A Cubic Perturbed, Hard Sphere Equation of State for Thermodynamic Properties and Vapor-Liquid Equilibrium Calculations

TAKESHI ISHIKAWA
W. K. CHUNG
and
BENJAMIN C.-Y. LU
Department of Chemical Engineering
University of Ottawa
Ottawa, Ontario, CANADA K1N 9B4

A cubic perturbed, hard sphere equation of state which combines the hard sphere expression of Scott and the empirical attractive term of Redlich and Kwong with two temperature dependent parameters has been successfully applied to the calculation of pure component properties and vapor-liquid equilibrium values.

SCOPE

A well-behaved equation of state can represent and predict thermodynamic properties of pure components and mixtures, including vapor-liquid equilibrium values which are important in equipment design for separation processes. Many attempts have been made in recent years to improve the applicability of simple analytical equations of state such as those proposed by van der Waals and by Redlich and Kwong for chemical engineering applications. Special attention has been given to the modification of the repulsive term RT/(V-b). The objective of this study is to apply a new and simple perturbed, hard sphere equation of state to thermodynamic properties and vapor-liquid equilibrium calculations and to compare the calculated results with those obtained from other equations of state recently proposed in the literature.

CONCLUSIONS AND SIGNIFICANCE

The new perturbed, hard sphere equation used in this study combines the analytical expression of Scott for the hard sphere compressibility factor and the empirical attractive term of the Redlich-Kwong (RK) equation of state. This equation possesses the qualities of realism and simplicity of the RK equation, contains only two temperature dependent parameters and remains a cubic one in terms of density (or volume). It is much simpler to use than the equations proposed by De Santis et al. (1976) and Oellrich et al. (1978).

The calculated results obtained for five pure component properties (vapor pressure, saturated liquid and vapor volumes, latent heat of vaporization and second virial coefficient) indicate that the new equation yields lower deviations from the literature values than the two more complicated equations mentioned above.

Comparisons made on vapor-liquid equilibrium (VLE) values for five binary systems at thirty-two isothermal conditions indicate that the new equation yields better representation of the data than the methods of Soave (1972) and Peng-Robinson (PR) (1976). Some of the binary data used by De Santis et al. (1976) for testing their equation were also used in this study. The calculated results indicate that the new equation yields lower deviation in the calculated values of pressure. Comparisons were also made on VLE values for a ternary system at two isothermal conditions between the calculated results obtained by the new equation and the method of Soave (1972). The new equation again yields better results.

Ever since van der Waals (1873) proposed his equation, the vdW equation, many modifications have been made in the literature to improve his model. One of the most successful ones was the two-parameter empirical equation proposed by Redlich and Kwong (1949):

$$P = \frac{RT}{V-b} - \frac{a}{T^{0.5}V(V+b)} \tag{1}$$

It has been suggested (Modell and Reid, 1974) that almost all property estimation systems in use today employ the Redlich-Kwong equation. A number of empirical modifications have been proposed in recent years to improve the applicability of Equation (1), the RK equation, to the calculation of vapor-liquid equilibrium values. For example, the universal constants *a* and *b* were replaced by substance dependent and/or temperature dependent parameters (Wilson, 1964; Chueh and Prausnitz, 1967; Lu et al., 1969; Zudkevitch and Joffe, 1970). In addition, much attention has been given in recent years to the perturbed, hard sphere equation of state by modifying the hard sphere term $RT/(V-b)$ of the vdW and the RK equations of state. For example, Carnahan and Starling (1972) replaced the $RT/(V-b)$ term of these two equations by an improved equation for rigid spheres,

---

Correspondence concerning this paper should be addressed to Benjamin C.-Y. Lu.

0001-1541-80-3732-0372-$00.95.

TABLE 1. VALUES OF THE COEFFICIENTS a_i AND b_i OF EQUATIONS (5) AND (6)

	a_0	a_1	a_2	a_3	b_0	b_1	b_2	b_3	Ref.
Methane	0.19650	1.16856	−1.38439	0.47037	0.13356	0.12888	−0.26165	0.19262	5,7
Ethane	0.20176	1.31256	−1.67980	0.61622	0.11802	0.17279	−0.31486	0.12735	2,4
Propane	0.24104	1.25456	−1.64596	0.59878	0.11493	0.17712	−0.31397	0.12452	2,3
n-butane	0.23612	1.35573	−1.81164	0.66445	0.10786	0.19593	−0.32967	0.12712	1,2
n-pentane	0.35919	0.85241	−1.09198	0.32006	0.12727	0.07994	−0.14135	0.03378	1,2
n-hexane	0.29758	1.19570	−1.62966	0.57754	0.09861	0.19188	−0.29559	0.10457	1,2
n-heptane	0.24812	1.40351	−1.87158	0.65585	0.02042	0.47134	−0.63328	0.24004	9
n-octane	−0.20696	3.10569	−3.93176	1.46918	−0.12905	1.00409	−1.26511	0.48891	9
i-butane	−0.18450	2.89176	−3.65663	1.39674	−0.03957	0.75459	−1.02007	0.40746	1
i-pentane	0.10878	1.81070	−2.34577	0.86703	0.02509	0.49251	−0.68686	0.26953	9
Ethylene	0.44641	0.30161	−0.29444	−0.00538	0.14054	0.07086	−0.15209	0.04310	1
Propylene	0.11730	1.63895	−2.02328	0.71485	0.05773	0.37461	−0.53234	0.20234	1
1-butene	−0.22174	2.85561	−3.41073	1.21951	−0.00685	0.56951	−0.72161	0.25950	1
Acetylene	1.15110	−2.24265	2.82209	−1.28905	0.33084	−0.67414	0.78921	−0.34625	1
Benzene	0.38936	0.65177	−0.78790	0.18743	0.11547	0.13103	−0.21122	0.06496	1
Carbon dioxide	−0.96550	5.68232	−6.94321	2.67340	−0.31758	1.71076	−2.11569	0.82464	1
Carbon monoxide	0.16664	1.47391	−1.92735	0.74838	0.10783	0.24471	−0.42244	0.17596	1
Nitrogen	0.79071	−1.07156	1.52277	−0.79841	0.26291	−0.38945	0.44179	−0.21436	8
Oxygen	0.46326	0.12814	−0.01032	−0.13075	0.19070	−0.10512	0.06006	−0.04248	8
Argon	0.22914	1.02460	−1.16633	0.36604	0.12583	0.16172	−0.29468	0.11138	6
Sulfur dioxide	0.03616	2.08022	−2.66063	0.98686	0.02529	0.47173	−0.64978	0.25346	1
Ammonia	−0.12433	2.43358	−3.10164	1.21720	0.01133	0.45682	−0.63062	0.25746	1

References for saturated properties used in the evaluation of Ω_a and Ω_b: 1. Canjar and Manning (1967); 2. Carruth and Kobayashi (1972); 3. Das and Eubank (1972); 4. Eubank (1971); 5. Goodwin and Prydz (1972); 6. Gosman et al. (1969); 7. Prydz and Goodwin (1972); 8. Wilson (1964); 9. Young (1910).

which they had developed in 1969, and reported that a general improvement was obtained in the accuracy of predicted enthalpies, densities, pressures and saturated fugacities from these two reformulated equations (CSvdW and CSRK) relative to the original vdW and RK equations. De Santis et al. (1976) made an attempt to develop a hard sphere equation of state by combining the hard sphere repulsion compressibility factor of Carnahan and Starling (1969) with an attractive term for vapor-liquid equilibrium calculations. The equation they obtained was practically identical to the CSRK equation, but with the RK attractive term in the form as that modified by Soave (1972) and the two parameters considered temperature dependent. Oellrich et al. (1978) used the same reformulation of the vdW equation as presented by Carnahan and Starling (1972) and applied the CSvdW equation to the calculation of properties of eight pure fluids, but with the two parameters of the equation considered temperature dependent and evaluated from supercritical density data, subcritical saturated liquid densities and vapor pressures.

Recently, in our search for a simple analytical equation of state, we made a study on the representation of pure component properties by means of the vdW and the RK equations of state together with their twelve variants. These variants were obtained by replacing the $RT/(V-b)$ term with the analytical expressions of the hard sphere compressibility factor proposed by Frisch et al. (Reiss et al., 1959; Helfand et al., 1961), Thiele (1963), Guggenheim (1965) and Scott (1971), in addition to that suggested by Carnahan-Starling (1969). The results of our study indicate that the variant which combines the hard sphere compressibility factor of Scott and the RK empirical attractive term

$$P = \frac{RT}{V}\frac{(2V+b)}{(2V-b)} - \frac{a}{T^{0.5}V(V+b)} \qquad (2)$$

appears to be superior to all the other variants of the vdW and the RK equations mentioned above for representing pure component properties which are relevant to vapor-liquid equilibrium calculations. The pure component properties selected for the evaluation included vapor pressure, saturated liquid and vapor volumes, latent heat of vaporization and second virial coefficient. It should be mentioned, however, that the parameters of the variants were considered as universal constants in all of the calculations.

Equation (2) is very attractive from the viewpoint that it is simple to use. It contains only two parameters and remains a cubic one in terms of volume. The purpose of this study is to evaluate the feasibility of improving Equation (2) for representing pure component properties by considering the two parameters temperature and substance dependent, and to evaluate the applicability of Equation (2) to calculating and predicting vapor-liquid equilibrium using these modified parameters.

PURE COMPONENT PARAMETERS

The quantities a and b of Equation (2) are related to the critical properties as follows:

$$a = \Omega_a R^2 T_c^{2.5}/P_c \qquad (3)$$

and

$$b = \Omega_b R\, T_c/P_c \qquad (4)$$

Equations (3) and (4) were obtained by applying the two conditions, $(\partial P/\partial V)_{T_c} = 0$ and $(\partial^2 P/\partial V^2)_{T_c} = 0$, to Equation (2) at the critical point. In this work, the parameters Ω_a and Ω_b were evaluated from vapor pressures and saturated liquid densities for twenty two arbitrarily selected pure compounds following a procedure similar to that proposed for modifying the RK equation (Chang and Lu, 1970). The references from which the saturated properties were obtained are reported in Table 1. The calculated Ω_a and Ω_b values were further correlated by means of Equations (5) and (6):

$$\Omega_a = \sum_{i=0}^{3} a_i T_r^{\,i} \qquad (5)$$

and

$$\Omega_b = \sum_{i=0}^{3} b_i T_r^{\,i} \qquad (6)$$

The values of the coefficients a_i and b_i of these two equations are also reported in Table 1. These values were used in the calcula-

TABLE 2. A SUMMARY OF DEVIATIONS BETWEEN CALCULATED AND LITERATURE VALUES OF FOUR SATURATED PROPERTIES
AVERAGE ABSOLUTE DEVIATIONS, %

Compound	N	$\|\Delta P/P\|_{av}$			$\|\Delta V^v/V^v\|_{av}$			$\|\Delta V^l/V^l\|_{av}$			$\|\Delta\lambda/\lambda\|_{av}$		
		PR	De Santis	This work	PR	De Santis	This work	PR	De Santis	This work	PR	De Santis	This work
Methane	29	1.63	5.10	0.48	3.26	7.12	1.82	7.73	5.05	0.54	3.44	4.50	1.60
Ethane	27	1.09	4.06	0.31	2.27	8.21	1.04	6.68	3.62	2.23	4.14	5.72	0.84
Propane	31	1.04	0.81	0.31	2.28	2.82	0.88	5.75	0.91	1.07	3.70	2.46	1.19
n-butane	28	0.97	0.87	0.22	1.50	2.95	2.06	4.59	1.13	0.91	2.42	3.52	2.64
n-pentane	30	0.32	0.58	0.18	1.10	3.65	2.57	4.71	0.78	0.74	1.72	4.41	3.78
n-hexane	43	1.43	2.25*	0.28	1.33	7.27*	3.31	4.10	1.33*	0.42	2.54	5.96*	4.13
i-butane	29	1.47	2.06	0.04	2.35	3.53	0.70	5.09	1.63	0.43	2.34	7.09	4.31
Ethylene	21	1.15	3.44	0.77	1.58	6.63	1.82	6.45	2.29	0.38	1.40	4.58	2.50
Propylene	26	0.58	0.87	0.07	1.39	2.84	1.75	5.26	0.79	0.27	1.97	3.07	2.18
Acetylene	22	1.57	1.53	0.32	0.97	5.49	3.59	5.00	1.36	0.51	4.37	3.56	3.37
Benzene	47	0.91	1.08†	0.16	2.80	2.79†	3.21	4.39	0.84†	0.29	3.20	2.98†	3.25
Carbon dioxide	32	0.65	2.24	0.18	1.31	5.27	2.69	4.62	2.00	0.36	4.09	7.30	4.65
Carbon monoxide	24	1.45	6.36**	0.20	2.97	10.58**	3.16	8.49	4.24**	0.34	2.68	5.40**	2.69
Nitrogen	18	1.41	7.01	0.74	4.36	10.86	3.18	8.12	4.50	0.88	4.10	8.06	4.72
Ammonia	29	0.54	2.85	0.28	5.27	7.57	9.55	15.40	1.72	0.65	4.35	9.65	11.56
Average		1.08	2.74	0.30	2.32	5.84	2.76	6.43	2.15	0.67	3.10	5.22	3.56

* $N=37$;
†$N=44$.
**$N=22$.

TABLE 3. COMPARISON OF CALCULATED RESULTS OBTAINED FROM THE CSvdW EQUATION PROPOSED BY OELLRICH ET AL. FOR FIVE COMPOUNDS WITH LITERATURE VALUES

		Average absolute deviations, %			
	N	$\|\Delta P/P\|_{av}$	$\|\Delta V^v/V^v\|_{av}$	$\|\Delta V^l/V^l\|_{av}$	$\|\Delta\lambda/\lambda\|_{av}$
Methane	29	0.82	6.62	1.38	7.34
Ethane	27	0.98	9.52	2.55	10.92
Propane	31	1.12	9.20	1.42	11.65
Nitrogen	18	2.02	4.39	1.42	7.79
Ammonia	29	1.86	19.72	2.53	19.27

tions of this study. The weighted average absolute deviations between the correlated and calculated Ω_a and Ω_b values are 0.00089 and 0.00028, respectively.

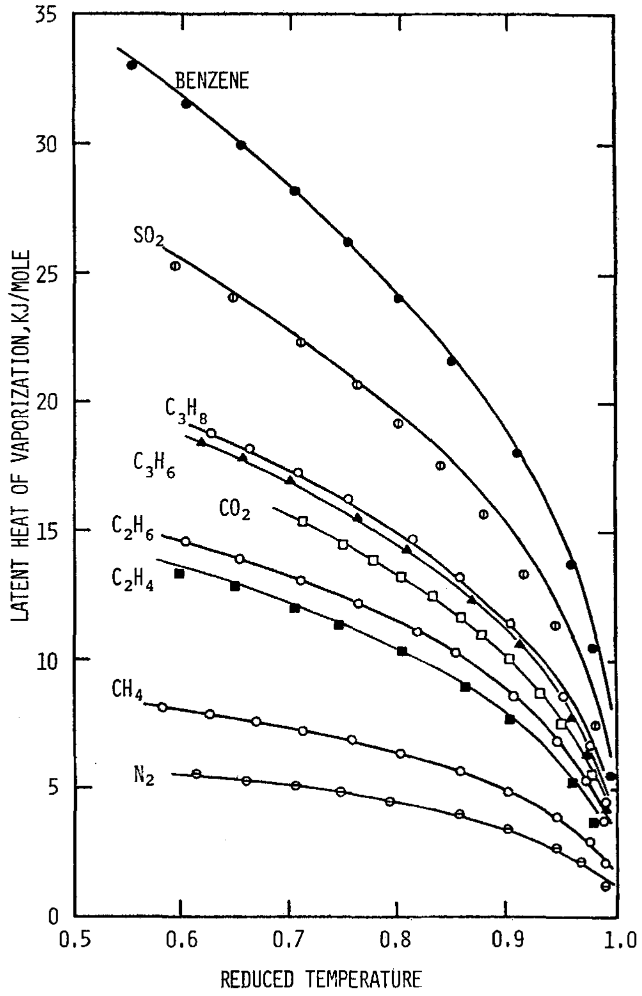

Figure 1. Comparison of calculated and literature values of latent heats of vaporization (———, calculated).

REPRESENTATION OF PURE COMPONENT PROPERTIES

The properties selected in this study for testing the capability of Equation (2) together with the Ω_a and Ω_b values represented by Equations (5) and (6) for representing pure component properties include four saturated properties (vapor pressure, liquid and vapor volumes and latent heat of vaporization) and second virial coefficient.

All the saturated properties were obtained from the compilation of Canjar and Manning (1967). The fifteen compounds selected for the calculation, as listed in Table 2, are those which have been studied by De Santis et al. (1976) but are available in the compilation so that comparisons can be made between the proposed equation and the CSRK equation of De Santis et al. The calculated results are reported in Table 2. Furthermore, the calculated results obtained from the cubic equation recently proposed by Peng and Robinson (1976) were also included in Table 2 for the purpose of comparison. It should be mentioned that some difficulties were encountered in convergence when the equation of De Santis et al. was used in the calculation for *n*-hexane, carbon monoxide and benzene. For this reason, the data points included in the calculation for these three compounds are not identical for the three equations as indicated in Table 2. The overall averages obtained are shown in Table 2, indicating that the proposed equation gives smaller deviations between the calculated and the literature values than the more complicated equation of De Santis et al. for all of the four saturated properties studied. The Peng-Robinson equation gives larger deviations than the proposed equation in the calculated values of vapor pressure and saturated liquid volume but gives slightly smaller deviations in the calculated values of saturated vapor volume and latent heat of vaporization. However, the proposed equation would give smaller average deviations than the Peng-Robinson equation in all of the four properties studied if the calculated results for ammonia were excluded in the

TABLE 4. A SUMMARY OF DEVIATION BETWEEN CALCULATED AND LITERATURE VALUES OF SECOND VIRIAL COEFFICIENTS FOR TEN COMPOUNDS

	Temperature range, °K	Data points	$\lvert \Delta B/B \rvert_{av} \cdot 100\%$		
			P.-R.	De Santis	This work
Argon	81-600	14	57.50	187.02	10.73
Nitrogen	75-700	14	29.51	81.77	15.74
Methane	110-600	16	113.94	315.44	9.53
Ethane	220-500	11	15.32	17.83	7.80
Propane	260-550	13	10.05	12.43	5.47
Propylene	280-500	8	10.97	10.51	5.48
n-butane	250-560	17	11.01	6.81	4.53
n-pentane	300-550	12	8.98	5.06	4.06
n-hexane	300-415	12	10.10	5.30	6.86
Benzene	300-440	8	13.04	7.16	8.92
Average		125	28.04	64.93	7.91

comparison. In addition, the CSvdW equation proposed by Oellrich et al. (1978) was also used to obtain the calculated results for methane, ethane, propane, nitrogen and ammonia. These five compounds were selected because they were also included in their study. The calculated results obtained are listed in Table 3. These results indicate that the proposed equa-

TABLE 5. COMPARISON OF CALCULATED AND EXPERIMENTAL VALUES FOR ELEVEN BINARY SYSTEMS AT FIFTY-THREE ISOTHERMAL CONDITIONS

	N	Temperature, °K	C_{12}	$\lvert \Delta P/P \rvert_{av} \cdot 100\%$	$\lvert \Delta y \rvert_{av}$	Ref.
Nitrogen-argon	7	112.00	0.0053	1.00	0.0007	Miller et al. (1973)
Nitrogen-methane	7	95.00	0.0470	1.25	0.0024	Parrish and Hiza (1974)
	9	100.00	0.0480	0.84	0.0023	Parrish and Hiza (1974)
	7	105.00	0.0500	1.20	0.0023	Parrish and Hiza (1974)
	9	110.00	0.0510	0.94	0.0024	Parrish and Hiza (1974)
	14	110.93	0.0460	0.58	—	Wilson (1964)
	8	113.71	0.0580	1.21	0.0034	TP-4 (1974)
	8	115.00	0.0550	1.04	0.0028	Parrish and Hiza (1974)
	8	120.00	0.0570	1.08	0.0036	Parrish and Hiza (1974)
	11	122.04	0.0610	1.04	0.0056	TP-4 (1974)
	9	138.44	0.0447	1.42	0.0074	Stryjek et al. (1972)
Methane-ethane	13	110.93	0.0040	1.18	—	Wilson (1964)
	4	130.37	0.0140	0.83	0.0003	TP-4 (1974)
	7	144.26	0.0120	0.54	0.0007	TP-4 (1974)
	10	158.15	0.0050	2.54	0.0017	TP-4 (1974)
	9	172.04	0.0120	1.12	0.0021	TP-4 (1974)
	11	186.11	0.0140	1.23	0.0030	TP-4 (1974)
	13	189.65	0.0130	1.30	0.0035	TP-4 (1974)
	16	190.94	0.0150	1.23	0.0033	TP-4 (1974)
Methane-propane	14	110.93	0.0060	1.07	—	Wilson (1964)
	3	130.37	0.0040	1.71	0.00002	TP-4 (1974)
	6	144.26	0.0100	3.38	0.00003	TP-4 (1974)
	8	158.15	0.0190	1.74	0.00007	TP-4 (1974)
	8	172.04	0.0180	0.81	0.0005	TP-4 (1974)
	9	187.54	0.0200	1.52	0.0010	TP-4 (1974)
	11	190.95	0.0210	0.37	0.0009	TP-4 (1974)
Methane-*n*-butane	3	144.26	0.0018	1.51	0.00003	TP-4 (1974)
	4	155.36	0.0007	4.25	0.00005	TP-4 (1974)
	5	166.50	0.0040	3.54	0.00006	TP-4 (1974)
	9	177.62	0.0060	2.54	0.0001	TP-4 (1974)
	7	189.06	0.0070	3.38	0.0004	TP-4 (1974)
	6	190.58	0.0070	4.14	0.0004	TP-4 (1974)
Methane-carbon monoxide	2	122.04	0.0460	1.78	0.0225	TP-4 (1974)
	4	130.37	0.0480	1.67	0.0141	TP-4 (1974)
Ethylene-propane	6	199.83	0.0185	0.19	0.0016	Elshayal and Lu (1975)
	6	227.90	0.0147	0.12	0.0014	Elshayal and Lu (1975)
	9	255.38	0.0147	0.22	0.0009	Elshayal and Lu (1975)
	13	273.06	0.0200	0.57	0.0010	Elshayal and Lu (1975)
Carbon dioxide-propane	12	277.59	0.1060	1.83	0.0064	Sage and Lacey (1955)
	17	294.26	0.1077	1.09	0.0047	Sage and Lacey (1955)
	18	310.90	0.1166	0.34	0.0092	Sage and Lacey (1955)
	15	327.59	0.1291	0.73	0.0081	Sage and Lacey (1955)
	11	344.26	0.1391	0.94	0.0070	Sage and Lacey (1955)
Carbon dioxide-*i*-butane	13	310.93	0.0990	1.29	0.0072	Besserer and Robinson (1973)
	8	344.26	0.1257	1.87	0.0120	Besserer and Robinson (1973)
Ethane-propylene	6	260.93	0.0060	0.10	0.0016	McKay et al. (1951)
	8	277.59	0.0060	0.32	0.0021	McKay et al. (1951)
	12	310.93	0.0110	0.40	0.0058	McKay et al. (1951)
	7	344.26	0.0100	0.22	0.0189	McKay et al. (1951)
n-hexane-benzene	10	303.15	0.0140	0.37	0.0019	Li et al. (1972)
	10	313.15	0.0132	0.32	0.0055	Li et al. (1972)
	10	323.15	0.0123	0.23	0.0012	Li et al. (1972)
	10	333.15	0.0113	0.19	0.0012	Li et al. (1972)

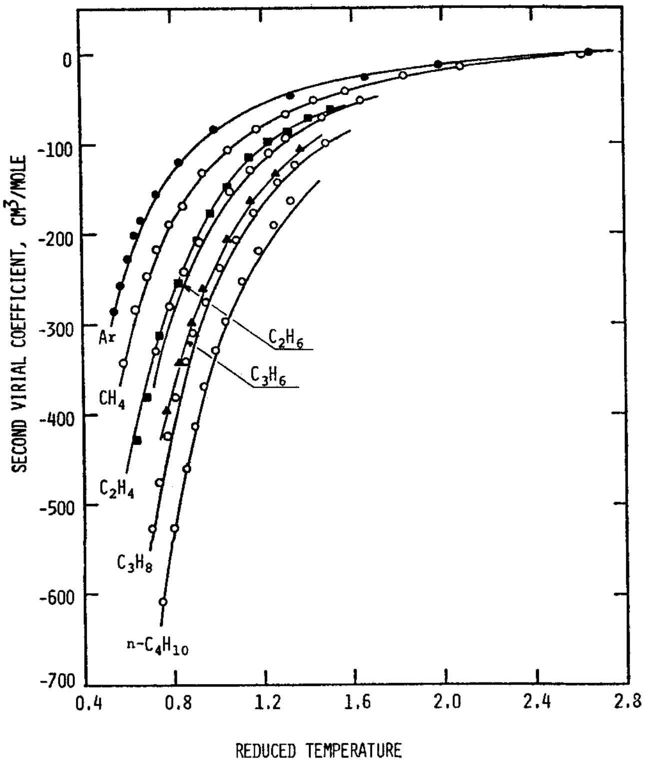

Figure 2. Comparison of calculated and literature values of second virial coefficients (———, calculated).

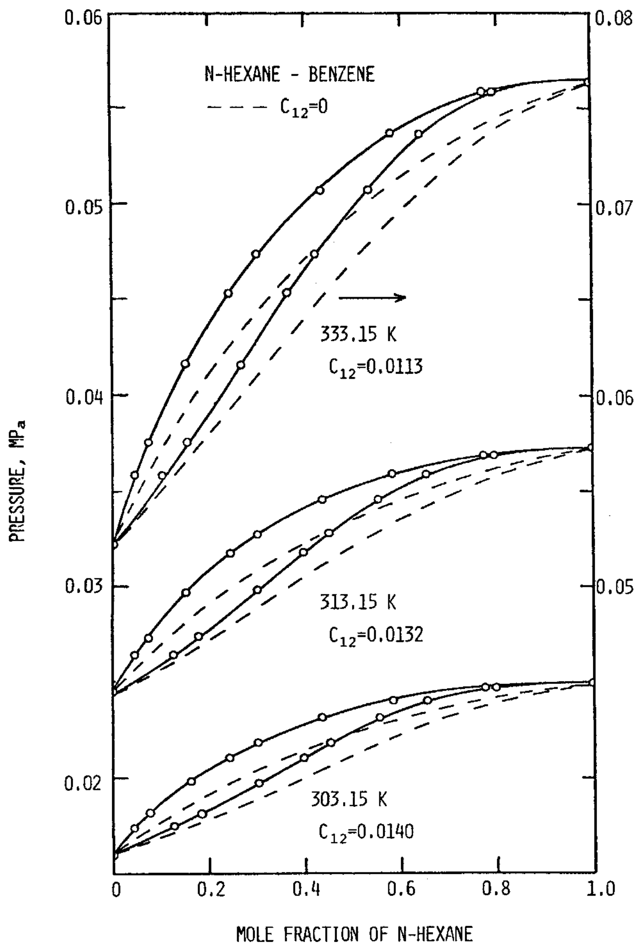

Figure 4. Calculated and experimental vapor-liquid equilibrium values for the binary system *n*-hexane-benzene (----, ———, calculated).

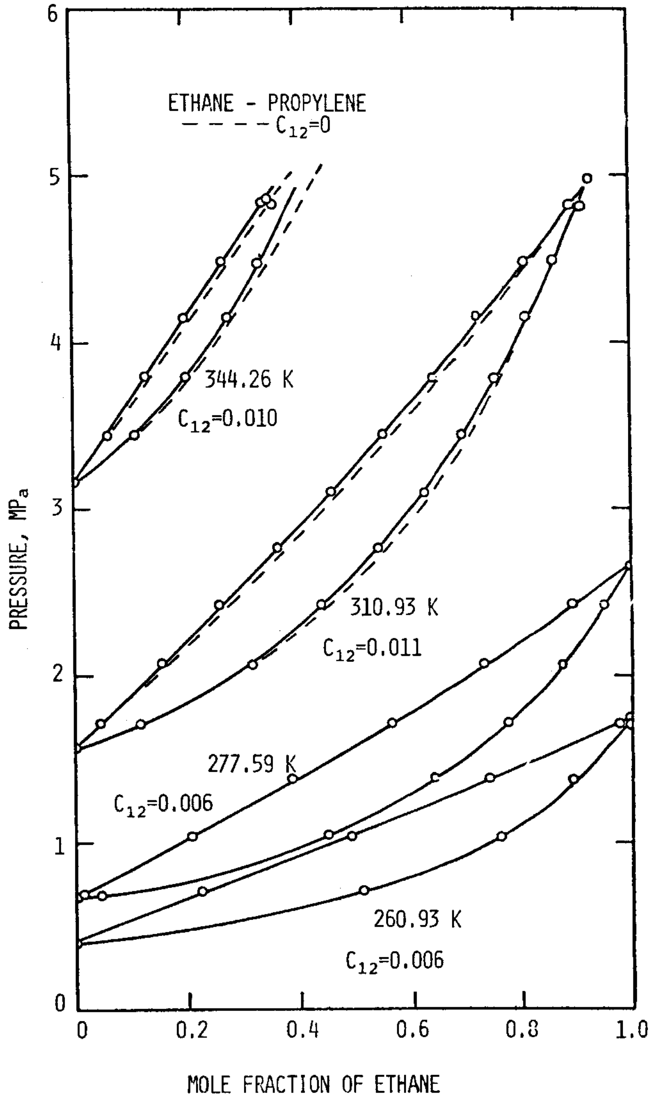

Figure 3. Calculated and experimental vapor-liquid equilibrium values for the binary system ethane-propylene (----, ———, calculated).

TABLE 6. COMPARISON OF CALCULATED RESULTS FOR FIVE BINARY SYSTEMS OBTAINED FROM THREE METHODS

	$\lvert\Delta y\rvert_{av}$	$\lvert\Delta P/P\rvert_{av} \cdot 100\%$
Peng-Robinson	0.0046	5.87
Soave	0.0040	5.12
This work	0.0023	1.47

tion represents the saturated properties studied better than the more complicated CSvdW equation. To illustrate the agreement obtained between the calculated values using Equation (2) and those available in the literature, values of latent heat of vaporization for nine compounds are plotted as a function of reduced temperature in Figure 1.

The proposed equation together with the CSRK equation of De Santis et al. and the Peng-Robinson equation were also used for calculating second virial coefficients for ten arbitrarily

TABLE 7. VALUES OF BINARY INTERACTION COEFFICIENT FOR MIXTURES OF NITROGEN (1), METHANE (2) AND ETHANE (3)

Temperature, °K	C_{12}	C_{13}	C_{23}
138.71	0.0447	0.0992	0.012
149.82	0.0391	0.0816	0.012

TABLE 8. COMPARISON OF CALCULATED AND LITERATURE VAPOR-LIQUID EQUILIBRIUM DATA FOR THE TERNARY SYSTEM NITROGEN (1)-METHANE(2)-ETHANE(3)

Temperature, °K	Pressure, MPa	N	This work $\lvert\Delta P/P\rvert_{av}\cdot 100\%$	This work $\lvert\Delta y\rvert_{av}$	Soave $\lvert\Delta P/P\rvert_{av}\cdot 100\%$	Soave $\lvert\Delta y\rvert_{av}$
138.71	0.69	7	3.14	0.0074	18.17	0.0307
	1.38	4	1.73	0.0052	21.33	0.0219
	2.07	5	2.70	0.0027	22.52	0.0068
	2.76	6	7.27	0.0027	19.53	0.0044
	3.45	4	12.06	0.0032	16.97	0.0033
	4.14	6	11.46	0.0027	9.45	0.0053
	Overall average		6.34	0.0041	17.72	0.0128
149.82	0.69	3	4.05	0.0096	14.08	0.0287
	1.38	3	2.79	0.0050	13.86	0.0222
	2.07	3	0.83	0.0035	10.26	0.0220
	2.76	4	1.43	0.0024	11.80	0.0111
	3.45	3	3.05	0.0023	13.51	0.0074
	4.14	2	4.58	0.0017	12.89	0.0034
	Overall average		2.61	0.0041	12.67	0.0158

selected pure compounds, using the values compiled by Dymond and Smith (1969). The calculated results, summarized in Table 4, indicate that the proposed equation gives the best representation. The agreement obtained between the calculated and literature values for seven compounds is depicted in Figure 2.

VAPOR-LIQUID EQUILIBRIUM CALCULATIONS

Application of Equation (2) to mixtures requires the definition of two quantities, a_m and b_m, which replace a and b in Equations (2), (3) and (4). The conventional mixing rules

$$a_m = \sum_i \sum_j y_i y_j a_{ij} \tag{7}$$

and

$$b_m = \sum_i y_i b_i \tag{8}$$

were used in this study for gas mixtures. The same rules were used for liquid mixtures with x replacing y in these equations. In this study, the mixing rule for a_{ij} as proposed by Redlich and Kwong (1949) was modified by the introduction of a binary interaction coefficient as suggested by Zudkevitch and Joffe (1970):

$$a_{ij} = (a_{ii}a_{jj})^{0.5}(1-C_{ij}) \tag{9}$$

The expression obtained from Equation (2) for calculating the fugacity coefficient of a component $i, \hat{\phi}_i^v$, in a vapor mixture is given by

$$\ln\hat{\phi}_i^v = \ln\left(\frac{\hat{f}_i^v}{y_iP}\right) = \frac{2b_i}{2V-b_m} - 2\ln\left(1-\frac{b_m}{2V}\right) - \frac{2\sum_{k=1}^{m} y_k a_{ki}}{RT^{1.5}b_m}\ln\left(\frac{V+b_m}{V}\right) + \frac{ab_i}{RT^{1.5}b_m^2}\left[\ln\left(\frac{V+b_m}{V}\right) - \frac{b_m}{V+b_m}\right] - \ln Z \tag{10}$$

The same expression is applicable to the calculation of the liquid fugacity coefficient ($\hat{\phi}_i^l = \hat{f}_i^l/x_iP$) by replacing y by Equations (10) with x. At equilibrium

$$\hat{f}_i^v = \hat{f}_i^l \tag{11}$$

and

$$K_i = y_i/x_i = \hat{\phi}_i^l/\hat{\phi}_i^v \tag{12}$$

Equations (7) to (12) are the working equations used in this study for vapor-liquid equilibrium (VLE) calculations. The calculated results for eleven binary systems at fifty-three isothermal conditions, summarized in Table 5, indicate that the proposed equation is suitable for VLE calculations. In the calculation, values of P and y were obtained from given T and x values. All the values of C_{12} were determined directly from vapor-liquid equilibrium values by minimizing the difference between the calculated and experimental values of system pressures of isothermal conditions. The influence of C_{12} on the calculated equilibrium values is demonstrated in Figures 3 and 4 for the binary systems ethane-propylene and n-hexane-benzene. The Ω_a and Ω_b values for a component in its supercritical region were obtained from Equations (5) and (6) at $T_r = 1$.

Comparisons of the calculated VLE results were made between the proposed equation, the Peng-Robinson equation and the Soave modification of the RK equation on the following five binary systems at thirty-two isothermal conditions: nitrogen-methane, carbon monoxide-methane, methane-ethane, methane-propane, methane-n-butane. The calculated results obtained by the Soave method for these systems have been reported by Kato et al. (1976). The weighted overall average deviations obtained by the three methods in $\lvert\Delta y\rvert_{av}$ and $\lvert\Delta P/P\rvert_{av}\cdot 100\%$ are listed in Table 6. The results indicate that the proposed equation yields better representation of the data than the other two methods.

In the work of De Santis et al., comparisons were made for several binary systems. They estimated that for the systems argon-nitrogen, ethane-propylene and ethylene-propane, estimated pressures on the average deviated from observations less than 2%. The deviations in P obtained by the proposed method for these systems as indicated in Table 5 are lower, and the mean deviation is less than 0.5%.

The applicability of the proposed equation for predicting multicomponent VLE values is demonstrated by means of the calculated values for the nitrogen (1)-methane (2)-ethane (3) ternary system at two isothermal conditions. The temperature selected are above the critical temperature of nitrogen. The C_{ij} values used in the proposed method are listed in Table 7. The calculated results obtained by the proposed method together with those obtained from the Soave method are compared with the experimental values (Gas Processors Association TP-4, 1974) in Table 8.

The satisfactory results obtained in this study indicate that Equation (2) is suitable for VLE calculations for systems containing nonpolar and slightly polar compounds.

ACKNOWLEDGMENT

The authors are grateful to the Natural Sciences and Engineering Research Council of Canada for continuing financial support.

NOTATION

a,b = parameters of the RK and the proposed equation of state
C_{ij} = binary interaction coefficient
f = fugacity
K = equilibrium ratio
m = number of components
N = number of observations
P = pressure
R = gas constant
T = absolute temperature
V = volume
x = mole fraction in liquid phase
y = mole fraction in vapor phase
Z = compressibility factor
Δ = difference
ϕ = fugacity coefficient
Ω_a, Ω_b = dimensionless parameters of the proposed equation of state

Subscripts

av = average value
c = critical property
i,ii,j,jj,k = component identification
i = order of series expansion
m = mixture
r = reduced

Superscripts

$\hat{}$ = solution property
i = order of series expansion
l = liquid
v = vapor

LITERATURE CITED

Besserer, G. J., and D. B. Robinson, "Equilibrium-Phase Properties of *i*-Butane-Carbon Dioxide System," *J. Chem. Eng. Data*, **18**, 298 (1973).

Canjar, L. N., and F. S. Manning, *Thermodynamic Properties and Reduced Correlations for Gases*, Gulf Publ. Co., Houston, Tex. (1967).

Carnahan, N. F., and K. E. Starling, "Equation of State for Non-attracting Rigid Spheres," *J. Chem. Phys.*, **51**, 635 (1969).

———, "Intermolecular Repulsions and the Equation of State for Fluids," *AIChE J.*, **18**, 1184 (1972)

Carruth, G. F., and R. Kobayashi, "Extension to Low Reduced Temperatures of Three-Parameter Corresponding States: Vapor Pressures, Enthalpies and Entropies of Vaporization, and Liquid Fugacity Coefficients," *Ind. Eng. Chem. Fundamentals*, **11**, 509 (1972).

Chang, S. D., and B. C.-Y. Lu, "Prediction of Partial Molal Volumes of Normal Fluid Mixtures," *Can. J. Chem. Eng.*, **48**, 261 (1970).

Das, T. R., and P. T. Eubank, "Thermodynamic Properties of Propane: Vapor-Liquid Coexistence Curve," *Adv. Cryog. Eng.*, **18**, 208 (1972).

De Santis, R., F. Gironi and L. Marrelli, "Vapor-Liquid Equilibrium from a Hard-Sphere Equation of State," *Ind. Eng. Chem. Fundamentals*, **15**, 183 (1976).

Dymond, J. H., and E. B. Smith, *The Virial Coefficients of Gases*, Clarendon Press, Oxford, England (1969).

Elshayal, I. M., and B. C.-Y. Lu, "Measurement and Total Pressures for Ethylene-Propane Mixtures," *Can. J. Chem. Eng.*, **53**, 83 (1975).

Eubank, P. T., "Thermodynamic Properties of Ethane: Vapor-Liquid Coexistence," *Adv. Cryog. Eng.*, **17**, 270 (1971).

Goodwin, R. D., and R. Prydz, "Densities of Compressed Liquid Methane and the Equation of State," *J. Res.*, **NBS 76A**, 81 (1972).

Gosman, A. L., R. D. McCarty and J. G. Hust, "Thermodynamic Properties of Argon from Triple Point to 300K at Pressures to 1000 Atmospheres," *NSRDS-NBS*, 27 (1969).

Guggenheim, E. A., "Variations on van der Waals' Equation of State for High Densities," *Mol. Phys.*, **9**, 199 (1965).

Helfand, E., H. L. Frisch and J. L. Lebowitz, "Theory of the Two- and One-Dimensional Rigid Sphere Fluids," *J. Chem. Phys.*, **34**, 1037 (1961).

Kato, M., W. K. Chung and B. C.-Y. Lu, "Modified Parameters for the Redlich-Kwong Equation of State," *Can. J. Chem. Eng.*, **54**, 441 (1976).

Li, I. P. C., Y.-W. Wong, S.-D. Chang and B. C.-Y. Lu, "Vapor-Liquid Equilibria in Systems *n*-Hexane-Benzene and *n*-Pentane-Toluene," *J. Chem. Eng. Data*, **17**, 492 (1972).

Lu, B. C.-Y., S.-D. Chang, I. M. Elshayal, P. Yu, D. Gravelle and D. P. L. Poon, "Low Temperature Phase Equilibria of Natural Gas Components," Proc. First Intern. Conf. Calorimetry and Thermodynamics, pp. 755-766, Warsaw (1969).

McKay, R. A., H. H. Reamer, B. H. Sage and W. N. Lacey, "Volumetric and Phase Behavior in the Ethane-Propane System," *Ind. Eng. Chem.*, **43**, 2112 (1951).

Miller, R. C., A. J. Kidnay and M. J. Hiza, "Liquid-Vapor Equilibria at 112.00K for Systems Containing Nitrogen, Argon and Methane," *AIChE J.*, **19**, 145 (1973).

Modell, M., and R. C. Reid, *Thermodynamics and its Applications*, Prentice-Hall, Englewood Cliffs, N. J. (1974).

Oellrich, L. R., H. Knapp and J. M. Prausnitz, "A Simple Perturbed-Hard-Sphere Equation of State Applicable to Subcritical and Supercritical Temperatures," *Fluid Phase Equilibria*, **2**, 163 (1978).

Parrish, W. R., and M. J. Hiza, "Liquid-Vapor Equilibria in the Nitrogen-Methane System Between 95 and 120K," *Adv. Cryog. Eng.*, **19**, 300 (1974).

Peng, D.-Y., and D. B. Robinson, "A New Two-Constant Equation of State.," *Ind. Eng. Chem. Fundamentals*, **15**, 59 (1976).

Prydz, R., and R. D. Goodwin, "Experimental Melting and Vapor Pressures of Methane," *J. Chem. Thermodynamics*, **4**, 127 (1972).

Redlich, O., and J. N. S. Kwong, "On the Thermodynamics of Solutions V," *Chem. Rev.*, **44**, 233 (1949).

Reiss, H., H. L. Frisch, and J. L. Lebowitz, "Statistical Mechanics of Rigid Spheres," *J. Chem. Phys.*, **31**, 369 (1959).

Sage, B. H., and W. N. Lacey, "Some Properties of the Lighter Hydrocarbons, Hydrogen Sulfide and Carbon Dioxide," A.P.I., Washington, D. C. (1955).

Scott, R. L., *Physical Chemistry, An Advanced Treatise*, D. Henderson, ed., Vol. 8A, Chapt. 1, Academic Press, New York (1971).

Soave, G., "Equilibrium Constant from a Modified Redlich-Kwong Equation of State," *Chem. Eng. Sci.*, **37**, 1197 (1972).

Stryjek, R., P. S. Chappelear and R. Kobayashi, "Low-Temperature Vapor-Liquid Equilibria of Nitrogen-Methane Systems," *J. Chem. Eng. Data*, **19**, 334 (1974).

Technical Publication TP-4, Low Temperature Data from Rice University for Vapor-Liquid and P-V-T Behavior, Gas Processors Association, Oklahoma 1974 (work performed by R. Kobayashi et al. data compiled by P. Chappelear).

Thiele, E. T., "Equation of State for Hard Spheres," *J. Chem. Phys.*, **39**, 474 (1963).

Van der Waals, J. D., Jr., "Over de continuiteit van den gas-en Vloeistoftoestand," doctoral dissertation, Leiden, Holland (1973).

Wilson, G. M., "Vapor-Liquid Equilibria of Nitrogen, Methane, Ethane and Propane Binary Mixtures at LNG Temperatures from Total Pressure Measurements," *Adv. Cryog. Eng.*, **20**, 164 (1975).

———, P. M. Silverberg and M. G. Zellner, Argon-Oxygen-Nitrogen Three Component System Experimental Vapor-Liquid Equilibrium Data," APL TDR 64-64, U.S. Department of Commerce, Washington, D. C. (1964).

Young, S., "The Vapor-Pressures, Specific Volumes, Heat of Vaporization and Critical Constants of Thirty Pure Substances," *Sci. Proc. Royal Dublin Soc.*, **12**, 374 (1910).

Zudkevitch, D., and J. Joffe, "Correlation and Prediction of Vapor-Liquid Equilibria with the Redlich-Kwong Equation of State," *AIChE J.*, **16**, 112 (1970).

Manuscript received June 25, 1979; revision received October 23, and accepted November 7, 1979.