Phase Behavior of CO_2/Hydrocarbon Systems: Amendments to Previously Predicted Phase Diagrams

S.E. Quiñones-Cisneros, M.B. Blackburn,* L.E. Scriven, SPE, and **H.T. Davis,** SPE, U. of Minnesota

Summary. In using the Peng-Robinson equation of state (PREOS) described by Sahimi *et al.*, we found discrepancies with their results. By using two separate methods of computation, we deduced that their method is correct, but that some code or implementation errors must have caused the observed discrepancies.

Introduction

The patterns of the phase behavior of CO_2/hydrocarbon mixtures have been studied previously[1,2] with the aid of the PREOS.[3] In developing a free-energy minimization (FEM) technique for calculating phase diagrams, we[4] found phase diagrams in serious disagreement with several of those published in Refs. 1 and 2. We were unable to trace the errors in the algorithm used by Sahimi *et al.* for the calculations reported in Refs. 1 and 2. Consequently, we wrote a new computer code based on Sahimi *et al.*'s method and recomputed the questionable phase diagrams. The results were phase diagrams in full agreement with those obtained by FEM[4] and in disagreement with those published in Refs. 1 and 2. This means that the computational method of Sahimi *et al.* is correct but that some error or errors in the original code or in its implementation led to incorrect phase diagrams.

The purpose of this paper is to present corrections to the phase diagrams in Refs. 1 and 2. A brief description of the methods is also given. A more extensive discussion of the FEM technique and its application is given in Ref. 4.

Computational Methods

The PREOS, Helmholtz free-energy density, and chemical potential for component i are as follows.

Pressure.

$$p=\frac{nkT}{1-nb}-\frac{n^2a(T)}{1+2nb-(nb)^2}. \quad (1)$$

Helmholtz free-energy density.

$$f=\sum_i n_i\mu_{ci}{}^+(T)+kT\sum_i n_i \ln n_i-nkT\ln(1-nb)$$
$$-\frac{a(T)n}{2\sqrt{2}b}\ln\left[\frac{1+nb(1+\sqrt{2})}{1+nb(1-\sqrt{2})}\right]. \quad (2)$$

Chemical potential.

$$\mu_{ci}=\mu_{ci}{}^+(T)+kT\ln\left(\frac{n_i}{1-nb}\right)+\frac{nkTb_i}{1-nb}-\frac{a(T)nb_i}{b[1+2nb-(nb)^2]}$$
$$-\left\{\frac{1}{2\sqrt{2}bn}\frac{\partial}{\partial n_i}[n^2a(T)]-\frac{a(T)b_i}{2\sqrt{2}b^2}\right\}\ln\left[\frac{1+nb(1+\sqrt{2})}{1+nb(1-\sqrt{2})}\right]. \quad (3)$$

In Eqs. 1 through 3, k=Boltzmann's constant, T=absolute temperature, $\mu_{ci}{}^+(T)$=chemical potential datum that drops out of phase-behavior diagram calculations, n_i=number density of Component i, $n=\Sigma_i n_i$=the total number density, b=excluded volume function given by

$$b=\sum_i x_i b_i, \quad (4)$$

and a=interaction energy function given by

$$a(T)=\sum_{i,j} x_i x_j a_{ij}(T), \quad (5)$$

where x_i=mole fraction of Component i ($x_i=n_i/n$). Values of the composition-independent parameters of the model, b_i and a_{ij}, are given by Sahimi *et al.* for the systems of interest here.

Sahimi *et al.* calculated two-phase equilibria from the equations of thermodynamic equilibrium at constant temperature,

$$\mu_{ci}(\mathbf{n}^\alpha)=\mu_{ci}(\mathbf{n}^\beta) \quad (6)$$

for each component, and

$$p(\mathbf{n}^\alpha)=p(\mathbf{n}^\beta), \quad (7)$$

where $\mathbf{n}^\alpha$=the set $\{n_1^\alpha, n_2^\alpha \ldots\}$ of component densities in Phase α. These nonlinear equations are solved by Newton's method aided by relaxation and zero-order continuation in thermodynamic parameters to move from one state to another. According to the phase rule, when there are C components there are C degrees of freedom in a two-phase system; i.e., C-intensive variables must be fixed to specify the system fully. For three-phase equilibria, the equations $\mu_{ci}(\mathbf{n}^\beta)=\mu_{ci}(\mathbf{n}^\gamma)$ and $p(\mathbf{n}^\beta)=p(\mathbf{n}^\gamma)$ must be added to Eqs. 6 and 7, and there are only $C-1$ degrees of freedom. The protocol of fixing the degrees of freedom and application of relaxation and continuation in Newton's method to compute the phase diagrams from the equilibrium equations is outlined by Sahimi *et al.*

The FEM approach for calculating phase diagrams is based on a stability analysis of the Gibbs free energy[5] and is similar to a method proposed by Michelsen.[6,7] In this method, the molar Gibbs free energy, G, is expressed as an explicit function of temperature, pressure, and the set $\mathbf{x}=\{x_i, x_2 \ldots\}$. This is done by solving the PREOS's for density as a function of T, p, and mole fractions $\mathbf{x}$. Because the PREOS is cubic in the density n, three different Gibbs functions may result. In such a case, one of the functions corresponds to mechanically unstable fluid and is not used in the calculations. The other two are used to define the Gibbs support function

$$D(\mathbf{x};\mathbf{z},T,p)=G(\mathbf{x},p,T)-\sum_i x_i\mu_{ci}(\mathbf{z},T,p), \quad (8)$$

where $\mathbf{z}$=mole fractions of a reference homogeneous phase. At a fixed temperature and pressure, the phase of composition $\mathbf{z}$ is globally stable if

$$D(\mathbf{x};\mathbf{z},T,p)\geq 0 \text{ for all } \mathbf{x}. \quad (9)$$

Starting with an initially assumed $\mathbf{z}$, one iteratively uses the condition in Eq. 9 to find coexistence compositions $\mathbf{x}^\alpha, \mathbf{x}^\beta \ldots$ such that Eq. 9 is satisfied and $\mathbf{z}$ lies along a tie-line (two coexistent phases) or in a tie-triangle (three coexistent phases) in ternary systems.

Phase Diagrams

We identified and recomputed all the erroneous phase diagrams that appear in Refs. 1 and 2 (see **Figs. 1 through 7**).

As stated earlier, we validated these phase diagrams by determining that both methods of calculation give the same results. The

*Now with Bloomsburg U.

Copyright 1991 Society of Petroleum Engineers

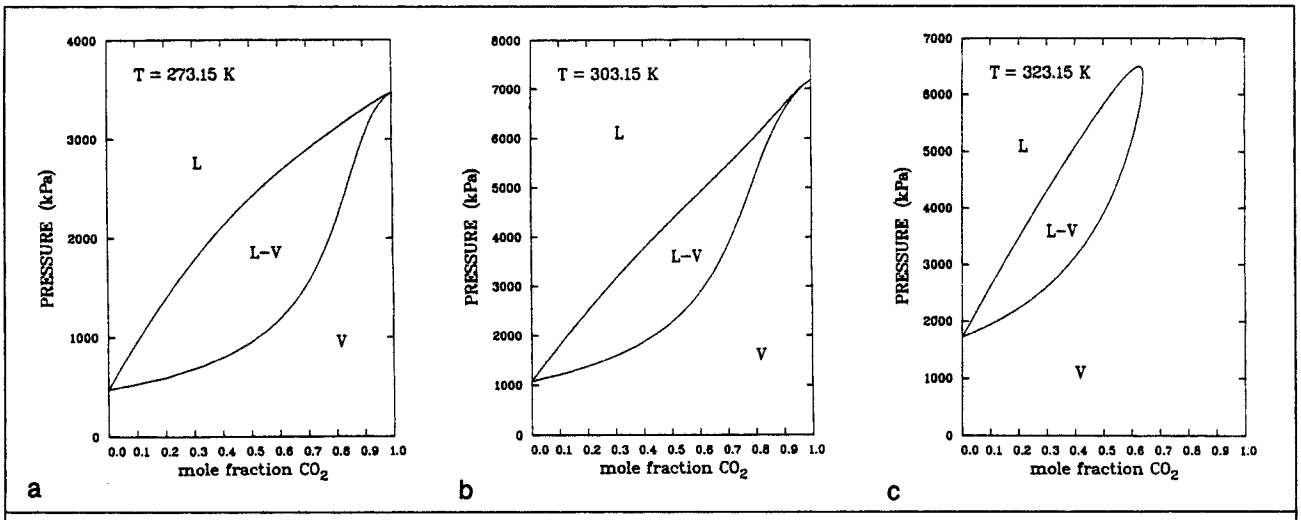


Fig. 1—Liquid/vapor binodals of CO_2/propane mixtures at (a) 273.15 K, (b) 303.15 K, and (c) 323.15 K. To replace Fig. 6 of Ref. 1.

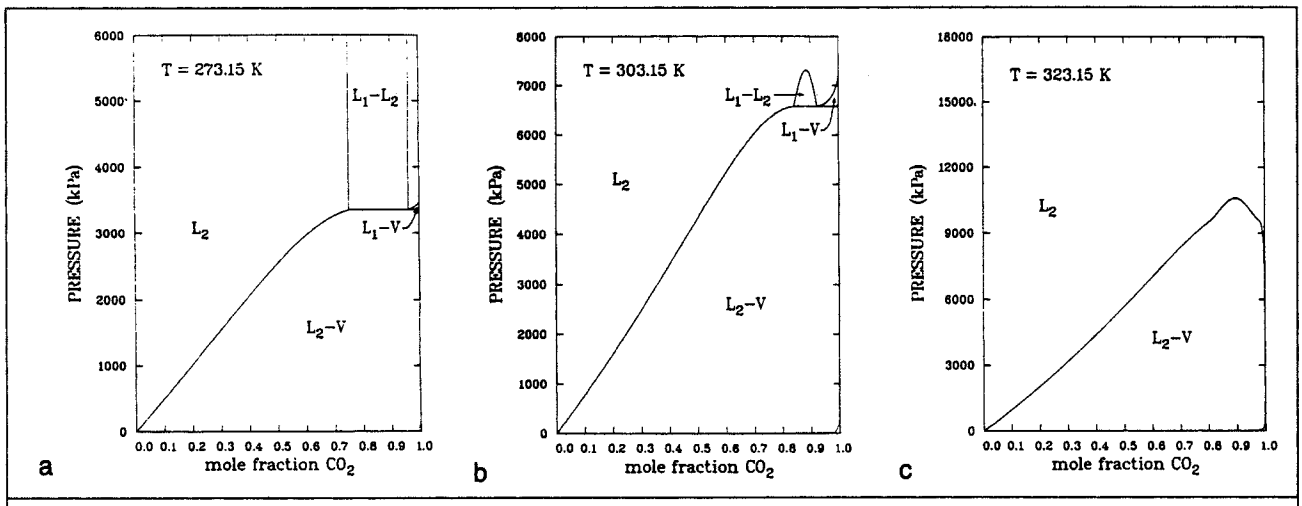


Fig. 2—Phase diagrams of CO_2/decane mixtures at (a) 273.15 K, (b) 303.15 K, and (c) 323.15 K showing liquid/vapor (L_1/V, L_2/V), liquid/liquid (L_1/L_2), and liquid/liquid/vapor (L_1/L_2/V) equilibria. To replace Fig. 8 of Ref. 1.

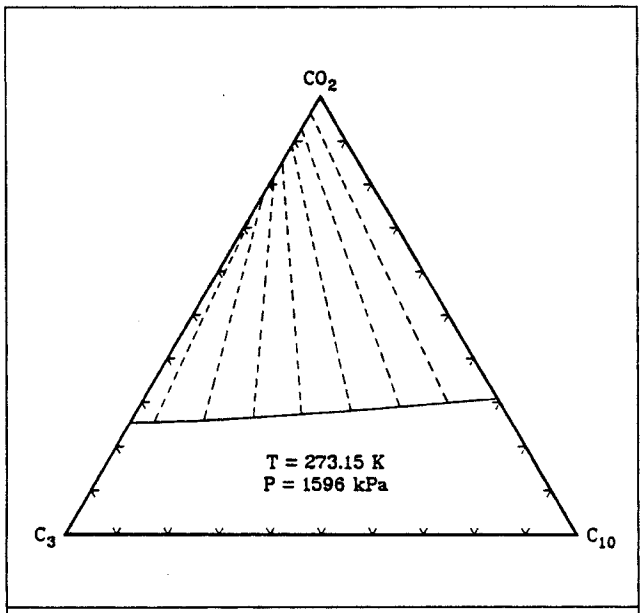


Fig. 3—CO_2/propane/decane at 1596 kPa and 273.15 K. To replace Fig. 12 of Ref. 1.

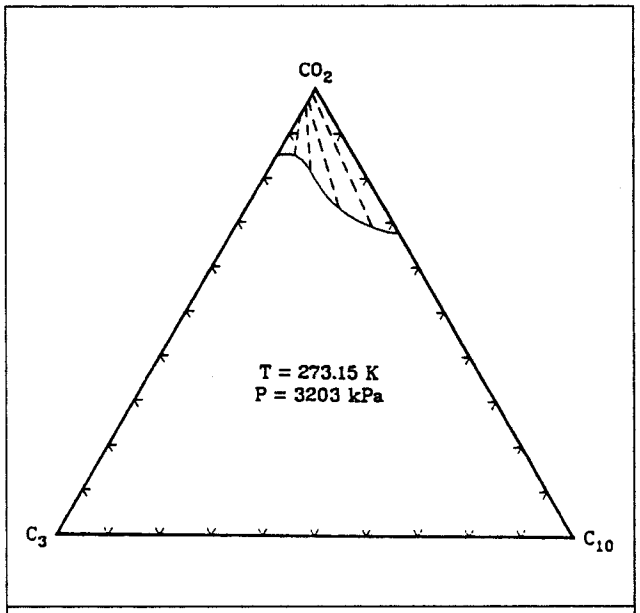


Fig. 4—CO_2/propane/decane at 3203 kPa and 273.15 K. To replace Fig. 13 of Ref. 1.

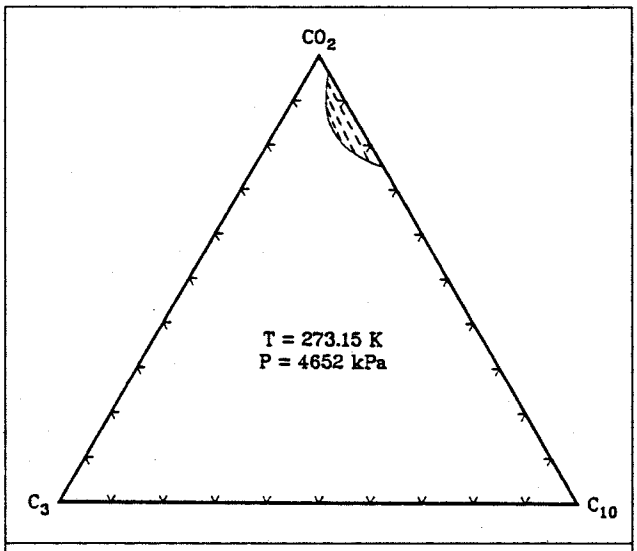


Fig. 5—CO_2/propane/decane at 4652 kPa and 273.15 K. To replace Fig. 14 of Ref. 1.

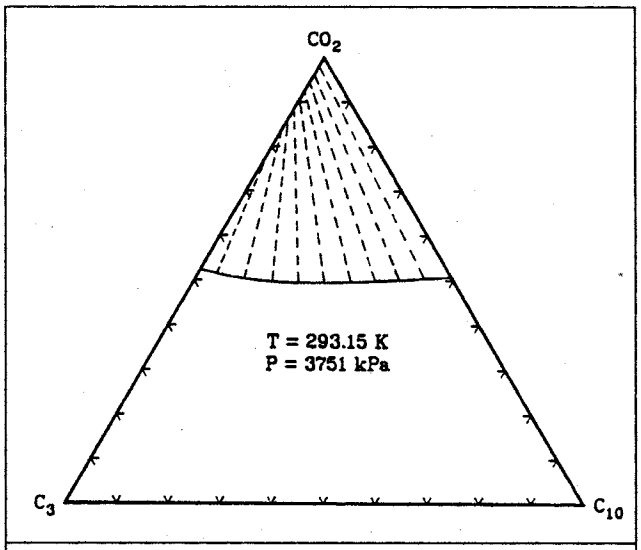


Fig. 6—CO_2/propane/decane at 3751 kPa and 293.15 K. To replace Fig. 15 of Ref. 1.

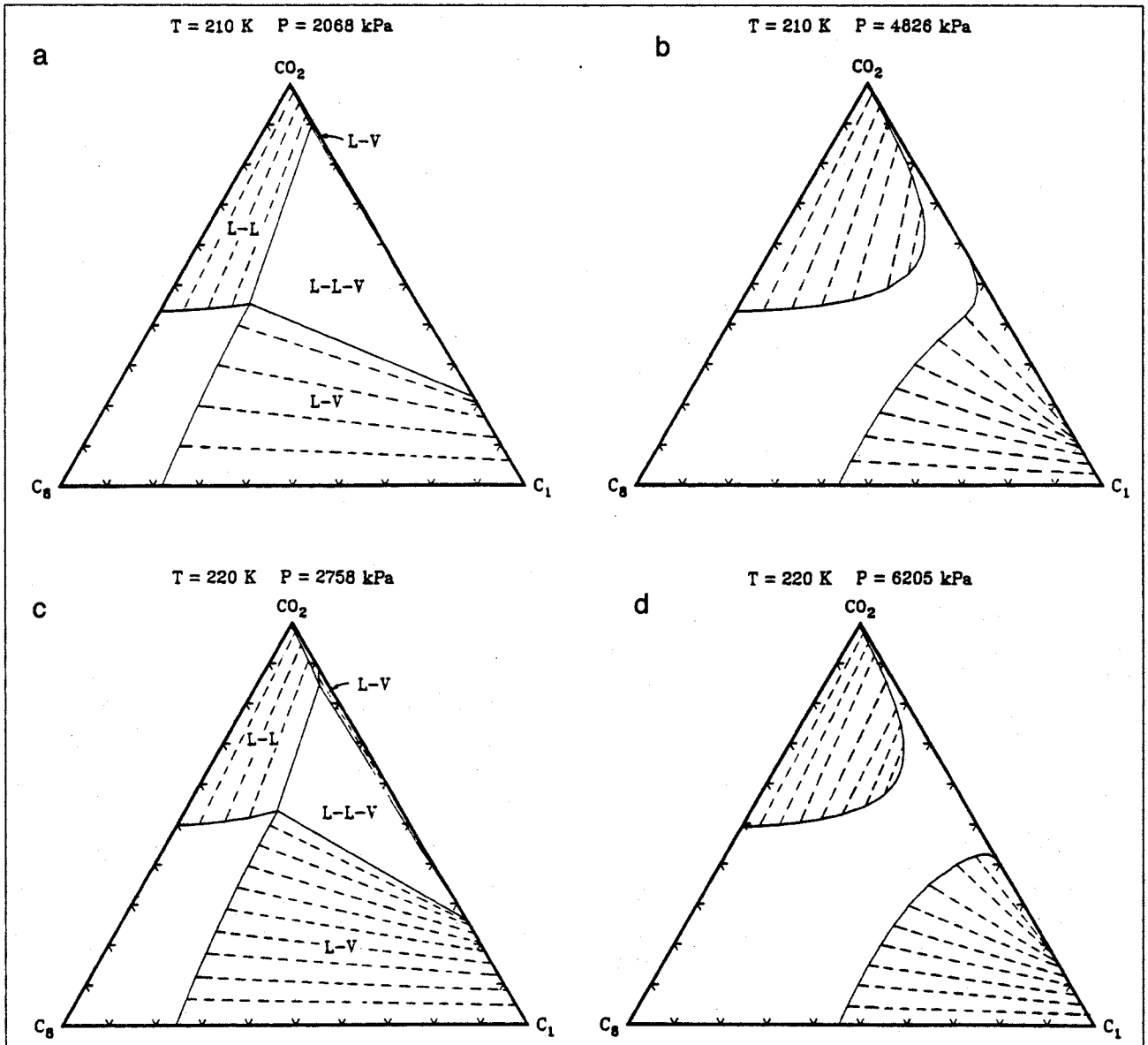
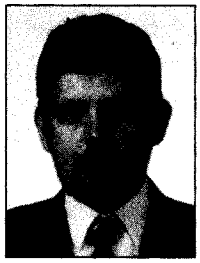


Fig. 7—CO_2/methane/octane at 210 and 220 K. To replace the Peng-Robinson model predictions in Fig. 9 of Ref. 2.

Authors



Davis Quiñones-Cisneros Scriven

Sergio E. Quiñones-Cisneros is a doctoral candidate in mechanics in the Aerospace Engineering and Mechanics Dept. at the U. of Minnesota in Minneapolis with research interests in phase behavior, particularly critical behavior. He holds an MS degree in chemical engineering from the U. of Minnesota. **Mariana B. Blackburn,** assistant professor of analytical chemistry at Bloomsburg U. in Bloomsburg, PA, has research interests in chemometrics, including the application of multivariate statistics to quantitative FT-IR spectroscopy and the theory of multicomponent calibration and analysis. She holds a PhD degree. (Photo unavailable.) **L.E. Scriven** is a professor in the Dept. of Chemical Engineering & Materials Science at the U. of Minnesota. His research interests include multiphase flow in porous media, oil recovery technology, and EOR methods. He holds a PhD degree in chemical engineering from the U. of Delaware. **H.T. Davis,** also a professor in the Dept. of Chemical Engineering & Materials Science at the U. of Minnesota, has research interests in multiphase flow in porous media, oil recovery technology, and EOR methods. He holds a PhD degree in chemical physics from the U. of Chicago.

diagrams for which those presented here are corrections are identified in the figure captions. The code used in calculating phase diagrams by the FEM method (Eq. 9) is available in Ref. 4. The code based on the equilibrium method (EM) (Eqs. 6 and 7) is available in an internal technical report.[8] In **Table 1**, we present a comparison of the results of the two codes. The parameters used in the calculations were chosen to match those used by Sahimi *et al.* There are more recent values of these parameters that are very slightly different from the ones they used, but these small differences have little effect on the results and are not the point of this paper. The fact that the independently developed codes implementing the two methods agree to at least six decimal places is the point. All the phase diagrams reported here were in similar agreement. The FEM calculations were done on a 512K Macintosh computer and the EM ones on an IBM XT computer.

Because we were unable to find the source of the errors in computation of the original phase diagrams or to determine any systematic pattern of error, we feel a comparative discussion of the original diagrams and those given below is meaningless.

TABLE 1—COMPARISON OF LIQUID/VAPOR COEXISTENCE COMPOSITIONS FOR A PROPANE/CO_2 MIXTURE AT 323.15 K

Pressure (MPa)	Mole Fraction CO_2			
	Liquid Phase		Vapor Phase	
	FEM	EM	FEM	EM
2.0	0.03077084	0.03077086	0.1197076	0.1197077
3.0	0.1439210	0.1439210	0.3762908	0.3762909
4.0	0.2624077	0.2624078	0.5090701	0.5090701
5.0	0.3883428	0.3883429	0.5887129	0.5887129
6.0	0.5265907	0.5265907	0.6361932	0.6361433
6.4950	0.6201939	0.6201940	0.6304512	0.6304511

Parameters Used in Calculations

	Propane	CO_2
T_c, K	369.8	304.26
P_c, MPa	4.250	7.376
ω_a	0.152	0.225
δ_{12}	0.124	

FEM = results of FEM method. EM = results of the equilibrium method of Sahimi *et al.* 1 atm = 1.01325 bar and R = 83.14 cm^3-bar/gmol-K.

Nomenclature

$a = \Sigma_{i,j} x_i x_j a_{ij}$
a_{ij} = intermolecular energy parameter
$b = \Sigma_i x_i b_i$
b_i = molecular volume parameter
C = number of molecular components in solution
D = Gibbs support function
f = Helmholtz free-energy density
G = Gibbs free energy
i = molecular component index
j = molecular component index
k = Boltzmann's constant
$n = \Sigma_i \rho_i$
n_i = number density of Component i
$\mathbf{n}^{\alpha}$ = set of component densities in Phase 2
p = pressure
p_c = critical pressure
T = absolute temperature
T_c = critical temperature
x_i = mole fraction of Component i
$\mathbf{x}$ = set of mole fractions
$\mathbf{z}$ = set of mole fractions
α = Phase α
β = Phase β
γ = Phase γ
δ_{12} = mixing parameter $= a_{12}/\sqrt{a_{11}a_{22}}$
μ_{ci} = chemical potential of Component i
$\mu_{ci}^{+}(T)$ = chemical potential datum of Component i
ω_a = acentric factor

Acknowledgment

The U.S. DOE provided financial support for the research reported here through DOE Project No. DOE-DE-AC19-85BC10842.

References

1. Sahimi, M., Davis, H.T., and Scriven, L.E.: "Thermodynamic Modeling of Phase and Tension Behavior of CO_2/Hydrocarbon Systems," *SPEJ* (April 1985) 235-54.
2. Kuan, D.Y. *et al.*: "Multicomponent CO_2/Water/Hydrocarbon Phase Behavior Modeling: A Comparative Study," *SPERE* (Jan. 1986) 61-72.
3. Peng, D. and Robinson, D.B.: "A New Two-Constant Equation of State," *Ind. & Eng. Chem. Fund.* (1976) **15**, 59-64.
4. Quiñones-Cisneros, S.E.: "Fluid Phase Equilibria from Minimization of the Free Energy," MS thesis, U. of Minnesota, Minneapolis, MN (Nov. 1987).
5. Baker, L.E., Pierce, A.C., and Luks, K.D.: "Gibbs Energy Analysis of Phase Equilibria," *SPEJ* (Oct. 1982) 731-42.
6. Michelsen, M.L.: "The Isothermal Flash Problem. Part I. Stability," *Fluid Phase Equilibria* (1982) **9**, 1-19.
7. Michelsen, M.L.: "The Isothermal Flash Problem. Part II. Phase-Split Calculation," *Fluid Phase Equilibria* (1982) **9**, 21-40.
8. Blackburn, M.B.: "Pascal Code for Computing Phase Diagrams for a Peng-Robinson Fluid," technical report, Dept. of Chemical Engineering & Materials Science, U. of Minnesota, Minneapolis, MN (1988).

SI Metric Conversion Factors

°F (°F+459.67)/1.8 = K
psi × 6.894 757 E+00 = kPa

SPERE

Original SPE manuscript received for review June 27, 1988. Paper (SPE 18584) accepted for publication July 25, 1990. Revised manuscript received April 30, 1990.