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A Simple Perturbation Term for the Carnahan-Starling Equation of State

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Abstract

A simple perturbation term is presented for the Carnahan-Starling (CS) hard-sphere reference equation of state (EOS). This perturbed CS EOS is compared with seven other two-parameter equations of state; it represents the critical isotherms of eight fluids with the lowest deviations in density and pressure. After a generalized temperature dependence is introduced for parameters a and b, the perturbed CS EOS is compared to the well-known Peng-Robinson equation. For nine nonpolar pure fluids, the perturbed CS EOS represents liquid densities significantly better, but it is not superior for vapor pressures. For mixtures, the CS reference term is given by the Boublik-Mansoori hard-sphere mixture EOS. Some calculations for binary mixtures are given, using conventional mixing rules for parameters a and b in the simple perturbation term.

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Introduction

Following the Ornstein-Zernike formulation for describing the equilibrium properties of fluids, much attention has been given toward developing a theoretical equation of state. For standard chemical engineering purposes, the most significant result of that attention is the Carnahan-Starling equation of state for hard spheres (Carnahan and Starling, 1969) and its extension to mixtures by Boublik (1971) and Mansoori (Mansoori et al., 1971).

For application to real fluids, it is necessary to add a perturbation term to the equation of Carnahan and Starling. Nearly 20 years ago, Carnahan and Starling (1972) suggested two perturbation terms: first, the perturbation term used by van der Waals in 1873 and second, the perturbation term used by Redlich and Kwong in 1949. These were obvious choices only because they were readily available; little effort was made to test their significance or applicability.

Following Carnahan and Starling's 1972 paper, perturbations were proposed by several chemical-engineering-oriented authors (Beret and Prausnitz 1975, Chen and Kreglewski 1977, Donohue and Prausnitz 1978, Oellrich et al. 1978, Johnston and Eckert 1981, Brandani and Prausnitz 1981, Johnston et al. 1982, Wong and Prausnitz 1985, Lee et al. 1985, Cotterman et al. 1986, Grenzheuser and Gmehling 1986, Nezbeda and Aim 1987, Wogatzki 1988, Pfennig 1989, Mulia and Yesavage 1989). In this work, we present a perturbation term which has a simple density dependence and does not introduce any new adjustable parameters beyond those commonly used in typical chemical-engineering calculations.

Our motivation for finding a simple but reasonable perturbation term follows from our belief that, despite its limited empirical success so far, the Carnahan-

Starling equation provides a better basis for development of a broadly applicable equation of state than does the popular hard-sphere reference equation used by van der Waals, Redlich-Kwong, Peng-Robinson and many others. These common equations have been remarkably successful for numerous (mostly hydrocarbon) vapor-liquid equilibrium calculations required in the natural-gas and petroleum industries but their extension to more complex systems has encountered severe difficulties.

Our particular interest is directed at developing an equation of state that may be used for three-phase (LLV) equilibria in asymmetric systems containing one highly polar component (e.g. water), one or more highly volatile components (e.g. hydrogen) and one or more heavy hydrocarbons (Dohrn and Brunner, 1987 and 1988). Toward that end, we make use of the hard-sphere-with-dipole reference EOS, proposed by Bryan (1987); we shall report on that work elsewhere (Dohrn and Prausnitz, 1990). As part of that work, however, we require a useful perturbation term for the CS reference EOS as described here.

Following van der Waals, it is useful to divide compressibility factor Z into a reference term and a perturbation term:

$$Z = Z_{ref} + Z_{pert} \tag{1}$$

For relatively simple fluids, Z_{ref} is a function of (v/b), where v is the molar volume and b is a molar molecular-size parameter which may depend on temperature. Nearly 120 years ago, van der Waals proposed that

$$Z_{ref}^{vdW} = \frac{v}{v - b} \tag{2}$$

and that proposal has dominated most equation-of-state work in the chemical-engineering community. Equation (2) has theoretical validity only at low densities,

as pointed out by van der Waals many years ago. For application to higher densities, attempts to correct Equation (2) were reported already early in this century.

Following the theoretical work of Percus and Yevick, who solved the Ornstein-Zernike equation for hard spheres, Carnahan and Starling (1969) proposed that

$$Z_{ref}^{CS} = \frac{1 + \eta + \eta^2 - \eta^3}{(1-\eta)^3} \tag{3}$$

where $\eta = b\rho/4$ and molar density $\rho = 1/v$.

For many practical purposes, Equation (2) is satisfactory; because of its algebraic simplicity, Equation (2) is used extensively. From a theoretical point of view, Equation (3) is far superior.

Calculation of critical isotherms

To describe the properties of a real fluid, it is necessary to add a perturbation to Equation (3). To find a simple but reasonable perturbation term, we used experimental data for the critical isotherms of several fluids (methane, ethane, propane, n-butane, carbon dioxide and argon) for pressures to 35 MPa.

A general form for the perturbation is

$$Z_{pert} = -\frac{4a}{RTb}\eta\Psi \tag{4}$$

where a is a molecular parameter reflecting intermolecular attractive forces and Ψ is a correction function that depends on reduced density η such that $\Psi \rightarrow 1$ as $\eta \rightarrow 0$. We find that a fair representation of the critical isotherm is obtained with

$$\Psi = 1 - 1.41\eta + 5.07\eta^2 \tag{5}$$

Unlike the Ψ proposed by Wogatzki (1988), Equation (5) first falls with rising η and then rises monotonically. For nonpolar fluids, our proposed equation of state is

$$\boxed{Z = \frac{1 + \eta + \eta^2 - \eta^3}{(1-\eta)^3} - \frac{4\,a}{RTb}\,\eta\,(1 - 1.41\eta + 5.07\eta^2)} \tag{6}$$

where, however, parameters a and b may depend on temperature.

Using the well-known criteria of the critical point,

$$\left(\frac{\partial P}{\partial v}\right)_T = 0 \qquad \left(\frac{\partial^2 P}{\partial v^2}\right)_T = 0 \tag{7}$$

we obtain parameters a_c and b_c at the critical temperature

$$a_c = \Omega_a R^2 T_c^2 / P_c \tag{8}$$

$$b_c = \Omega_b R T_c / P_c \tag{9}$$

where Ω_a and Ω_b are constants, specific for each equation of state, as shown in Table 1. Ω_a and Ω_b have a strong influence on the critical compressibility Z_c, so that the number of significant figures for Ω_a and Ω_b can lead to a significant change of Z_c.

Table 1 shows Equation (6) and several other two-parameter equations of state. The reference terms are either the Carnahan-Starling Z^{CS} or the van der Waals Z^{vdW} [Equations (3) or (2)]. The perturbation terms are expressed by correction function Ψ in Equation (4). Critical compressibilities Z_c were calculated with constants Ω_a and Ω_b as given in Table 1. Equation (6) and the Carnahan-Starling(CS)-Peng-Robinson equation have the smallest critical compressibilities Z_c. Many equations of state with

a Carnahan-Starling reference term have values of Z_c that lie between 0.34 and 0.36. For most fluids, experimental critical compressibilities are smaller than 0.3.

To illustrate the performances of different EOS, Fiqure 1 shows calculated and observed critical isotherms for n-butane; the experimental data are by Haynes and Goodwin (1982). The experimental data are not well-represented by any of the equations of state but best by Equation (6). At high pressure, the CS-van der Waals equation predicts densities that are much too small, while the CS-Peng-Robinson equation predicts densities that are much too high.

Since small differences in the critical temperature and the critical pressure can have a significant influence on calculated critical isotherms, Table 2 presents the values of T_c and P_c used in this study. Table 3 gives relative deviations between calculated and experimental molar densities. Experimental data were taken from Angus et al. (1971, 1976, 1978, 1979, 1980), Goodwin et al. (1976 and 1982) and Haynes and Goodwin (1982). For all fluids shown, Equation (6) gives the smallest deviations; the Peng-Robinson equation is second best. It is surprising that newer equations, like the Mulia-Yesavage equation, do not perform better than the CS-Redlich-Kwong-Soave equation. Due to large deviations at higher pressures, the CS-Peng-Robinson equation is worse than the CS-van der Waals equation. Close to the critical point, where isotherms in a pressure-density diagram are very flat, density deviations provide a sensitive means to detect deviations from experiment. In this region, pressure deviations are small for all equations of state, since they were forced to reproduce the critical pressure. However, in steep parts of the critical isotherms, i.e. at high densities. pressure deviations provide a good way to describe the performance of an EOS. Table 4 gives pressure deviations for eight fluids and seven

EOS. Equation (6) shows the smallest deviations; the CS-van der Waals equation shows the largest deviations.

Temperature dependence of parameters a and b

Using experimental density and vapor-pressure data, the effect of temperature on a and on b is given by

$$\frac{a}{a_c} = a^{(1)} \tanh\left(a^{(2)} \left|T_R - 1\right|^{0.7}\right) + 1 \tag{10}$$

$$\frac{b}{b_c} = b^{(1)} \tanh\left(b^{(2)} \left|\ln T_R\right|^{0.8}\right) + 1 \tag{11}$$

where $T_R = T/T_c$. The coefficients are related to acentric factor ω by

$$a^{(1)} = 0.367845 + 0.055966\,\omega \tag{12}$$

$$a^{(2)} = (-1)^m (0.604709 - 0.008477\,\omega) \tag{13}$$

$$b^{(1)} = 0.356983 - 0.190003\,\omega \tag{14}$$

$$b^{(2)} = (-1)^m (1.37 - 1.898981\,\omega) \tag{15}$$

$$m = 0 \quad \text{for } T_R < 1 \qquad \text{and} \qquad m = 1 \quad \text{for } T_R \geq 1 \tag{16}$$

The acentric factors used in this work are given in Table 2. Equations (10) and (11) show no discontinuities in their derivatives with respect to T_R when $T_R = 1$. The coefficients in Equations (12) - (15) were determined with an optimization routine (Pfennig, 1989) by fitting vapor pressures and densities of 13 fluids (more than 2500 data points). For nine fluids, Table 5 shows deviations for molar densities and vapor pressures calculated with the new equation of state and with the Peng-Robinson equation. Equation (6) reduces the liquid-density deviations by a factor of three to four. However, the Peng-Robinson equation gives slightly better vapor pressures for most of the fluids.

Figure 2 shows the temperature dependence of parameters a and b for methane and for n-octane. At low and high temperatures, parameter a does not change significantly with rising or falling temperature. The steepest slope of the curve is at the critical point (T_R=1). For parameter a, the curves for methane and for n-octane lie close together, while for parameter b, the curves differ significantly from each other. The large effect of acentric factor on the temperature dependence of b follows from our objective function which gives emphasis to liquid-density data. Liquid densities are highly sensitive to b.

Figure 3 presents experimental and calculated liquid densities for propane at 140, 240 and 340 K. The deviations of Equation (6) [coupled with Eqs. (10) - (16)] are much smaller than those for the Peng-Robinson equation.

Mixtures

For the reference term of a mixture, we use the Boublik-Mansoori equation (Boublik, 1971, Mansoori et al. 1971) as discussed by Dimitrelis (1986). For a mixture of N components

$$Z_{ref} = \frac{1 + (3\frac{DE}{F} - 2)\eta + (3\frac{E^3}{F^2} - 3\frac{DE}{F} + 1)\eta^2 - \frac{E^3}{F^2}\eta^3}{(1-\eta)^3} \tag{17}$$

with

$$D = \sum_i^N \xi_i \sigma_i \qquad E = \sum_i^N \xi_i \sigma_i^2 \qquad F = \sum_i^N \xi_i \sigma_i^3 \tag{18}$$

and

$$\sigma_i = \left(\frac{3}{2}\frac{b_i}{\pi N_A}\right)^{1/3} \qquad \eta = \frac{1}{6}\pi N_A F \rho \tag{19}$$

where N_A is Avogadro's number and ζ_i is the mole fraction of component i. The perturbation term of the compressibility factor for mixtures is

$$Z_{pert} = -\frac{4\, a_M}{RTb_M}\eta\,(1 - 1.41\eta + 5.07\eta^2) \tag{20}$$

where a_M and b_M are parameters a and b for the mixture. For mixtures of nonpolar fluids, we use the conventional one-fluid mixing rules:

$$a_M = \sum_i^N \sum_j^N \xi_i\, \xi_j\, a_{ij} \qquad a_{ij} = \sqrt{a_{ii}\, a_{jj}}\,\frac{\sqrt{b_i\, b_j}}{b_{ij}}\left(1 - k_{ij}\right) \tag{21}$$

$$b_M = \sum_i^N \sum_j^N \xi_i\, \xi_j\, b_{ij} \tag{22}$$

where k_{ij} is a binary interaction parameter. When $b_{ij}=0.5(b_i+b_j)$, b_M in the perturbation term is linear in mole fraction; in that event, η has the same value for the reference term and the perturbation term [Equation (19)]. It is important to note that the one-fluid assumption has been made here only for the perturbation term. The reference term is not based on a one-fluid assumption.

To illustrate the applicability of Equations (17) - (22), using $b_{ij}=0.5(b_i+b_j)$, we present some results for the system hydrogen - n-hexane. This system is of interest to us here because of its high asymmetry and because data are available for both phase compositions and densities (Nichols et al., 1957). To determine the pure-component parameters for hydrogen, "classical" values for T_c, and ω were used (T_c = 43.6 K, P_c = 2.05 MPa, and ω = 0) (Prausnitz et al., 1986). The properties of pure hydrogen are well described by Equations (6) and (10) - (16) for temperatures higher than 100 K.

Figure 4 shows a pressure-composition diagram for the hydrogen - n-hexane system at 277.59 K (k_{12} = 0.355), 377.59 K (k_{12} = 0.349) and 477.59 K (k_{12} = 0.444). For 277.59 and 377.59 K, agreement with experiment is very good; for 477.59 K, agreement is only fair, but better than that for the other equations of state. Table 6 compares results using the Peng-Robinson equation, the Redlich-Kwong-Soave equation and Equations (17) - (22). The interaction parameters of the new equation are smaller and the temperature dependence of k_{12} for Equations (17) - (22) is weaker than those for the other EOS. The phase compositions as well as molar densities are best represented by Equation (6).

Phase-compostion and density data are also availabe for the carbon dioxide - n-butane system (Kalra et al., 1976; Hsu et al., 1985). Figure 5 shows a pressure-composition diagram for 255.98 K (k_{12} = 0.197), 319.26 K (k_{12} = 0.195) and 377.59 K (k_{12} = 0.211). Agreement with experiment is good. Results using the Peng-Robinson EOS, the Redlich-Kwong-Soave EOS and Equations (17) - (22) are compared in Table 7. For all EOS, agreement with experimental data is good; for this system, the proposed perturbed CS equation is better only for liquid densities. For both systems, used in this study, the deviations of the liquid-phase densities of the Redlich-Kwong-Soave equation are more than four times larger than those of the proposed perturbed CS equation.

Phase-equilibrium calculations were performed with a flash program developed at the Technische Universität Hamburg-Harburg (Dohrn and Brunner, 1989). An efficient density-finding routine, developed at the University of California, Berkeley, (Topliss, 1985) was integrated into the main program.

Conclusions

A simple perturbation term is proposed for the Carnahan-Starling reference EOS. When applied to pure nonpolar fluids using only conventional parameters, the perturbed CS EOS provides improved liquid densities, but calculated vapor pressures are no better than those from the Peng-Robinson EOS. For mixtures of nonpolar fluids, it appears that the perturbed CS EOS provides better description of densities; however, calculated phase compositions are not necessarily better than those provided by conventional equations of state. Nevertheless, a perturbed CS EOS is of potential interest in chemical engineering because, unlike its essentially empirical competitors, it provides a good basis for extension to more complex mixtures where essentially empirical EOS are unsatisfactory.

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List of Symbols

Symbol	Dimension	
a	kJ m^3/kmol^2	equation of state parameter
$a^{(1)}$	-	constant in Eqs. (10), (12) and (13)
b	m^3/kmol	equation of state parameter
$b^{(1)}$	-	constant in Eqs. (11), (14) and (15)
D	m	molecular size parameter, Eqs. (17) and (18)
E	m	molecular size parameter, Eqs. (17) and (18)
F	m	molecular size parameter, Eqs. (17) - (19)
k_{ij}	-	binary mixture interaction parameter
m	-	exponent, Eqs. (13), (14) and (16)
N	-	number of components
N_A	-	Avogadro's number
P	Pa	pressure
R	J/(mol K)	gas constant, 8314.39 J/(mol K)
T	K	temperature
T_R	-	reduced temperature
v	m^3/kmol	molar volume
Z	-	compressibility factor

Greek letters

Symbol	Dimension	
η	-	reduced density
Ψ	-	correction function, defined in Eqs. (4) and (5)
ρ	kmol/m^3	molar density
σ_i	m	molecular diameter of component i

ξ_i	-	mole fraction in either the liquid or the vapor phase
ω	-	acentric factor
Ω_a	-	constant in Eq. (8)
Ω_b	-	constant in Eq. (9)

Subscripts

M	mixture
c	critical
i	component i
j	component j
pert	perturbation term
ref	reference term

Superscripts

CS	Carnahan-Starling
vdW	van der Waals

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Table 1. Properties of Some Two-Parameter Equations of State at the Critical Temperature

	Z_{ref} Eqs. (1)-(3)	Ψ Eq. (5)	Z_c	Ω_a Eq. (8)	Ω_b Eq. (9)
Equation (6)	Z^{CS}	$1-1.41\eta+5.07\eta^2$	0.298	0.550408	0.187276
CS-van der Waals	Z^{CS}	1	0.366	0.496388	0.187295
CS-Redlich-Kwong	Z^{CS}	$\frac{1}{1+4\eta}$	0.324	0.461883	0.105000
Wong-Prausnitz	Z^{CS}	$\frac{1}{1+0.8\eta}$	0.336	0.480554	0.157866
CS-Peng-Robinson	Z^{CS}	$\frac{1}{1+8\eta-16\eta^2}$	0.273	0.511598	0.097750
Mulia-Yesavage	Z^{CS}	$\frac{1}{1+0.8\eta-1.6\eta^2}$	0.350	0.498966	0.170911
Redlich-Kwong	Z^{vdW}	$\frac{1}{1+4\eta}$	0.327	0.42748	0.08664
Peng-Robinson	Z^{vdW}	$\frac{1}{1+8\eta-16\eta^2}$	0.321	0.45724	0.07780

Table 2. Pure Component Data

	Ar	H_2	H_2*)	N_2	CO_2	CH_4	C_2H_6	C_3H_6
T_c	150.86	33.19	43.60	126.2	304.21	190.56	305.33	365.37
P_c	48.98	13.15	20.50	34.	73.83	45.95	48.71	46.65
ω	0.001	-0.216	0.0	0.039	0.225	0.008	0.099	0.144

	C_3H_8	C_4H_{10}	C_5H_{12}	C_6H_6	C_7H_8	C_8H_{18}	$C_{16}H_{34}$
T_c	369.85	425.16	469.65	562.2	540.3	568.8	722.
P_c	42.48	37.96	33.69	48.9	27.4	24.9	14.1
ω	0.153	0.199	0.251	0.212	0.349	0.398	0.742

*) "Classical" values, used in Equation (6).

Table 3. Average absolute deviations (%) between experimental and calculated densities of critical isotherms for different equations of state.
P = 0 to 35 MPa

	Total	CH_4	C_2H_6	C_3H_6	C_3H_8	C_4H_{10}	CO_2	Ar	N_2
Equation (6)	3.92	3.58	4.16	3.25	4.40	5.36	3.91	2.40	4.29
Peng-Robinson	4.59	4.41	4.91	3.66	4.99	5.93	4.53	3.13	5.17
CS-Redlich-Kwong	5.60	5.30	5.96	4.72	6.16	7.40	4.68	3.77	6.79
Redlich-Kwong	6.12	5.07	7.22	6.36	7.60	9.06	7.16	1.88	4.61
Mulia-Yesavage	8.79	7.43	10.71	8.57	10.86	12.29	10.31	3.17	6.99
Wong-Prausnitz	9.11	7.73	11.08	8.87	11.21	12.61	10.71	3.36	7.32
CS-van der Waals	12.38	11.40	14.66	11.78	14.80	16.23	13.38	5.71	11.06
CS-Peng-Robinson	13.79	17.35	13.66	11.94	13.77	13.37	8.78	12.60	18.84

Table 4. Average absolute deviations (%) between experimental and calculated pressures of critical isotherms for different equations of state. P = 0 to 35 MPa

	Total	CH_4	C_2H_6	C_3H_6	C_3H_8	C_4H_{10}	CO_2	Ar	N_2
Equation (6)	6.48	7.32	5.55	5.16	6.38	7.10	4.41	6.38	9.54
Peng-Robinson	7.37	8.79	6.51	5.87	7.29	7.96	4.36	7.31	10.84
CS-Redlich-Kwong	8.94	10.70	8.33	7.42	9.26	10.13	4.62	8.25	12.79
Redlich-Kwong.	15.42	14.65	17.06	14.68	20.92	23.81	17.77	4.79	9.71
CS-Peng-Robinson	16.05	20.59	15.68	14.09	16.49	16.65	8.39	14.93	21.58
Wong-Prausnitz	22.86	23.51	25.20	21.94	29.59	32.29	24.79	9.15	16.41
Mulia-Yesavage	22.89	23.50	25.24	21.88	29.78	32.68	24.65	9.16	16.20
CS-van der Waals	47.94	51.95	51.84	44.55	59.85	64.88	45.64	24.35	40.47

Table 5. Average absolute deviations (%) between experimental and calculated vapor pressures and molar densities for the new equation and the Peng-Robinson (PR) equation; 215 data points, T_R = 0.5 to 1. P = 0 to 35 MPa

(%)	Deviations					
	Vapor Pressure		Saturated Densities		Liquid Density	
	Eq. (6)	PR	Eq. (6)	PR	Eq. (6)	PR
carbon dioxide	0.57	0.66	2.32	2.75	1.43	3.64
benzene	0.28	0.60	1.99	1.77	0.87	3.14
methane	2.98	1.08	3.39	4.81	0.71	10.63
propane	2.68	0.38	1.48	2.46	1.28	6.18
n-butane	2.34	0.66	2.01	2.79	1.20	5.27
n-pentane	0.67	0.54	1.01	1.40	1.41	3.17
n-heptane	0.72	0.70	0.68	0.57	1.05	1.82
n-octane	0.86	0.40	-	-	0.88	2.33
n-hexadecane	2.79	3.02	-	-	0.56	11.68
Total	1.54	0.89	1.84	2.36	1.04	5.36

Table 6. Root mean square deviations of phase compositions and average absolute deviations of molar densities for the hydrogen - n-hexane system. T = 277.59 to 477.59 K, P = 0 to 42 MPa (Nichols et al., 1957)

	Interaction Parameter k_{12}	Deviations			
		Phase composition, mol%		Density, %	
		liquid	vapor	liquid	vapor
Equation (6)	0.349 ... 0.444	0.755	1.029	1.873	0.948
Peng-Robinson	0.406 ... 0.653	1.452	1.026	2.318	2.497
Redlich-Kwong-Soave	0.348 ... 0.684	1.773	1.656	8.027	1.362

Table 7. Root mean square deviations of phase compositions and average absolute deviations of molar densities for the carbon dioxide - n-butane system. T = 319.26 K, 344.26 K and 377.59 K for densities (Hsu et al., 1985) plus 255.98 K (Kalra et al., 1976) for phase compositions; P = 0 to 7 MPa.

	Interaction Parameter k_{12}	Deviations			
		Phase composition, mol%		Density, %	
		liquid	vapor	liquid	vapor
Equation (6)	0.195 ... 0.211	0.958	1.127	2.791	3.969
Peng-Robinson	0.219 ... 0.235	0.714	0.870	3.453	2.754
Redlich-Kwong-Soave	0.222 ... 0.252	0.729	0.624	12.935	2.823

Captions

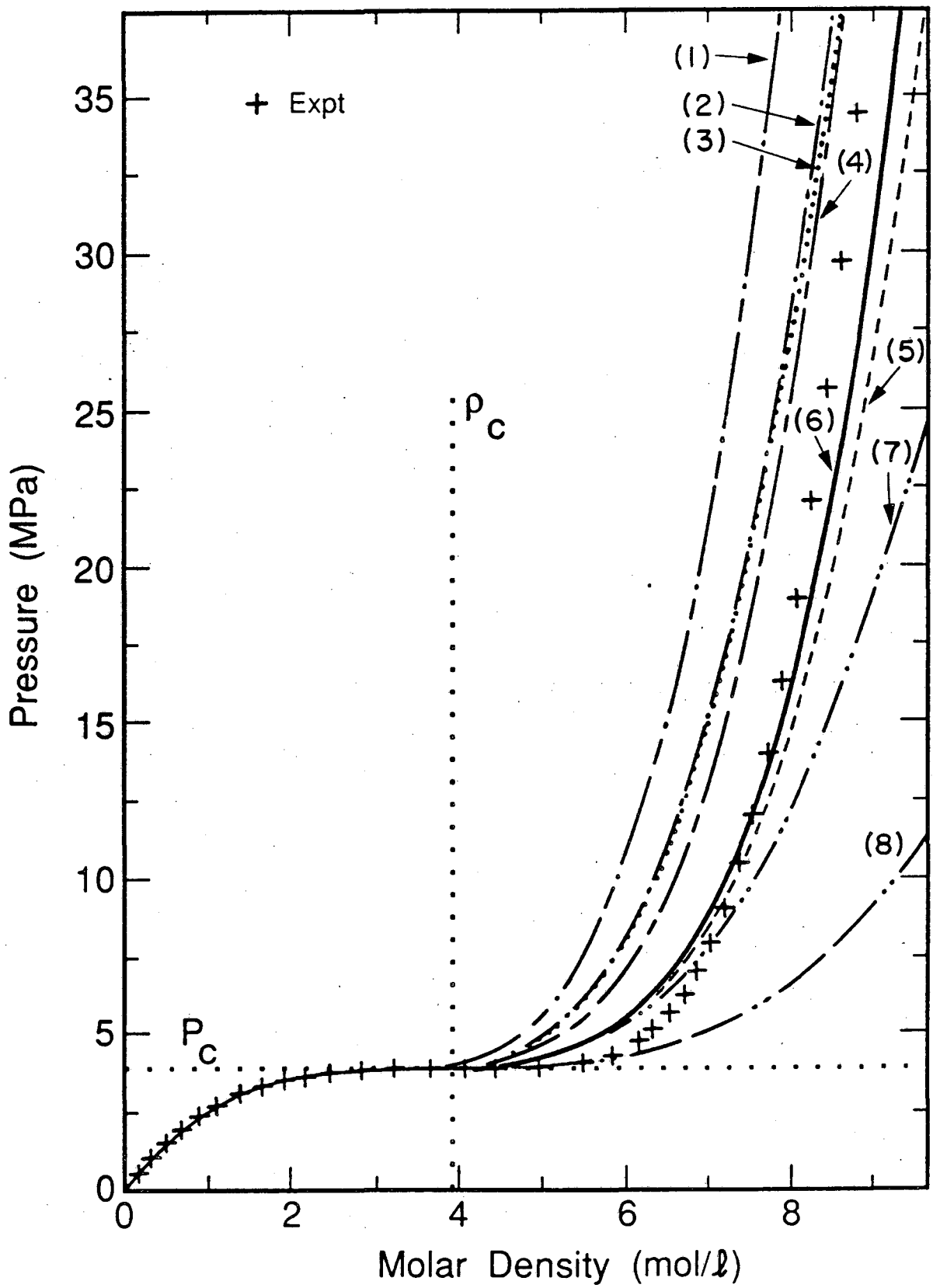
Fig. 1: Critical isotherm of n-butane, T = 425.16 K. + experimental (Haynes and Goodwin, 1982). Calculated results: (1) — – · — – · CS-van der Waals EOS; (2) — · — · Mulia-Yesavage EOS; (3) ····· Wong-Prausnitz EOS; (4) — – — – Redlich-Kwong EOS; (5) - - - - Peng-Robinson EOS; (6) ———— Equation (6); 7) – ·· – ·· CS-Redlich-Kwong EOS; (8) — — ·· — — ·· CS-Peng-Robinson EOS.

Fig. 2: Temperature dependence of parameters a and b for methane and n-octane. Calculated with Eqs. (11), (14) and (15): ——— methane; — · — · n-octane

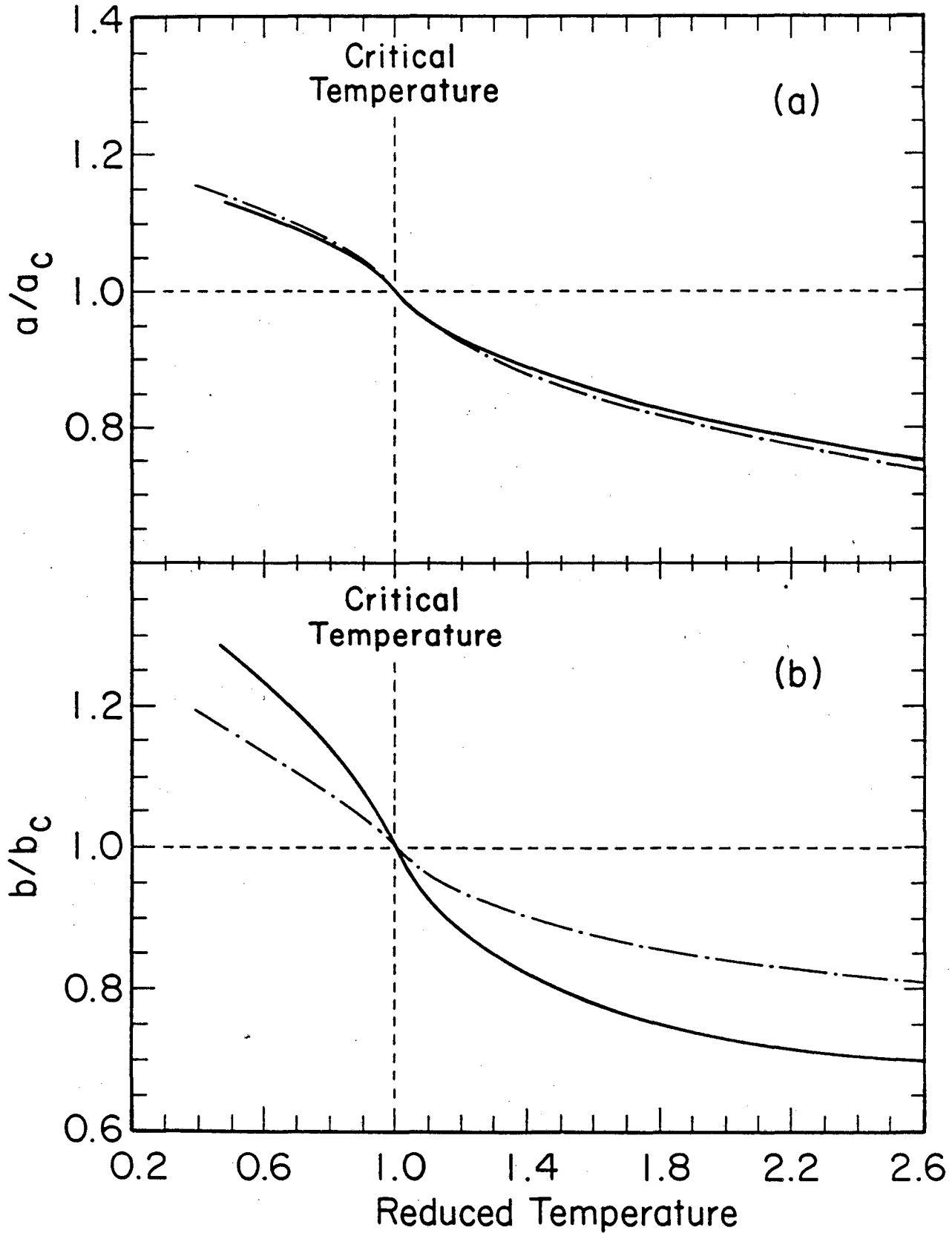
Fig. 3: Reduced liquid densities of propane as a function of reduced temperature. • experimental (Goodwin and Haynes, 1982); (1) 140 K; (2) 240 K; (3) 340 K; ——— calculated with Equation (6); - - - - calculated with the Peng-Robinson EOS.

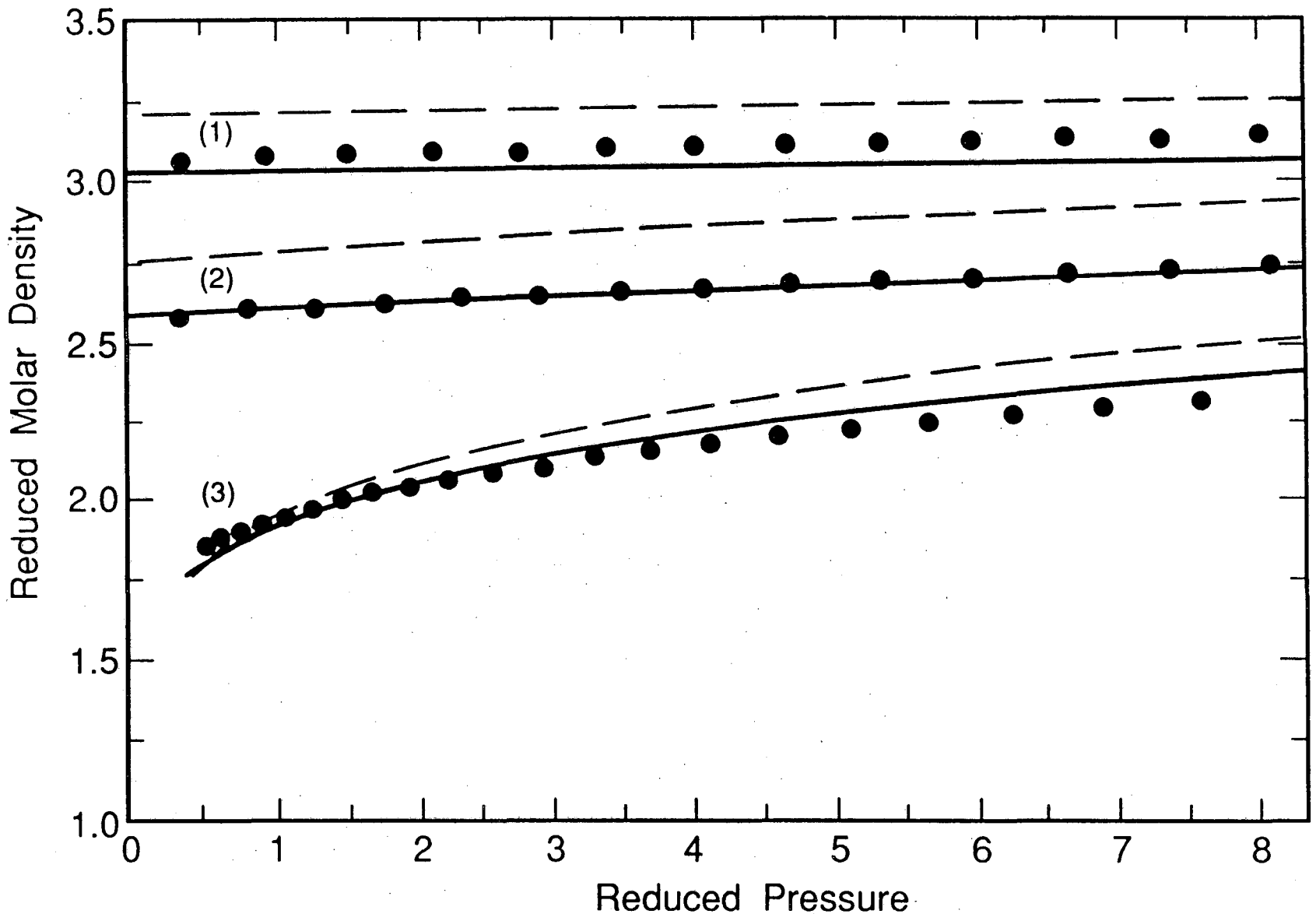
Fig. 4: Pressure-composition diagram for the system hydrogen - n-hexane. • experimental (Nichols et al., 1957); (1) 277.59 K; (2) 377.59 K; (3) 477.59 K; ——— calculated with the new equation [Eqs. (17) - (22)].

Fig. 5: Pressure-composition diagram for the system carbon dioxide - n-butane. • experimental (Kalra et al., 1976: (1); Hsu et al., 1985: (2) and (3)); (1) 255.98 K; (2) 319.26 K; (3) 377.59 K; ——— calculated with the new equation [Eqs. (17) - (22)].


+ Expt
(1)
(2)
(3)
(4)
(5)
(6)
(7)
(8)
ρ_c
P_c
Pressure (MPa)
Molar Density (mol/ℓ)
0
5
10
15
20
25
30
35
0
2
4
6
8

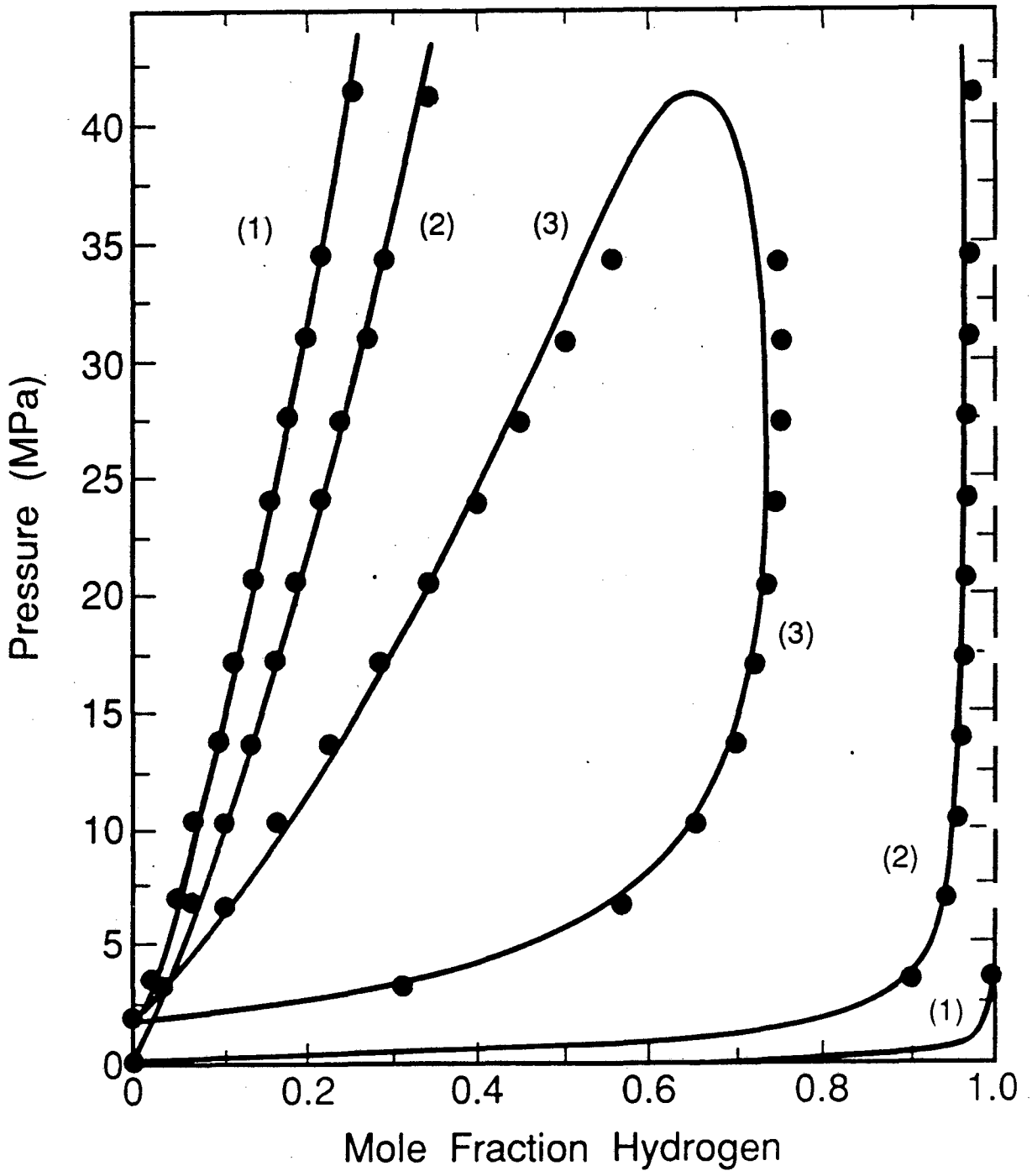
1


Critical
Temperature
(a)
a/a_c
1.4
1.2
1.0
0.8
Critical
Temperature
(b)
b/b_c
1.2
1.0
0.8
0.6
0.2
0.6
1.0
1.4
1.8
2.2
2.6
Reduced Temperature

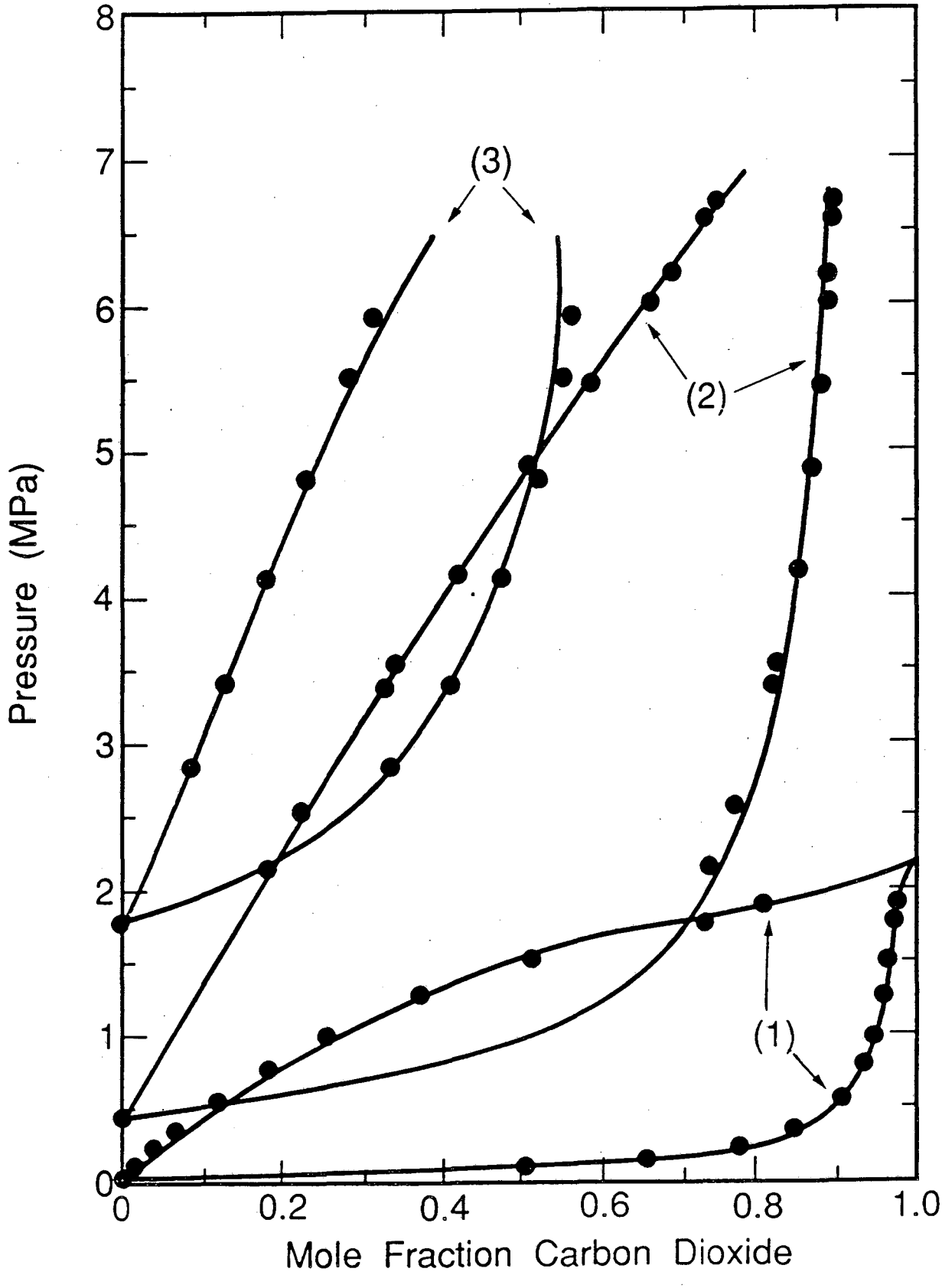


3

Prausnitz/Dobrn-1 (1/11/90)


Pressure (MPa)
Mole Fraction Hydrogen
0
5
10
15
20
25
30
35
40
0
0.2
0.4
0.6
0.8
1.0
(1)
(2)
(3)
(3)
(2)
(1)

4


Pressure (MPa)
Mole Fraction Carbon Dioxide
0
1
2
3
4
5
6
7
8
0
0.2
0.4
0.6
0.8
1.0
(1)
(2)
(3)

5

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