of the importance of petroleum and the vast amount of data which is available in the field of petroleum the papers which are reported in this monograph are applied to petroleum fluids.

There has been a great deal of activity in data collection and correlation of thermodynamic properties of petroleum fluids during the past few decades (Bowman 1949, Cavett 1964, Edmister 1984, Lydersen 1955, Reid, et al. 1977). But due to the changing emphasis of petroleum industry every so often towards new processes and applications, the existing thermodynamic data become insufficient and the correlations tend to be inaccurate for extrapolation purposes. This problem can be corrected by the development and use of accurate phase equilibrium predictive techniques which: (i) can have extrapolative capacity, (ii) will have multi-property prediction capability and, (iii) can have universal characteristics applicable for varieties of petroleum fluids. For industries engaged in gas and petroleum process design, these features are not only desirable, but also essential. These requirements justify development of new and more universal characterization techniques.

Phase equilibrium calculations which are based on more accurate characterization techniques perform much better in the extrapolation regions than the equally accurate empirical correlations. They will be also applicable to a wider variety of petroleum fluids over a broader range of temperature and pressure provided appropriate techniques for the choice of equation of state and mixing rules are used (Benmekki and Mansoori 1986, Reid, et al. 1977). There is a considerable incentive, therefore, to develop general usage

characterization techniques with universal applicability to variety of petroleum fluids.

In complex mixtures, such as petroleum reservoir fluids, coal derived liquids, polymer solutions, or vegetable oils consisting of a large number of components, it is rather difficult to identify every component and their concentrations. There exist two techniques for characterizing such fluid mixtures: The "pseudocomponent method" and the concept of "continuous mixtures" which stems from the idea of continuous thermodynamics.

### PSEUDOCOMPONENT METHOD

For complex mixtures certain components can be clearly specified. The remaining components may be lumped together into a number of pseudocomponents with certain molecular characteristics (Cotterman and Prausnitz 1985, Edmister 1984, Hoffman 1968, Reid, et al. 1977, Riazi 1979, Stalkup 1983). Then, in calculating thermodynamic properties of such mixtures and prediction of their phase behavior one may treat such a system as a mixture consisting of a certain number of real and pseudo components. For example, the chemical analysis of petroleum fluids is frequently reported up to  $C_6$  or  $C_7$  hydrocarbons and the remaining part is lumped into a fraction named  $C_{6+}$  or, more commonly,  $C_{7+}$  fraction. Then certain data, such as the true boiling point (TBP), of the plus fraction are used to characterize such fractions in order to perform phase equilibrium and other thermodynamic property calculations for the petroleum fluid. In many cases we are left with the problem of dealing with the TBP-residue which may constitute up to 15 mole percent of the total mixture while the plus fraction may be up to 60-70 mole percent of the mixture. Considering these we can expect that the characterization and choice of pseudocomponents will have a profound effect on the phase equilibrium calculation of petroleum fluids.

A two-parameter equation of state, such as the Peng-Robinson, requires values for four thermodynamic properties for each component in the mixture to be modeled. Two critical properties, pressure and temperature, are needed. The acentric factor, which represents the deviation of the molecular conformation from a sphere, is also required. A binary interaction coefficient, a correction factor used to account for dissimilar components in the mixture, is another input to the equation of state. If there are six components in the mixture, the equation of state requires 15 binary interaction parameters, i.e.,  $(n^2 - n)/2$ . This subset of input variables is used by the equation of state to predict thermodynamic properties of the mixture, such as saturation pressure, liquid volume in the two phase region, composition of equilibrium phases, etc. If the density of the mixture is also to be correctly modeled, a value of the volumetric shift parameter is required. Finally, when viscosity is to be predicted by the equation of state, attention must be given to the input value of the critical volume for each component. Hence a complete description of a mixture of  $n=20$  components requires  $(n^2 - n)/2 + 5n = 290$  variables.

The values of the critical properties of many volatile components, particularly paraffins with less than ten or twelve carbon atoms, are found in the literature as well as many thermodynamic properties of their binary and ternary mixtures. These values are often used without adjustment in the equation of state when estimates of phase behavior are required. The predictions of the equation of state are slightly improved by regressing against the binary interaction parameters. The problem is much more difficult when dealing with a pseudocomponent. Typically the pseudocomponent is defined by a range of boiling points. The range may cover as many as 10 paraffin carbon numbers (for  $C_n > 20$ ). The difficulty lies in the assignment of average, or representative, carbon number and the properties appropriate to represent the behavior of the fraction. Even the procedure for determining the number of fractions to divide the  $C_{7+}$  portion of the complex mixture into is unclear.

Numerous correlation for calculation of characteristic properties of petroleum fractions have been compiled in the literature (Bowman 1949, Cavett 1964, Edmister 1984, Lydersen 1955, Reid, et al. 1977, Riazi 1979, Taylor, and Edmister 1971). These include such properties as molecular weight, normal boiling point, Watson characterization factor, critical properties, acentric factor, and several other correlations for energetics, heats of vaporization, etc. To develop a pseudocomponent characterization technique one or more of these properties may be utilized.

## CONTINUOUS MIXTURE METHOD

In the continuous mixture characterization of complex mixtures instead of mole fractions, a distribution function is introduced to describe the composition of many-component mixtures (Blum, and Stell 1979, Cotterman and Prausnitz 1985, Du and Mansoori 1986, 1987, Flory 1979, Gualtieri, et al. 1982, Kehlen, Ratzsch 1985, Koningsveld 1969, Ratzsch, and Kehlen 1983, Scott 1949).

For a complex 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 mixture such as molecular weight or boiling point with mean value of  $I_0$  and variance of  $\eta$ .

The composition distribution function  $F(I, I_0, \eta)$  is normalized such that

$$\int_1 I F(I) dI = 1 \quad (1)$$

over the entire range of  $I$ . Various investigators have proposed several distribution functions for the composition distribution functions of continuous mixtures (Cotterman and Prausnitz 1985, Du and Mansoori 1986, 1987, Kehlen et al. 1985, Schulz 1939, Walpole, and Myers 1985). To choose a

certain continuous distribution function, some general knowledge about compositions of the many-component mixtures under consideration is necessary (Leontaritis and Mansoori 1989). 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 distribution function  $F(I)$ :

$$Z = Z[T, P, F(I)] \quad (2)$$

$I$  is an independent variable such as molecular weight or boiling point.

From the expression of the compressibility factor, one can derive other thermodynamic properties such as the chemical potential for such a mixture. For example, an expression for the chemical potential of a fraction in a continuous mixture is generally needed for phase equilibrium calculations can be derived as the following form.

$$\mu(I) = \mu^{\circ}(I) + \int_v^{\infty} [\partial P / \partial F(I) - RT/v] dv - RT \ln(v/[RTF(I)]) + RT \quad (3)$$

or

$$\mu(I) = \mu^{\circ}(I) + d(v, T, I_0, \eta; I) - RT \ln(v/[F(I, I_0, \eta)]) \quad (4)$$

where  $\mu^{\circ}(I)$  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 multi-phase 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 (Du and Mansoori 1986, 1987):

$$T = T^L = T^V \quad (5)$$

$$P = P^L[v^L, T, F^L(I)] = P^V[v^V, T, F^V(I)] \quad (6)$$

$$\mu^L(I) = \mu^V(I) \quad I \in (0 \Rightarrow \infty) \quad (7)$$

Since the distribution function variable  $I$  changes from some initial value of  $I_1$  to very large values, Eqn. (6) is representative of a multitude of equations.

To show the difference between discrete and continuous vapor-liquid equilibrium concepts, Table (1) illustrates comparative balance equations of a continuous mixture and a discrete mixture.

**Table (1)**  
Comparison of the balance equations of a continuous mixture and a discrete mixture

	<u>Continuous Mixture</u>	<u>Discrete Mixture</u>
Total material balance	$n_f = n_L + n_V$	$n_f = n_L + n_V$
Component material balance	$n_f F_f(l) = n_L F_L(l) + n_V F_V(l)$ $F_f(l) = \Phi_L F_L(l) + \Phi_V F_V(l)$	$n_f z_i = n_L x_i + n_V y_i$ $z_i = \Phi_L x_i + \Phi_V y_i$
Normalization Conditions	$\int_1 F_f(l) dl = 1$ $\int_1 F_L(l) dl = 1$ $\int_1 F_V(l) dl = 1$	$\sum_i z_i = 1$ $\sum_i x_i = 1$ $\sum_i y_i = 1$
Average molecular weight	$M_f = \int_1 F_f(l)  dl $ $M_L = \int_1 F_L(l)  dl $ $M_V = \int_1 F_V(l)  dl $	$M_f = \sum_i z_i M_i$ $M_L = \sum_i x_i M_i$ $M_V = \sum_i y_i M_i$

Using eqn. (3), we can rewrite the phase equilibrium conditions for a one-family continuous mixture.

$$P = P^L(T, v^L, I_o^L, \eta^L) = P^V(T, v^V, I_o^V, \eta^V) \quad (8)$$

$$\begin{aligned} & \delta^L(T, v^L, I_o^L, \eta^L; (I)) - RT \ln\{v^L / [F(I_o^L, \eta^L; (I))]\} \\ & = \delta^V(T, v^V, I_o^V, \eta^V; (I)) - RT \ln\{v^V / [F(I_o^V, \eta^V; (I))]\} \quad I \in (0 \Rightarrow \infty) \end{aligned} \quad (9)$$

It is necessary to use an equation of state to calculate pressure and the chemical potentials in the equilibrium liquid and vapor phases. Generally, it is impossible to solve eqn's. (8) and (9) 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, or vegetable oils, we need to use computational algorithms for the phase behavior predictions of continuous mixtures with wide ranges of molecular weight distribution (Du and Mansoori, 1986, 1987).

## DISCUSSION

The papers presented in this monograph are a collection of the works by

various investigators around the world who have been involved with the problem of  $C_7^+$  characterization for various practical applications:

In the first paper Helle and Friedemann make comparisons between various existing characterization methods by using such methods for three different petroleum reservoir fluid data. Through their study it is demonstrated that the choice of characterization method certainly affects the outcome of reservoir fluid PVT prediction.

In the second paper Whitson, Anderson, and Sfreide introduce a method for dividing the  $C_7^+$  fraction of crude oil and condensate fluids into an arbitrary number of discrete pseudocomponents using Gauss-Laguerre quadrature and the gamma distribution model. They demonstrate that their proposed method can be applied simultaneously to variety of mixtures. They observe that a small adjustment in measured  $C_7^+$  molecular weight may have a significant effect on the predicted phase behavior of reservoir fluids. They also conclude that it is not possible to predict the equilibrium oil composition and  $C_7^+$  properties in a saturated reservoir based only on the gas-cap composition through  $C_7^+$ .

In the third paper Benmekki and Mansoori present a new pseudoization technique which is applicable for equation of state calculation of phase behavior of multicomponent mixtures. The major advantage of this technique is that it is independent of the kind of mixing rules which may be used for parameters of the equation of state under consideration. In this technique Benmekki and Mansoori use a pseudobinary representation to evaluating a lumping parameter which accounts for the mixture-like character of pseudocomponents. The method proposed is shown to be quite versatile and applicable for variety of multicomponent calculations.

In the fourth paper Stewart, Phelps, and Ball present the results of their various chromatography and spectroscopy analysis which are applicable for  $C_7^+$  characterization of complex mixtures. Their results indicate that combined chromatography and spectroscopy analysis can provide detailed compositional and structural insights into the  $C_7^+$  fraction of reservoir oils.

In the fifth paper Warzinski, McKeegan, and Holder introduce a new method for characterization of heavy and complex materials, such as coal-derived residuum, by utilizing the properties of fluids near their critical points. This is achieved by the incorporation of an experimental system which promote reflux of less-soluble components onto a packed bed.

In the sixth paper Carrier, Rogalski, and Peneloux study the rules for choosing pseudocomponents by optimally regrouping petroleum fluid fractions in order to perform more accurate flash calculations than the

existing techniques through equations of state. They conclude that a successful pseudocomponent technique must satisfy the experimental composition data as closely as possible. They also investigate the possibility of reducing experimentally established compositions of petroleum fluids with the pseudoization technique in order to cut down the computer time for vapor-liquid equilibrium calculations of complex mixtures.

In the seventh paper Pedersen, Thomassen, and Fredenslund report some experimental phase equilibria data of North Sea reservoir oils. Then, they use the measured physical property data to correlate the parameters of an empirical equation of state. When the predicted results do not agree with the experimental phase behavior data they further adjust the molecular weight of the plus-fractions in order to fit the experimental data better. This report is a good example of the route that the practicing engineers have been taking in their trial and error efforts of characterizing the plus-fractions of complex mixtures.

In the eighth paper Chung introduces a new characterization technique which is based on boiling point and specific gravity as the input parameters. As a result of this technique the author develops an internally consistent method for the prediction of thermodynamic properties and viscosity of petroleum components and fractions.

In the ninth paper Yu, Wu, and Batycky introduce a new procedure and correlation for the  $C_7^+$  characterization of bitumen using a cubic thermodynamic equation of state. The results of their correlations can be useful in the design of separation systems involving bitumen.

In the tenth paper Shealy introduces a method of describing the phase behavior of oils in petroleum reservoir compositional simulators using equations of state as it is used in petroleum production industry. Since the computer time is a major problem in such simulators the goal of this work is to reduce the computational time by sacrificing some accuracy in the predictions.

In the eleventh paper Stange, Majeed, and Overa demonstrate the application of  $C_7^+$  fraction characterization in the operation of an off-shore gas-condensate transportation and terminal system. This paper clearly demonstrate the economic and technological risks which are encountered using inaccurate  $C_7^+$  fraction characterizations.

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# Pseudoization Techniques and Heavy Fraction Characterization with Equation of State Models

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## ABSTRACT

A pseudoization technique is developed which is independent of the kind of mixing rules used for characterizing the parameters of the equations of state. This technique uses a pseudobinary representation to evaluate a lumping parameter which accounts for the mixture-like character of the pseudocomponent. This is to reduce original mixture characterization to a minimum number of components. The method is versatile and can be used to tune the equation of state to any laboratory PVT data. The validity of the technique is demonstrated by several sample calculations such as phase split isotherms and phase envelopes of a gas condensate and other reservoir oils. The pseudoternary diagram representation of solvent-oil systems are predicted and they are shown to be in agreement with the original mixture characterization. Accuracy of prediction of such pseudoternary diagrams, which are widely used in vaporizing-gas-drive enhanced oil recovery processes, is demonstrated as a further test of the proposed method.

## INTRODUCTION

The computational efficiency and cost of simulation of processes involving complex fossil fuels (petroleum, coal-liquids, etc.) using equations of state depend a great deal on the number of components (real and pseudocomponents) chosen to describe the fluid under study. In general the number of components necessary to describe such complex fluids is higher than ten. The computer capacity of storage and computation time increase considerably with the increase in the number of components. Several methods have been reported to characterize pseudocomponents and heavy-end fractions (Hong 1982; Mehra et al. 1982; Withson 1983; Gonzalez et al. 1986; Wu and Batycky 1986). Most of these methods are based on arbitrary mixing rules and empirical pseudoization techniques where the pseudocomponents are treated as pure components. None of the methods proposed to date seem to offer an advantage over the other available techniques. More recently, a semi-empirical concept has been proposed to account for the mixture-like character of the pseudocomponent (Schlijper 1986). This concept has brought about improvement in describing phase behavior of complex fluids. In the present report, a new technique is presented that uses a nonlinear regression-based phase behavior program to characterize pseudocomponents. The method takes into consideration the effect of

temperature in calculating the lumping parameters by adjusting critical properties of the pseudocomponents evaluated from mixing rules.

In the second section of this report a review of the available methods for evaluating the properties of pseudocomponents is presented. In the third section an algorithm for the evaluation of the lumping parameters and the pseudobinary interaction parameters is described. Finally, in the fourth section computational results are presented for a synthetic oil mixture, a gas condensate system, and a reservoir oil.

#### PSEUDOCOMPONENT PROPERTIES

In lumping components into pseudocomponents to represent a complex many-component fluid one can use mixing rules to determine the pseudocomponent properties for substitution into the equation of state. These properties include critical temperature ( $T_c$ ), critical pressure ( $P_c$ ), critical volume ( $V_c$ ), critical compressibility factor ( $Z_c$ ), acentric factor ( $\omega$ ), molecular weight (MW), and binary interaction parameters ( $k_{ij}$ ). There are numerous sets of mixing rules available in the literature to characterize pseudocomponents.

Kay's rules (Kay 1938) are the simplest form of mixing rules by which the pseudocomponent properties are obtained by summing the products of the component properties and a weighting factor which is usually the relative molar fraction for the group of components used in a pseudocomponent,

$$P_{cm} = \sum_i^m x_i P_{ci} \quad (1)$$

$$T_{cm} = \sum_i^m x_i T_{ci} \quad (2)$$

$$V_{cm} = \sum_i^m x_i V_{ci} \quad (3)$$

$$\omega_m = \sum_i^m x_i \omega_i \quad (4)$$

$$MW_m = \sum_i^m x_i MW_i \quad (5)$$

In connection with evaluation of cross-parameters,  $a_{ij}$ , of cubic equations of state and the cross-second virial coefficient,  $B_{ij}$ , of the virial equation, Prausnitz and Gunn (1958) adopted the Lorentz-Berthelot type combining rules. The complete system of pseudocomponent properties includes:

$$T_{cij} = (T_{ci} T_{cj})^{0.5} \quad (6)$$

$$V_{cij}^{1.3} = \frac{V_{ci}^{1.3} + V_{cj}^{1.3}}{2} \quad (7)$$

$$T_{cm} = \sum_i^m \sum_j^m x_i x_j (1 - k_{ij}) (T_{ci} T_{cj})^{0.5} \quad (8)$$

$$V_{cm}^{1.3} = \frac{1}{2} \sum_i^m \sum_j^m x_i x_j (V_{ci}^{1.3} + V_{cj}^{1.3}) \quad (9)$$

$$Z_{cm} = 0.5(Z_{ci} + Z_{cj}) \quad (10)$$

$$\omega_m = 0.5(\omega_i + \omega_j) \quad (11)$$

$$P_{cm} = \frac{Z_{cm} R T_{cm}}{V_{cm}} \quad (12)$$

An alternate procedure for characterizing pseudocomponents has been developed by Mehra et al. (1982) as the following:

$$T_{cm} = \frac{1}{8} \frac{1}{V_{cm}} \sum_i^m \sum_j^m x_i x_j (V_{ci}^{1.3} + V_{cj}^{1.3})^3 (T_{ci} T_{cj})^{1.2} \quad (13)$$

$$Z_{cm} = 0.2905 - 0.085 \omega_m \quad (14)$$

Then several weighting factors,  $\phi_i$ , have been defined with various mixing rules which have been summarized by Hong (1982) and they include:

molar average,

$$\phi_i = x_i \quad (15)$$

surface fraction,

$$\phi_i = \frac{x_i V_{ci}^{2.3}}{\sum_i^m x_i V_{ci}^{2.3}} \quad (16)$$

weight fraction average,

$$\phi_i = \frac{x_i MW_i}{\sum_i x_i MW_i} \quad (17)$$

and the mixing rules for  $T_{cm}$  includes a  $P_c$  weighting factor,

$$T_{cm} = \sum_i^m \sum_j^m \phi_i \phi_j (T_{ci} T_{cj})^{1/2} (1 - k_{ij}) \quad (18)$$

where

$$\phi_i = \frac{x_i P_{ci}}{\sum_i x_i P_{ci}} \quad (19)$$

This is just to mention a few of a score of proposed mixing and combining rules for evaluating pseudocomponent properties. Statistical mechanical considerations can be used to derive other mixing rules for a specific equation of state. For example the pseudocomponent mixing rules for the Peng-Robinson equation of state (Peng and Robinson 1976) one can obtain the following expressions for properties of pseudocomponents:

$$T_{cm} = \frac{\sum_i^m \sum_j^m x_i x_j (T_{ci} T_{cj})^{1/2} \left( \frac{T_{ci}}{P_{ci}} + \frac{T_{cj}}{P_{cj}} \right)}{2 \sum_i^m x_i \frac{T_{ci}}{P_{ci}}} \quad (20)$$

$$P_{cm} = \frac{T_{cm}}{\sum_i^m x_i \frac{T_{ci}}{P_{ci}}} \quad (21)$$

To derive these expressions the dimensions of parameters  $a$  and  $b$  for the Peng-Robinson equation of state with pressure and temperature are taken into account. It is observed that the contribution of more complex mixing rules over the simple ones, Equations 1-5, in defining pseudocomponents is insignificant. There is no physical significance behind the mixing rules for the pseudocomponent binary unlike parameters. In this report a pseudobinary interaction parameter between any two different pseudocomponents is evaluated with the regression program in order

to match the calculation with the the exact compositional description of the mixture.

#### DESCRIPTION OF THE ALGORITHM

Let us assume the equation of state which is considered for phase equilibrium calculation is in the following form:

$$Z = Z(v, T, a_m, b_m) \quad (22)$$

where its mixing rules can be shown by the following general expressions:

$$a_m = a_m(x_i, x_j, a_{ij}); \quad i, j = 1, 2, \dots, c \quad (23)$$

$$b_m = b_m(x_i, x_j, b_{ij}); \quad i, j = 1, 2, \dots, c \quad (24)$$

with the following combining rules:

$$a_{ij} = (1 - k_{ij}) (a_i a_j)^{1/2} \quad (25)$$

$$b_{ij} = (1 - l_{ij}) \frac{(b_i + b_j)}{2} \quad (26)$$

where  $k_{ij}$  and  $l_{ij}$  are generally non-zero parameters when  $i \neq j$  and  $k_{ij} = l_{ij} = 0$  for  $i = j$ .

Provided one knows the exact number of components of the multicomponent mixture this equation of state can be used for phase equilibrium calculation of that mixture. In the proposed technique it is assumed that one can group the ( $c$ ) components of the mixture to ( $s$ ) pseudocomponents (for example  $s=3$  when one wants to represent the data in a ternary diagram). Then the equation of state of the multicomponent mixture can be shown in the following form:

$$Z = Z(v, T, a_m, b_m) \quad (27)$$

where

$$a_m = a_m(\xi_i, \xi_j, A_{ij}^{ps}); \quad i, j = 1, 2, \dots, s \quad (28)$$

$$b_m = b_m(\xi_i, \xi_j, B_{ij}^{ps}); \quad i, j = 1, 2, \dots, s \quad (29)$$

with the following combining rules:

$$A_{ij}^{ps} = (1 - \kappa_{ij}) (A_i^{ps} A_j^{ps})^{1/2} \quad (30)$$

$$B_{ij}^{ps} = (1 - \lambda_{ij}) \frac{(B_{ii}^{ps} + B_{jj}^{ps})}{2} \quad (31)$$

It should be pointed out that contrary to the case of Eqs. 25 and 26 parameters  $\kappa_{ij}$  and  $\lambda_{ij}$  will be in general non-zero parameters for both cases of  $i \neq j$  and  $i = j$ . When  $i = j$  parameters  $\kappa_{ii}$  and  $\lambda_{ii}$  will be called "Lumping Parameters" and when  $i \neq j$  parameters  $\kappa_{ij}$  and  $\lambda_{ij}$  will be called "Pseudobinary Interaction Parameters". In Eqs. 28 and 29  $\xi_i$  and  $\xi_j$  are "Group Mole Fractions" and  $A^{ps}_{ii}$ ,  $A^{ps}_{jj}$ ,  $B^{ps}_{ii}$ ,  $B^{ps}_{jj}$  are pseudocomponent parameters associated with each group.

At this stage we have to address three questions: (i) How to define the pseudocomponent parameters? (ii) How to calculate the lumping parameters? (iii) How to calculate the pseudobinary interaction parameters?

#### (i) Definition of Pseudocomponent Parameters

The existing techniques available for calculation of pseudocomponent parameters have already been reviewed in the previous section. In the present technique one can use any of the available techniques without loss of generality. So long as the same pseudocomponent calculation technique is used for defining pseudocomponents the present technique will predict the same phase behavior for the multicomponent system under consideration. However, in all the calculations which follow one must not switch from one pseudocomponent calculation technique to another.

#### (ii) Calculation of Lumping Parameters

These parameters are calculated by assuming that a pseudocompound with equation of state parameters  $A^{ps}_{ii}$  and  $B^{ps}_{ii}$  can represent properties of a lumped group of compounds. Parameters  $A^{ps}_{ii}$  and  $B^{ps}_{ii}$  are then calculated by matching properties of a pseudocompound with the mixture properties of the group of compounds which are lumped together. This technique of calculation makes the numerical value of lumping parameters dependent on the kind of mixing rules used for evaluating the pseudocomponent parameters, temperature, and composition of the compounds in the pseudocomponent.

#### (iii) Calculation of Pseudobinary Interaction Parameters

After the pseudocomponent parameters are defined and the lumping parameters are calculated pseudobinary interaction parameters can be calculated by matching the properties of every pseudobinary mixture with a true multicomponent mixture consisting of all the compounds appearing in the pseudobinary mixture. This technique of calculation makes the numerical value of pseudobinary interaction parameters dependent on temperature and composition of the compounds in the pseudobinary mixture. In some cases the temperature at which the system fluid is studied is higher than the critical temperature of the heavier pseudocomponent in the pseudobinary representation. Under such condition the regression analysis cannot be performed unless the pseudocritical properties obtained from mixing rules are adjusted or the grouping configuration is modified.

## APPLICATIONS

As an example the Peng-Robinson equation of state which has received a wide acceptance in process engineering calculations is chosen with the computational methods described in this paper. The experimental data of the mixtures studied in this investigation are not reported since the objective of this research is not to evaluate the performance of the equation of state but to test the proposed pseudoization technique vis a vis the computation performed with the original mixture characterization.

### First Application

A synthetic oil (Metcalf and Yarborough 1979) of 10 components (the binary interaction parameters and the composition are given in Table 1 and 2, respectively) is selected to test the proposed technique.

Table 1. Binary Interaction Parameters Used with the Peng-Robinson Equation of State.

	CO2	C1	C2	C3	C4	C5	C6	C7	C8	C10	C14
CO2	-										
C1	.092	-									
C2	.132	.000	-								
C3	.124	.014	.000	-							
C4	.133	.013	.010	.000	-						
C5	.122	.023	.010	.000	.000	-					
C6	.110	.042	.010	.000	.000	.000	-				
C7	.100	.035	.010	.000	.000	.000	.000	-			
C8	.114	.049	.010	.000	.000	.000	.000	.000	-		
C10	.150	.047	.010	.000	.000	.000	.000	.000	.000	-	
C14	.150	.045	.010	.000	.000	.000	.000	.000	.000	.000	-

Table 2. Synthetic Oil Composition Used for the First Application.

Components	Molar fraction (%)
Methane	35
Ethane	3
Propane	4
n-Butane	6
n-Pentane	4
n-Hexane	3
n-Heptane	5
n-Octane	5
n-Decane	30
n-Tetradecane	5

When the heavy-end fractions are described by the molecular weight, the specific gravity, and the boiling point, empirical correlations (Cavett 1962; Standing 1982) are used to estimate the properties (critical pressure and temperature and acentric factor) of the fractions. A lumping configuration is selected such that the synthetic mixture is reduced to 3 pseudocomponents, consisting of  $[C_1]$  (methane),  $[C_2-C_6]$

(C2-C6) / C7+

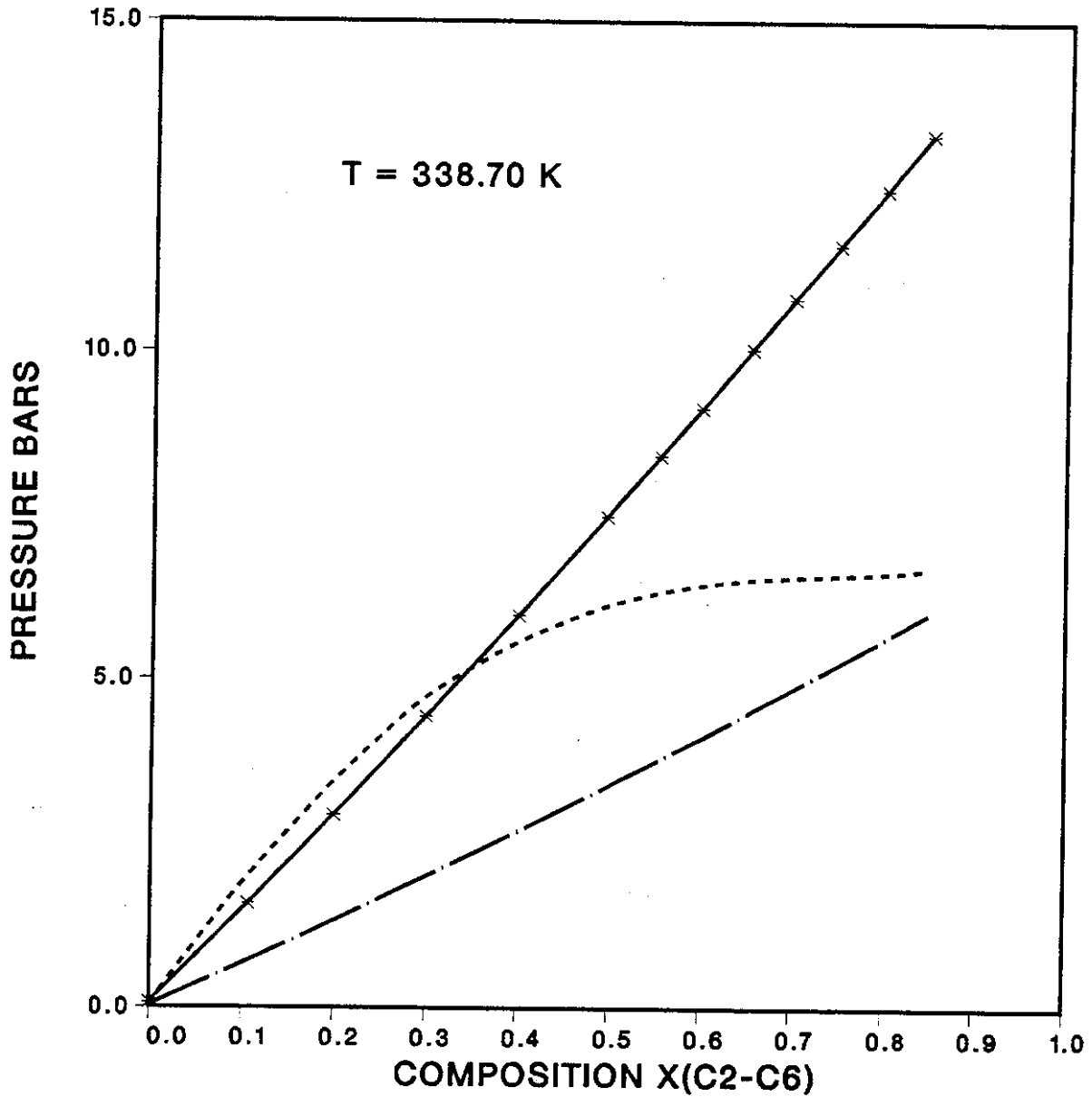


Figure 1. P-X diagram for the [C2-C6]/[C7+] pseudobinary system at 338.70K. Chain-dotted line: calculation without the lumping and pseudobinary interaction parameters; dots: calculation with the pseudobinary parameters but without the lumping parameter; solid line: calculation with the lumping and pseudobinary interaction parameters; symbols: exact multicomponent calculation

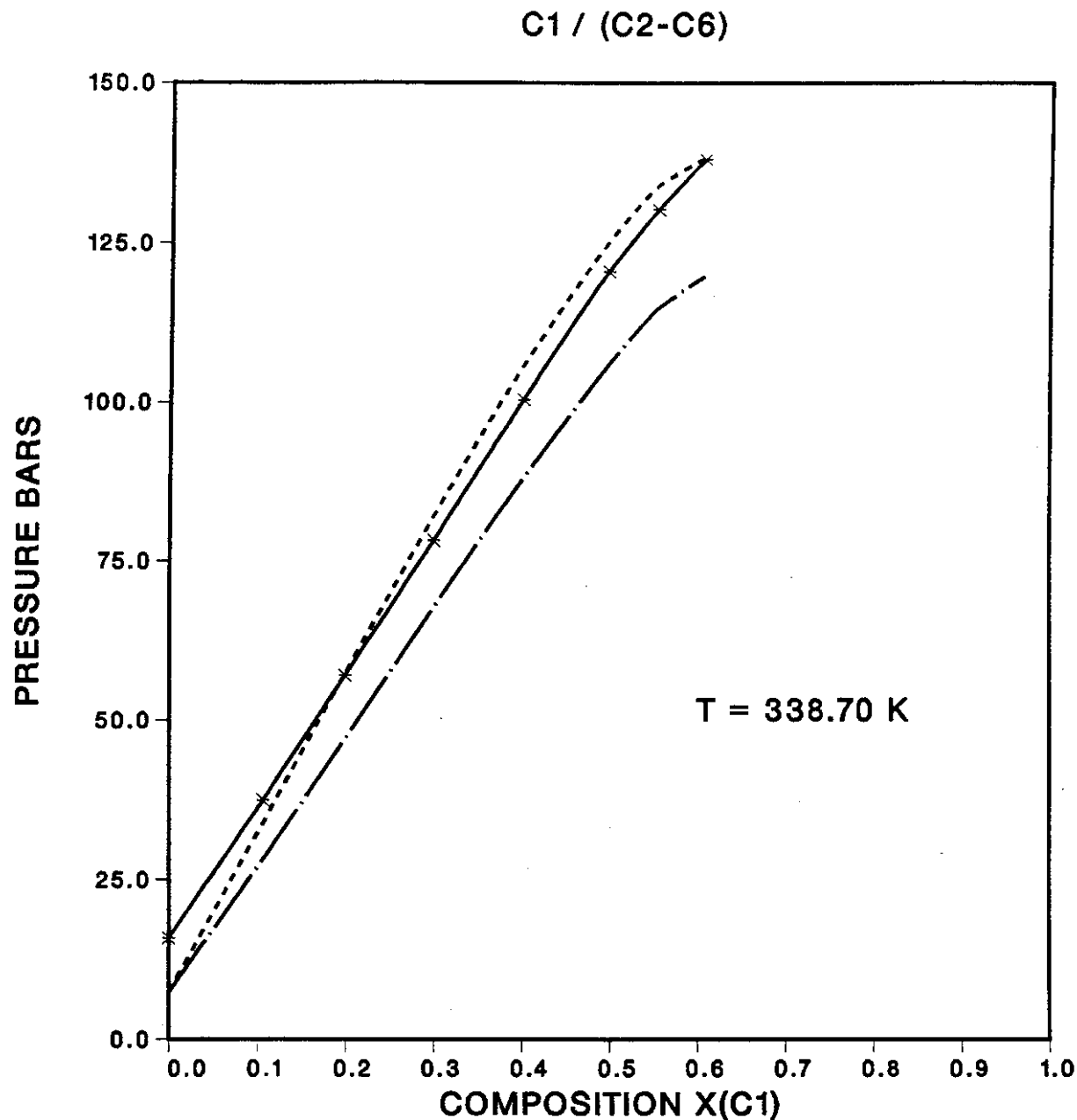


Figure 2. P-X diagram for the [C1]/[C2-C6] pseudobinary system at 338.70K. Chain-dotted line: calculation without the lumping and pseudobinary interaction parameters; dots: calculation with the pseudobinary parameters but without the lumping parameter; solid line: calculation with the lumping and pseudobinary interaction parameters; symbols: exact multicomponent calculation

C1 / C7+

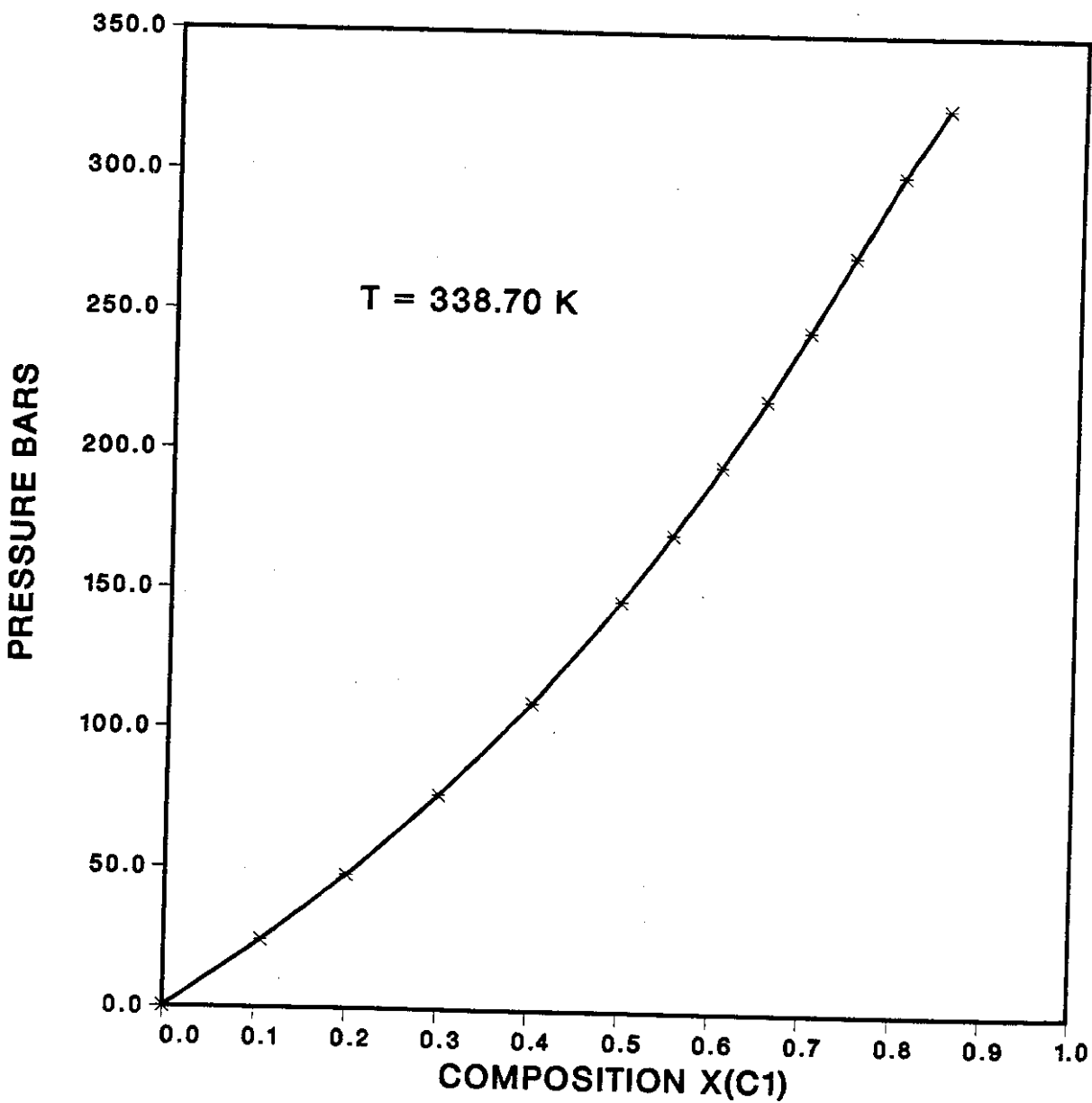


Figure 3. P-X diagram for the [C1]/[C7+] pseudobinary system at 338.70K. Solid line: calculation with the lumping and pseudobinary interaction parameters; symbols: exact multicomponent calculation.

(C1-CO2) / (C2-C6)

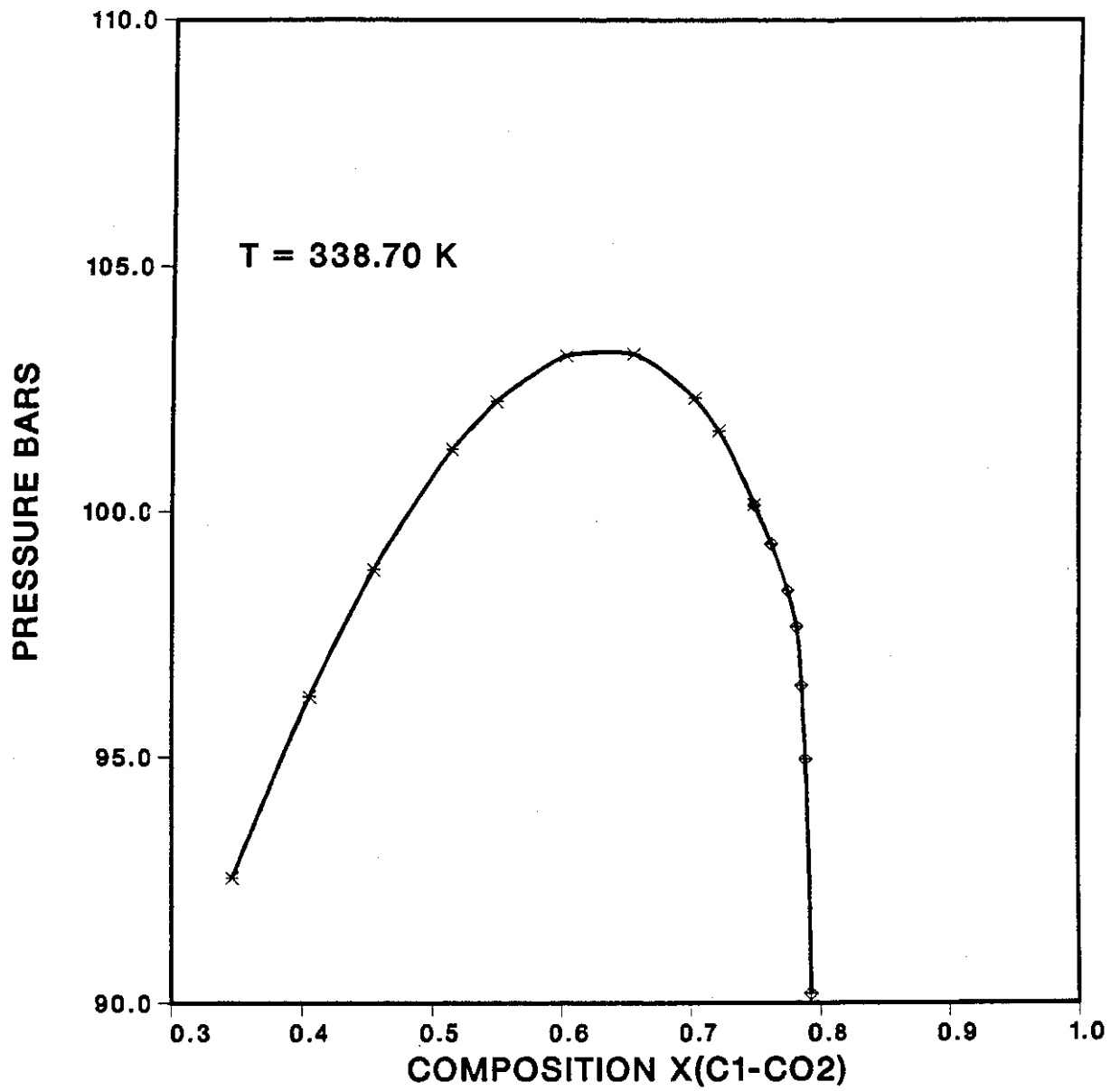


Figure 4. P-X diagram for the [C1-CO2]/[C2-C6] system at 338.70K. Solid line: calculation with pseudoization technique; symbols: exact multicomponent calculation.

(C1-CO2) / C7+

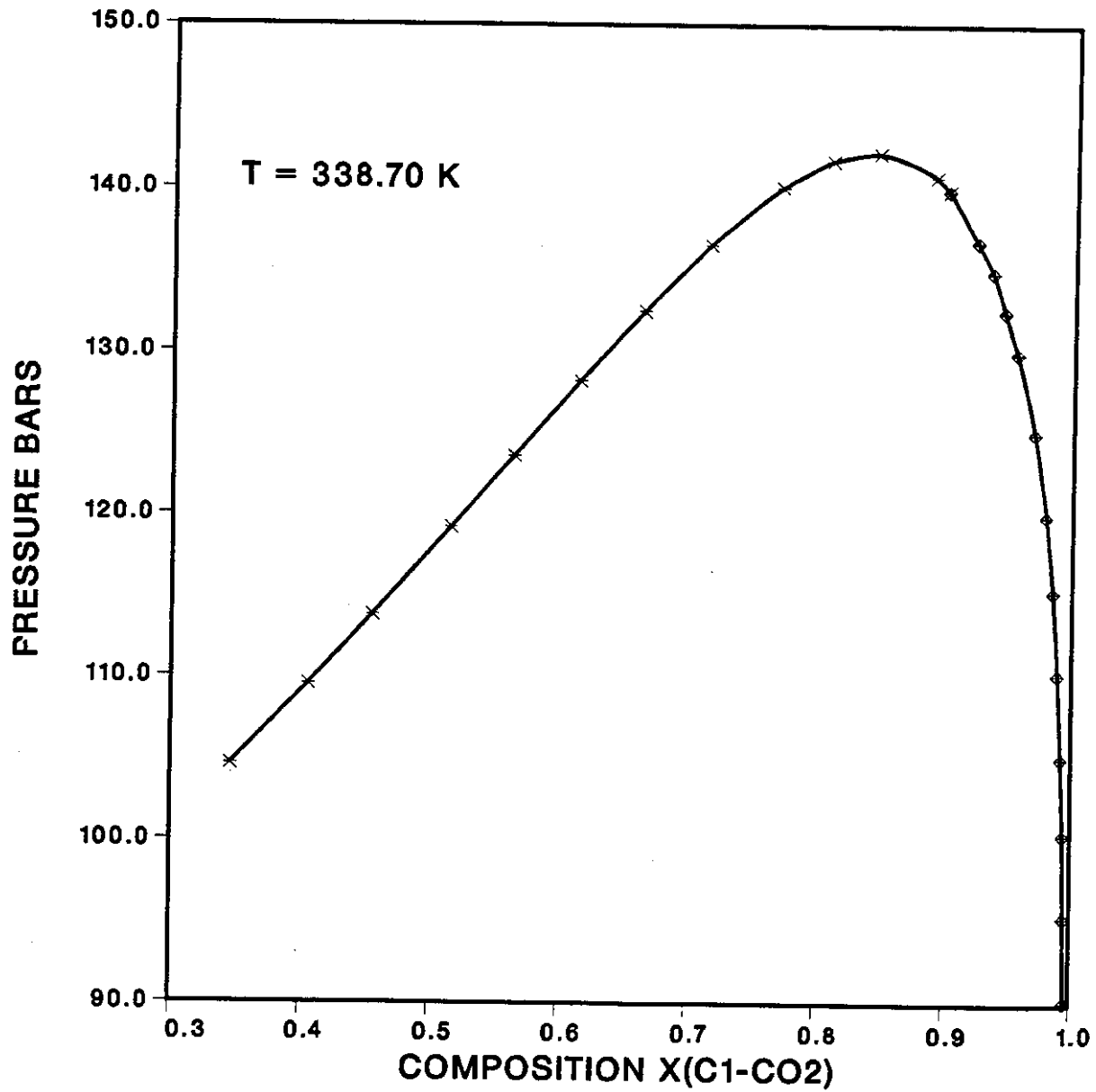


Figure 5. P-X diagram for the [C1-CO2]/[C7+] system at 338.70K. Solid line: calculation with pseudoization technique; symbols: exact multicomponent calculation.

# CO<sub>2</sub> / SYNTHETIC OIL

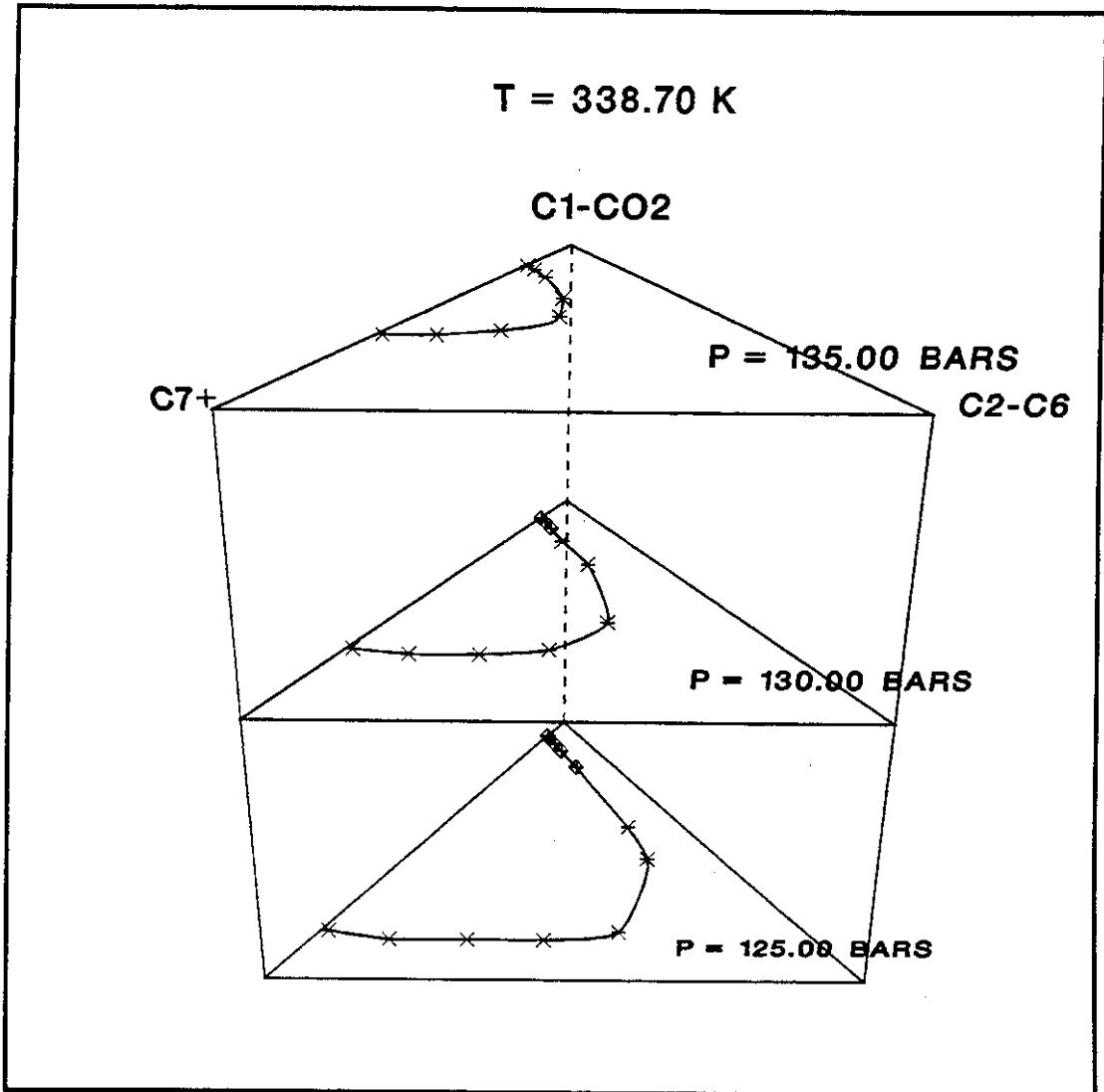


Figure 6. Pseudoternary diagram for CO<sub>2</sub>/synthetic oil at 338.70K. Solid line: calculation with pseudoization technique; symbols: exact multicomponent calculation.

(ethane to hexane), and [C<sub>7</sub>+] (heptane and heavier fractions). The computer program based on the proposed technique performs a specified number of bubble-point-pressure calculations which will be used in the objective function of the regression analysis. Figure 1 shows the P-X diagram of the [C<sub>2</sub>-C<sub>6</sub>]+[C<sub>7</sub><sup>+</sup>] pseudobinary system where the symbols represent the calculation with the exact compositional description of the synthetic mixture. The dash-dotted line is the calculation with 2 pseudocomponents but without the pseudobinary interaction parameters and lumping parameters. The dashed line is the result with two pseudocomponents and the pseudobinary interaction parameter, but, without the lumping parameters. The solid line is obtained with two pseudocomponents, the pseudobinary interaction parameter and the lumping parameters. Figure 2 illustrates the same calculations as in Figure 1 for the [C<sub>1</sub>]+[C<sub>2</sub>-C<sub>6</sub>] pseudobinary system. In Figure 3 the P-X diagram of the [C<sub>1</sub>]+[C<sub>7</sub><sup>+</sup>] pseudobinary system is reported where only the pseudobinary interaction parameter is evaluated to match the exact calculation represented by the symbols. For this particular example two lumping parameters are only needed, one lumping parameter for the [C<sub>2</sub>-C<sub>6</sub>] group and a second lumping parameter for the [C<sub>7</sub><sup>+</sup>] group.

Figures 4-6 are for prediction of the phase behavior of a vaporizing gas drive process with CO<sub>2</sub> as the injected gas and the synthetic oil as the reservoir oil. The objective here is to test the performance of the proposed technique at different pressures and in all ranges of composition of solvent and oil. The P-X diagrams shown in Figures 4 and 5 are used to evaluate the binary interaction parameters between CO<sub>2</sub> and the pseudocomponents of the synthetic mixture. The predicted pseudoternary diagram for this system is shown in Figure 6 where it is demonstrated that the agreement between the exact calculation and the lumping technique is excellent.

#### Second Application

A P-T phase envelope of a gas condensate (Wu and Batycky 1986) system (high in methane and low in heavy hydrocarbons) with the composition as in Table 3 is constructed and it is reported by Figure 7. In this calculation 4 pseudocomponents are chosen which are [CH<sub>4</sub>], [N<sub>2</sub>], [CO<sub>2</sub>,C<sub>2</sub>-C<sub>5</sub>], and [C<sub>6</sub>+].

Table 3. Gas Condensate Composition Used for the Second Application.

Components	Molar fraction (%)
Methane	76.34
Ethane	8.86
Propane	4.29
i-Butane	0.79
n-Butane	1.26
i-Pentane	0.56
n-Pentane	0.58
Hexane <sup>+</sup>	4.06
Nitrogen	0.94
Carbon dioxide	2.32

# PHASE ENVELOPE OF GAS CONDENSATE

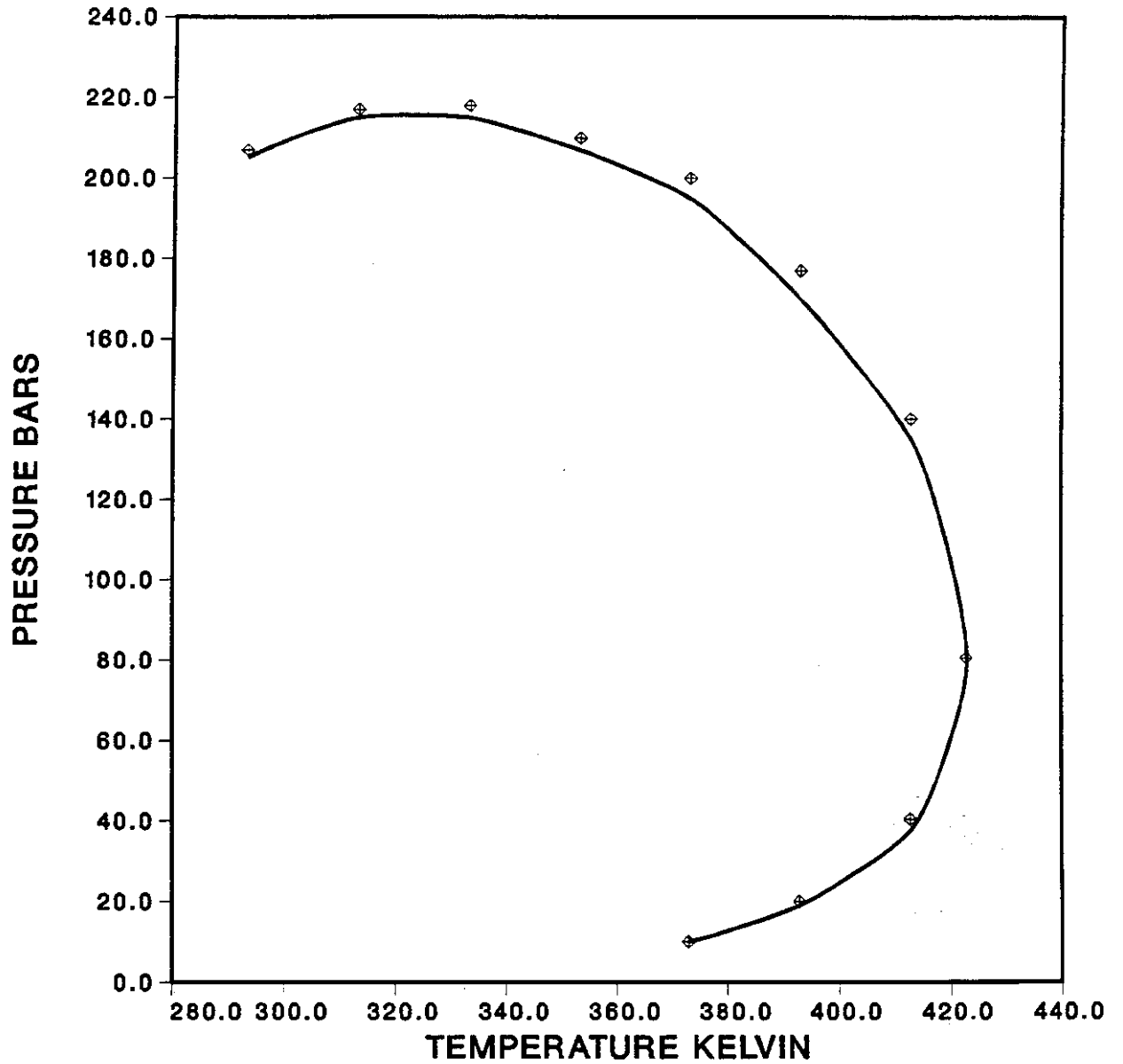


Figure 7. Phase envelope of gas condensate at 338.70K. Solid line: calculation with pseudoization technique; symbols: exact multicomponent calculation.

# PHASE EQUILIBRIA OF CO<sub>2</sub> / OIL

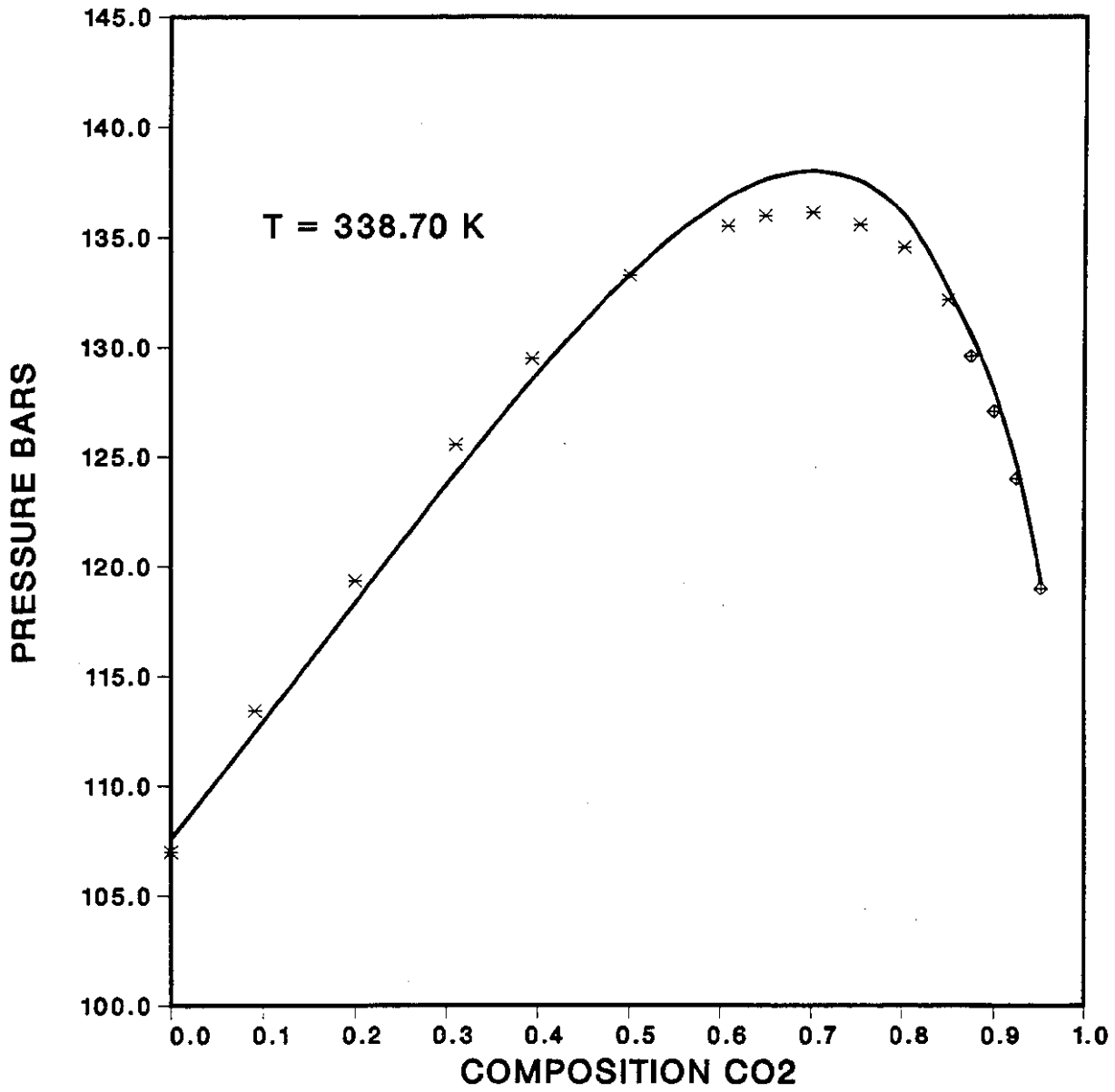


Figure 8. P-X diagram for CO<sub>2</sub>/reservoir oil at 338.70K. Solid line: calculation with pseudoization technique; symbols: exact multicomponent calculation.

Also, a P-X diagram of carbon dioxide-reservoir oil system (Wu and Batycky 1986) with the composition as in Table 4 is constructed using the same 4 pseudocomponents and it is reported by Figure 8. In both of these cases the results of calculations obtained with the present approach are in very good agreement with the exact multicomponent calculations.

Table 4. Reservoir Oil Composition used for the Second Application.

Components	Molar fraction (%)
Methane	32.54
Ethane	9.09
Propane	7.73
i-Butane	1.36
n-Butane	4.28
i-Pentane	1.67
n-Pentane	2.30
Hexane <sup>+</sup>	38.41
Nitrogen	1.19
Carbon dioxide	0.63

### Third Application

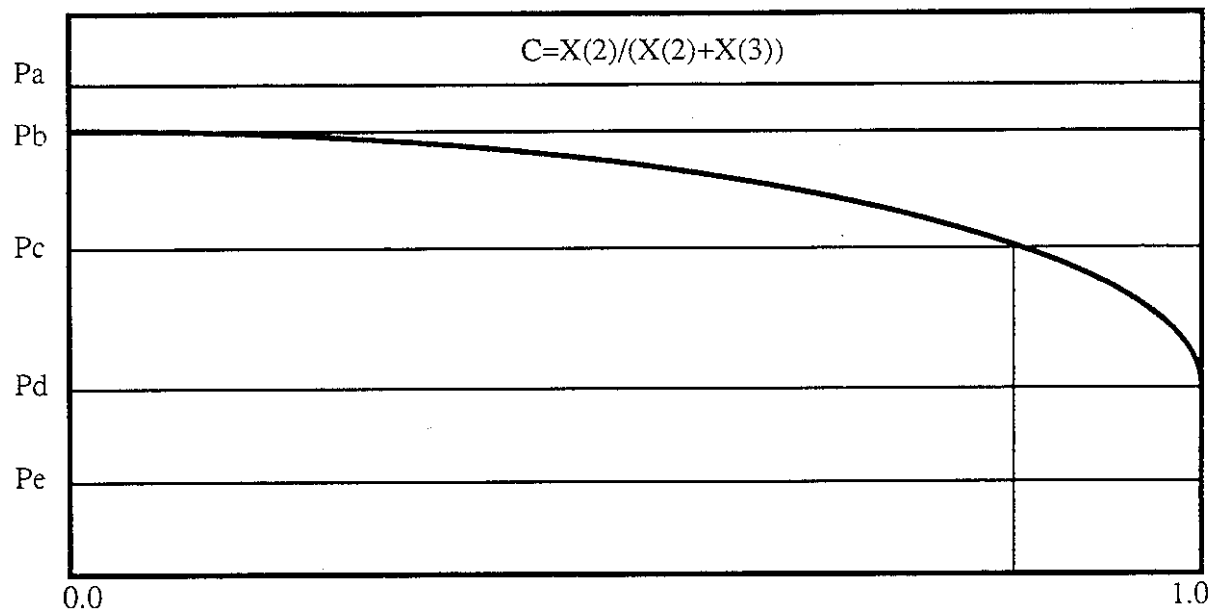
The final application is to establish a relationship between the cricondenbar locus of P-X diagram of a multicomponent mixture and the phase separation regions of the pseudoternary diagram of the same mixture. This kind of relationship is of significant importance in application of pseudoization techniques in high pressure processes such as supercritical fluid extraction of heavy compounds from mixtures and miscible flood enhanced oil recovery.

For every multicomponent mixture at a given composition one can plot a P-T diagram. For the same mixture, provided the temperature and relative composition of c-1 components are kept constant, one can plot a P-X diagram (pressure versus composition of one component). In the present computation we characterize our mixture by three pseudocomponents [heavy (3), intermediate (2), and light (1)] and we study the P-X diagrams by varying the ratio of compositions of heavy and intermediates. Rather than plotting various P-X diagrams the locus of the cricondenbars of such mixtures versus  $C=X(2)/[X(2)+X(3)]$  are reported by Figures 9 and 10. Also reported in Figures 9 and 10 are the pseudoternary diagrams related to the same mixtures at different pressures.

The major difference between Figures 9 and 10 is the difference in shapes of the cricondenbar loci. These two shapes (one a decreasing function of C and the other having a minimum point) are the only possible trends that one can produce by choosing all possible relative compositions for the light, intermediate, and heavy fractions of a multicomponent mixture.

Figure 9 shows the cases when a multicomponent mixture may exhibit an open phase-envelope ( $P < P_d$ ), a closed phase-envelope ( $P_d \leq P < P_b$ ), or no phase-envelope ( $P \geq P_b$ ) in a pseudoternary diagram representation. In no case one can observe two

Cricondenbar



Cc

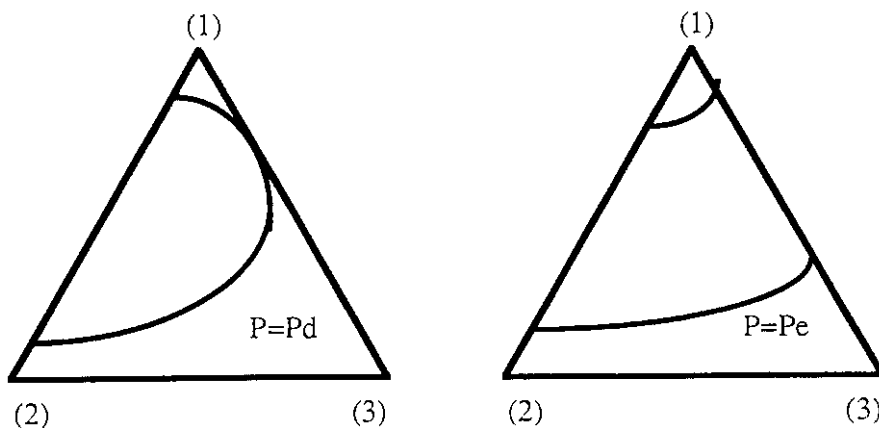
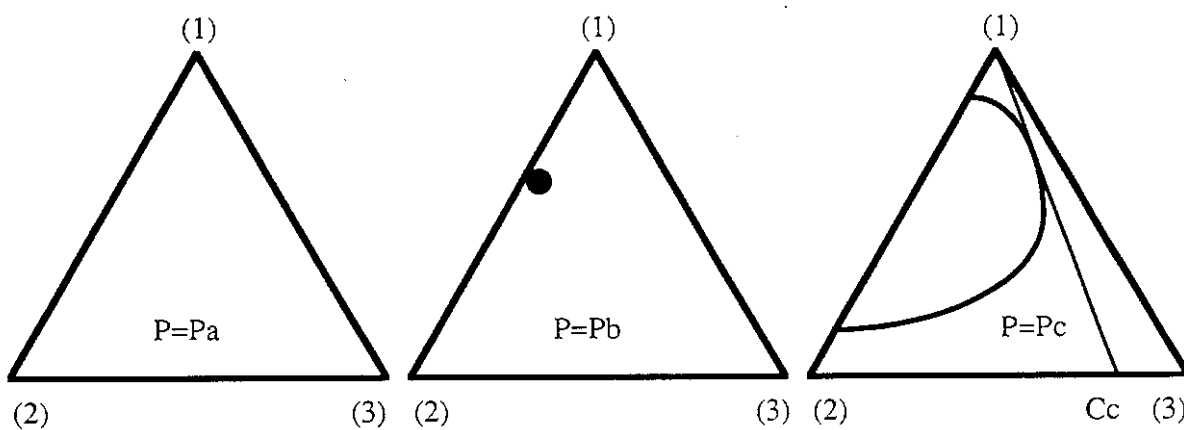


Figure 9. Relationship between cricondenbar locus of P-X diagram and phase separation regions in pseudoternary diagram

Cricondenbar

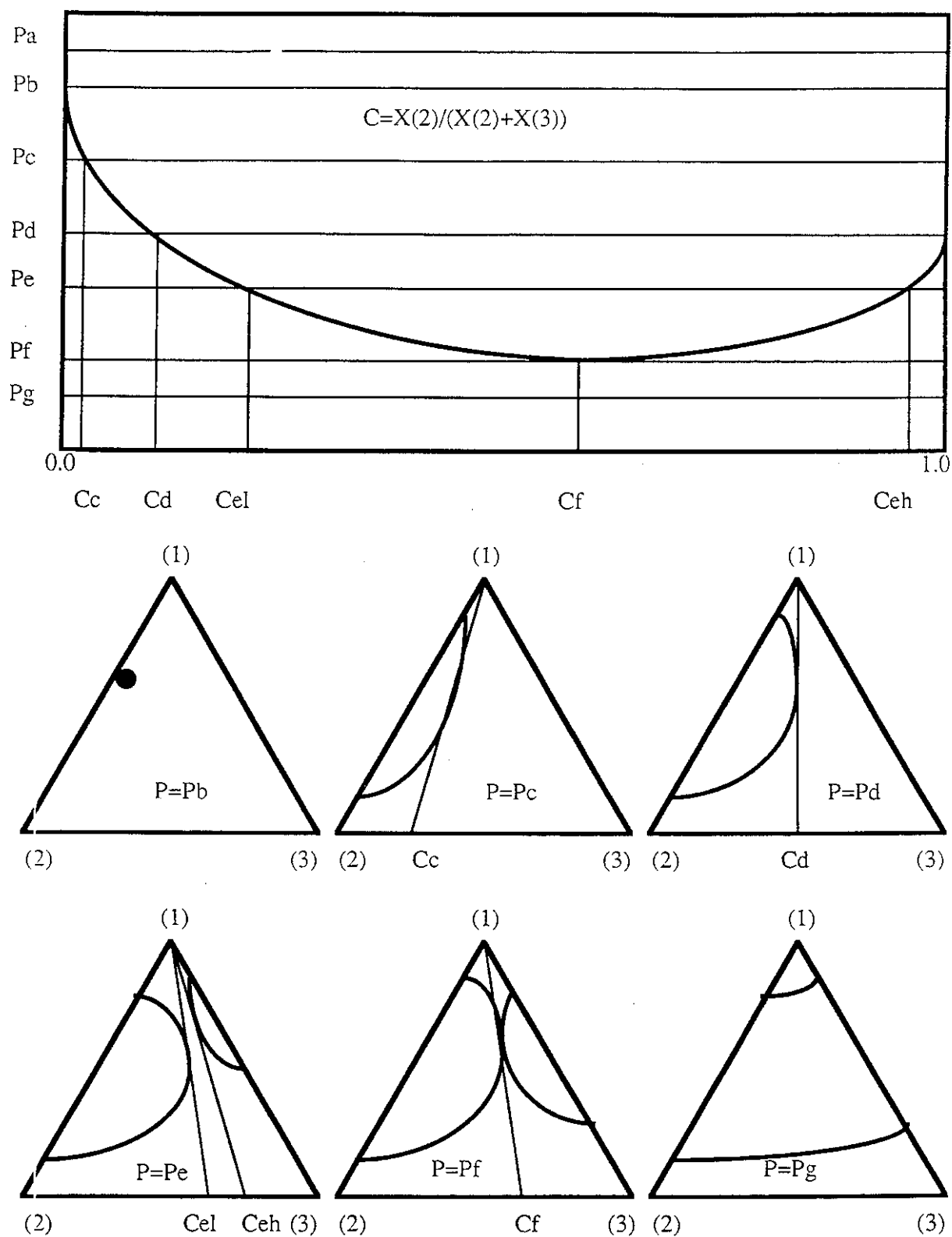


Figure 10. Relationship between cricondenbar locus of P-X diagram and phase separation regions in pseudoternary diagram

closed phase-envelopes when the cricondenbar locus is monotonic with respect to C as it is the case of Figure 9.

Figure 10 shows the cases when a multicomponent mixture may exhibit an open phase-envelope ( $P < P_f$ ), Two closed phase-envelopes ( $P_f \leq P < P_d$ ), one closed phase-envelope ( $P_d \leq P < P_b$ ), or no phase-envelope ( $P \geq P_b$ ) in a pseudoternary diagram representation. The reason for observing two closed phase-envelopes in this case is because the cricondenbar locus has a minimum with respect to  $C = X(2)/[X(2)+X(3)]$ .

## CONCLUSION

The technique proposed here enables one to use a reduced compositional fluid representation in phase behavior simulation without any loss in modeling accuracy. The non-linear regression-based phase behavior algorithm described in this report can have several applications in the simulation processes involving equations of state. These include adjustment of equation of state parameters to match laboratory PVT data, characterization of heavy end fractions, and most importantly large-scale simulation of petroleum field reservoirs. The algorithm is versatile and can be used with any generalized equation of state.

## ACKNOWLEDGMENT

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