

## **Prediction of Critical Properties of Mixtures from the PRSV-2 Equation of State: A Correction for Predicted Critical Volumes**

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The predictive capability of the Peng–Robinson–Stryjek–Vera (PRSV-2) equation of state (1986) for critical properties of binary mixtures was investigated. The procedure adopted by Heidemann and Khalil (1980) and discussed by Abu-Eishah et al. (1998) was followed. An optimized value for the binary interaction parameter based on minimization of error between experimental and predicted critical temperatures was used. The standard and the average of the absolute relative deviations in critical properties are included. The predicted critical temperature and pressure for several nonpolar and polar systems agree well with experimental data and are always better than those predicted by the group-contribution method. A correction is introduced here to modify the predicted critical volume by the PRSV-2 equation of state, which makes the average deviations between predicted and experimental values very close to or even better than those predicted by the group-contribution method.

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**KEY WORDS:** binary mixtures; critical properties; critical volume; equation of state.

### **1. INTRODUCTION**

Critical properties of a fluid or fluid mixtures are important for describing fluid phase behavior, predicting physical properties, developing equations of state, and designing supercritical-fluid extraction processes, and compression and refrigeration units [1]. For commonly used pure substances, these critical constants have been determined experimentally. Beside direct measurements, critical properties of mixtures are often estimated using various correlating methods. Li and Kiran [2] divided the bases of the

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existing correlating methods into six groups and gave references on each of them. These groups are (a) graphical approach, (b) equation of state approach, (c) excess property approach, (d) conformal solution (corresponding state principle) approach, (e) thermodynamic potential approach, and (f) group-contribution approach.

The prediction of true critical properties of multicomponent systems is an important aspect of the general problem of predicting the overall phase behavior of a system. Knowledge of the critical behavior of mixtures is important in order to determine the existing phase conditions or permissible operating ranges in reactors and mass transfer equipment.

Fluid-property predictions and design calculations in the critical region are often the most difficult to make, and a knowledge of the precise location of the critical point for the system under study is of utmost importance. Prediction of critical properties is also important in modeling the phase behavior exhibited by gas mixtures for the simulation of enhanced oil-recovery processes [3].

Evaluation of critical points for multicomponent mixtures based on an equation of state has attracted considerable attention in recent years. In this approach the second and third derivatives of the molar free energy with respect to composition at constant temperature and pressure must be equal to zero. Determination of the critical properties for mixtures involves a simultaneous solution of an extended form of these derivatives and an equation of state. Several attempts have been made using the Redlich-Kwong equation of state [4, 5], the Peng-Robinson equation of state [6, 7], the Soave-Redlich-Kwong equation of state [8-12], the Teja-Patel equation of state [7], Deiters' as well as Guggenheim equations of state [13], and the simplified perturbed hard-chain-theory equation of state [14]. More details about the capability of these equations are summarized elsewhere [15].

The Heidemann-Khalil method [10], compared to the Peng-Robinson rigorous method [6], is far superior: it is much more efficient, requires less computational effort, and does not need the evaluation of a very large number of high order determinants. Also, the partial derivatives required using the Helmholtz free energy concept are much more rapidly evaluated than those using the Gibbs free energy concept [11].

## **2. APPLICATION OF HEIDEMANN-KHALIL APPROACH TO THE PRSV-2 EQUATION OF STATE**

The Peng-Robinson-Stryjek-Vera (PRSV-2) equation of state has been successfully used for vapor-liquid equilibrium calculations over a wide range of temperatures and yields a good representation of the saturation

pressure of pure compounds even at low, reduced temperatures [16, 17]. Therefore, the PRSV-2 equation of state has been chosen here to test its ability to predict the critical properties of binary mixtures following the Heidemann and Khalil approach [10]. The Peng–Robinson equation of state in its modified form is given by

$$P = RT/(v - b) - a(T)/\{v(v + b) + b(v - b)\} \quad (1)$$

with pure compound parameters

$$a = \alpha[0.457235(RT_c)^2/P_c] \quad (2)$$

$$b = 0.077796RT_c/P_c \quad (3)$$

$$\alpha = [1 + \kappa(1 - T_r^{0.5})]^2 \quad (4)$$

and

$$\kappa = \kappa_o + [\kappa_1 + \kappa_2(\kappa_3 - T_r)(1 - T_r^{0.5})](1 + T_r^{0.5})(0.7 - T_r) \quad (5)$$

where

$$\kappa_o = 0.378893 + 1.4897153\omega - 0.17131848\omega^2 + 0.0196544\omega^3 \quad (6)$$

As recommended by Stryjek and Vera [16, 17], Eq. (5) is used in this work for  $T_r \leq 0.7$ , while  $\kappa = \kappa_o$  is used for  $T_r > 0.7$ . The pure-compound critical properties ( $P_c$ ,  $T_c$ ,  $\omega$ ), and the pure-component parameters ( $\kappa_1$ ,  $\kappa_2$ , and  $\kappa_3$ ) were taken from Stryjek and Vera [16, 17] and Proust and Vera [18] for the  $\kappa_1$  of some other pure compounds that have not been given before. For mixtures, the following mixing rules are applied:

$$a = \sum_i^N \sum_j^N x_i x_j a_{ij} \quad (7)$$

and

$$b = \sum_i^N x_i b_i \quad (8)$$

For the cross parameter,  $a_{ij}$ , the conventional one-binary interaction parameter form is used.

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

where  $k_{ij}$  is the binary interaction parameter between component  $i$  and component  $j$ . The optimized values of  $k_{ij}$  for all the studied systems are

listed in Appendix A. The optimization procedure is based on the minimization of the sum of the squares of the relative errors in the critical temperature for a given set of data.

In terms of the compressibility factor,  $Z$ , Eq. (1) can be written as

$$Z^3 - (1 - B)Z^2 + (A - 3B^2 - 2B)Z - (AB - B^2 - B^3) = 0 \quad (10)$$

where  $A = aP/(RT)^2$  and  $B = bP/RT$ .

Equation (10), as a cubic equation, gives three roots for  $Z$ : either all real or one real and two complex conjugate roots. When applied to mixtures, the largest positive real root is taken as the value of  $Z$  when the mixture is in the vapor phase, while the smallest positive real root is taken for  $Z$  when the mixture is in the liquid phase. In the case of a single positive real root (or three equal positive real roots) in a given phase, a pure component exists.

The fugacity of component  $i$  as a function of temperature, volume, and mole numbers derived from the PRSV-2 equation is [17]

$$\ln f_i = \frac{b_i}{b_m} (Z - 1) - \ln\{(Z - B)/x_i P\} - \frac{A}{2\sqrt{2}B} \left( \frac{2\sum x_i a_{ij}}{a_m} - \frac{b_i}{b_m} \right) \ln \left( \frac{Z + (1 + \sqrt{2})B}{Z + (1 - \sqrt{2})B} \right) \quad (11)$$

where  $x_i$  is the mole fraction of component  $i$  in the mixture.

If the Helmholtz free energy is expanded around some test point ( $T_o, V_o, n_{1o}, n_{2o}, \dots, n_{No}$ ) according to the approach of Heidemann and Khalil [10], one gets

$$\begin{aligned} & \left[ A - A_o - \sum_i^N (\partial A / \partial n_i) \Delta n_i \right] \\ &= \frac{1}{2} \sum_j^N \sum_i^N (\partial^2 A / \partial n_j \partial n_i) \Delta n_i \Delta n_j \\ &+ \frac{1}{3!} \sum_k^N \sum_j^N \sum_i^N (\partial^3 A / \partial n_k \partial n_j \partial n_i) \Delta n_i \Delta n_j \Delta n_k + O(\Delta n^4) \end{aligned} \quad (12)$$

The stability of the test point is assured if the quadratic term in Eq. (12) is positive-definite, i.e., is equal to zero. At such a point, the stability is determined by the properties of the cubic and higher-order terms in Eq. (12). If we note that

$$(\partial A / \partial n_i) |_{T, v, n_j \neq n_i} = RT \ln f_i \quad (13)$$

then the derivative elements in the quadratic and cubic terms in Eq. (12) at constant  $T$ ,  $P$ , and  $n_j \neq n_i$  become

$$(\partial^2 A / \partial n_j \partial n_i) = RT \{ \partial \ln f_i / \partial n_j \} \quad (14)$$

and

$$(\partial^3 A / \partial n_k \partial n_j \partial n_i) = RT \{ \partial^2 \ln f_i / \partial n_k \partial n_j \} \quad (15)$$

That is, the first and second partial derivatives of fugacity with respect to the number of moles of the constituents  $j$  and  $k$  have to be evaluated. The expressions that have been developed for these derivatives, from the PRSV-2 equation of state with conventional mixing rules, are summarized in Appendix B for reference.

The necessary condition for a point to lie on the limit of stability is that the matrix  $\mathbf{Q}$  with elements

$$q_{ij} = (\partial^2 A / \partial n_j \partial n_i) |_{T,v} = RT \{ \partial \ln f_i / \partial n_j \} |_{T,v} \quad (16)$$

should have a zero determinant, i.e.,

$$\det(\mathbf{Q}) = 0 \quad (17)$$

and the cubic term in Eq. (12) must vanish, i.e.,

$$C = \sum_k^N \sum_j^N \sum_i^N n_T^2 \{ \partial^2 \ln f_i / \partial n_k \partial n_j \} \Delta n_i \Delta n_j \Delta n_k = 0 \quad (18)$$

The resulting two nonlinear equations, (17) and (18), have been solved simultaneously for the critical temperature and volume. The critical pressure is then calculated from the PRSV-2 equation of state itself. A correction is introduced to the calculated critical volume as follows. The compressibility factor of the mixture,  $Z$ , is calculated using Eq. (10) at the calculated  $T_c$  and  $P_c$ . Then the corrected value of the critical volume is calculated as the value of  $v_c$  calculated from the PRSV-2 equation of state minus one-half the value of  $ZRT_c/P_c$ .

The flowchart of the computational procedure described by Heidemann and Khalil [10] and followed in this work is shown elsewhere [15]. The experimental critical data used in this work are those of Hicks and Young [19] and Ref. 20 for the water-acetic acid system. The pure-component properties have been taken from Stryjek and Vera [16, 17] and Proust and Vera [18]. The data of Reid et al. [21] have been used for the pure-component properties that are not available in Refs. 16–18.

### 3. RESULTS AND DISCUSSION

The algorithm described in Fig. 1 and discussed earlier [15] has been applied to the PRSV-2 equation of state to predict the critical properties of 21 binary mixtures. Among these systems are paraffins, aromatics, alcohols, water, ethers, hydrogen sulfide, sulfur dioxide, carbon dioxide, acetic acid, ammonia, and others. The pure-component properties of the systems studied in this work are listed in Table AI (Appendix A). The calculated optimum values of the conventional binary-interaction parameters for the systems studied are listed in Table AII in Appendix A. The criteria used to compare predicted and experimental critical properties are the standard deviation, SD, and the average of the absolute relative deviations, AD, defined below

$$SD = \left[ \sum_i^M (\text{exp. value} - \text{calc. value})^2 / (M - 1) \right]^{0.5} \quad (19)$$

$$AD = \left[ \sum_i^M |\text{exp. value} - \text{calc. value}| / \text{exp. value} \right] \times 100 / M \quad (20)$$

where  $M$  is the number of points in a given set of data.

It is first noted that all systems studied have continuous critical curves, and the critical locus of each of these systems exhibits a critical temperature that varies monotonically with composition. A point of minimum critical temperature has been noticed on the critical loci of several systems (propane–hydrogen sulfide and butane–ammonia mixtures). This minimum critical temperature is an indication of the formation of a positive azeotrope, i.e., an azeotrope with a minimum in its boiling temperature [22].

The effect of using different mixing rules (zero interaction parameter, conventional and two-parameter Margules-type) on the predicted critical properties by the PRSV-2 equation of state has been studied in a previous paper [15].

Using a conventional one-binary interaction parameter type, Table I shows the standard deviation, SD, and the average absolute relative deviation, AD, in critical temperature and pressure for 11 nonpolar systems. The average standard deviation for all these systems is 2.53 K, with a maximum SD of about 7.80 K for the critical temperature (when the convergence is oscillatory as it is in the case for the methane–H<sub>2</sub>S system). For the critical pressure the average SD is about 2.23 bar, with a maximum SD of about 9.87 bar for methane–H<sub>2</sub>S. Note that the uncertainties in the experimental values are typically about 0.6 K for the critical temperature and 0.2 bar for the critical pressure [23]. On the other hand, the average AD for all the

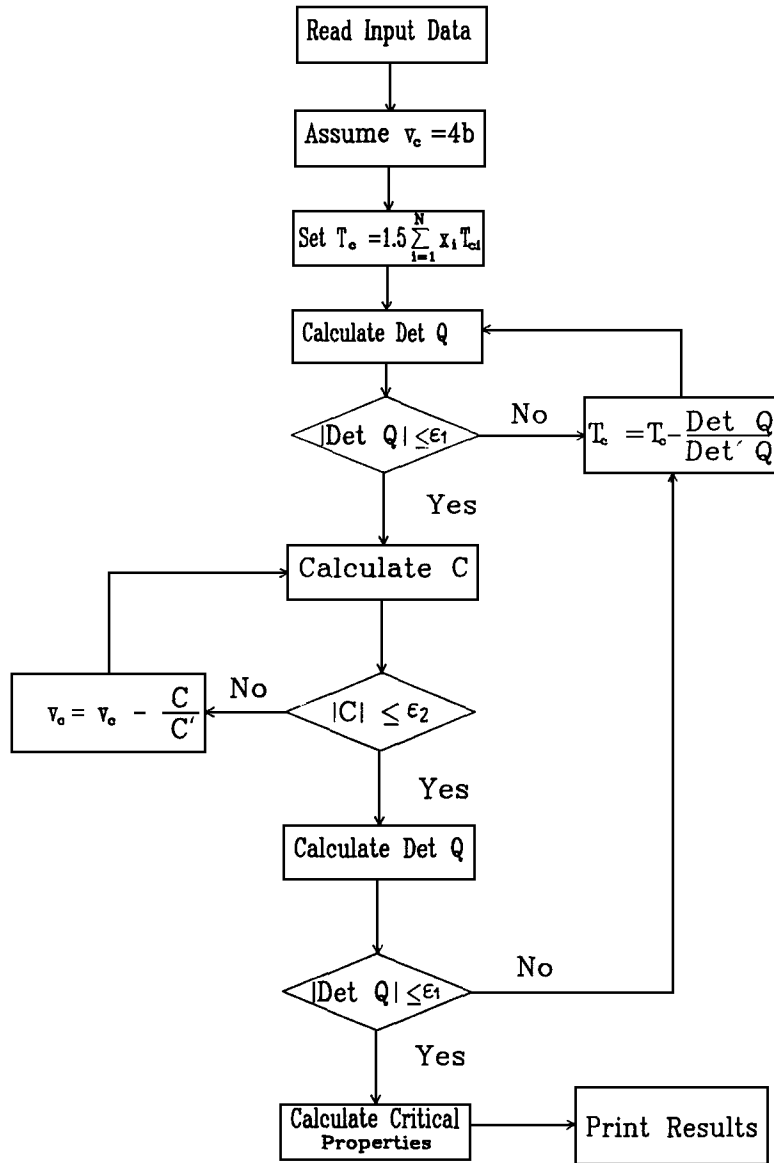


Fig. 1. Schematic flowchart for the calculation procedure of the critical properties of a mixture.

**Table I.** Standard and Average Deviations in Critical Properties for Some Nonpolar Mixtures Using PRSV-2 Equation of State Before and After Critical-Volume Correction ( $v_c = v_p/C_c$ )

Mixture	<i>M</i>	$T_c$		$P_c$		$v_c$		Corrected $v_c$	
		SD (K)	AD (%)	SD (bar)	AD (%)	SD (ml·mol <sup>-1</sup> )	AD (%)	SD (ml·mol <sup>-1</sup> )	AD (%)
CO <sub>2</sub> -H <sub>2</sub> S	8	1.06	0.27	2.29	2.13	9.08	8.74	2.18	1.98
Methane-H <sub>2</sub> S <sup>a</sup>	13	7.80	2.41	9.87	7.69	8.86	7.67	4.19	3.47
Ethane-H <sub>2</sub> S	6	0.29	0.07	0.34	0.25	16.00	11.44	3.13	2.19
Ethane-butane	12	0.70	0.13	0.77	1.02	27.80	14.21	2.18	1.11
Ethane-heptane <sup>a</sup>	10	3.95	0.78	2.04	2.31	40.12	12.00	16.01	4.29
Propane-H <sub>2</sub> S	8	0.68	0.16	1.40	2.07	19.90	12.37	1.28	0.60
Propane-CO <sub>2</sub>	5	1.17	0.29	0.98	0.99	14.78	8.16	2.36	1.28
Propane-octane <sup>a</sup>	7	2.98	0.41	0.85	1.52	53.93	12.00	25.14	5.70
Butane-CO <sub>2</sub>	5	1.70	0.41	1.82	1.77	21.57	11.61	5.47	3.39
Butane-heptane	5	0.81	0.13	0.61	1.31	75.31	21.41	9.42	2.64
Heptane-ethylene <sup>a</sup>	8	6.69	1.10	3.50	3.12	53.15	14.23	17.34	6.67
Overall average		2.53	0.56	2.23	2.21	30.96	12.17	7.49	3.03

<sup>a</sup> Oscillatory convergence.

nonpolar systems listed in Table I is about 0.56% for the critical temperature (with a maximum of 2.41%) and about 2.21% for the critical pressure (with a maximum of 7.69%).

For the 10 polar systems studied, the SD and AD in critical properties are shown in Table II using the conventional mixing rules. The average SD in the critical temperature for all of those systems is 1.84 K (with a maximum of 5.44 K when the convergence is oscillatory as it is in the case for the benzene-ethanol system). The average SD in the critical pressure for the systems listed in Table II is 4.20 bar (with a maximum of about 8.86 bar for benzene-ethanol). On the other hand, the average AD in the critical temperature for these systems is 0.33% (with a maximum of 0.83%), and that in the critical pressure is 4.95% (with a maximum of about 10.34%).

Table III shows a comparison between the calculated SD and AD for the PRSV-2 equation of state (using conventional mixing rules) without and with critical volume correction and those of the work of Li and Kiran [2] (which are based on the group contribution method). The method of Li and Kiran does not need experimentally adjusted interaction parameters to predict the critical properties. It is clear that the prediction of the critical temperature and pressure is always much better on the basis of the PRSV-2 equation of state. The average absolute relative deviations, AD, for the



**Table II.** Standard and Average Deviations in Critical Properties for Some Polar Mixtures Using PRSV-2 Equation of State Before and After Critical-Volume Correction ( $v_c = v_p/C_c$ )

Mixture	<i>M</i>	$T_c$		$P_c$		$v_c$		Corrected $v_c$	
		SD (K)	AD (%)	SD (bar)	AD (%)	SD (ml·mol <sup>-1</sup> )	AD (%)	SD (ml·mol <sup>-1</sup> )	AD (%)
Butane–ammonia	6	1.92	0.42	6.75	7.98	32.24	23.10	6.70	3.80
Methanol– 1-butanol	4	0.19	0.03	5.03	6.05	57.54	28.26	8.66	3.15
Benzene–methanol	8	0.87	0.13	8.86	10.34	49.77	28.82	12.66	5.51
Benzene–ethanol <sup>a</sup>	7	5.44	0.70	3.31	4.67	50.48	24.83	8.20	3.20
Ethylene– chloroform <sup>a</sup>	4	4.21	0.83	6.61	4.96	14.18	10.28	8.31	5.82
1-Butanol–diethyl ether	4	0.73	0.11	0.81	1.52	56.25	18.37	7.97	2.24
SO <sub>2</sub> –dimethyl ether	4	0.58	0.10	1.75	2.34	29.40	17.53	2.53	1.41
SO <sub>2</sub> –diethyl ether	4	0.41	0.06	2.77	4.17	35.35	15.42	3.38	1.22
SO <sub>2</sub> –methyl ethyl ether	5	0.95	0.18	0.39	0.52	30.96	16.02	2.65	1.14
Water–acetic acid	8	0.97	0.11	—	—	84.24	54.54	1.30	0.80
Overall average		1.84	0.33	4.20	4.95	39.50	20.35	6.24	2.83

<sup>a</sup> Oscillatory convergence.

systems listed in Table III, are 0.24 and 1.68% for the critical temperature and 2.53 and 10.45% for the critical pressure.

On the other hand, the PRSV-2 predictive capability of the critical volumes is not as good as its predictive capability of the critical temperature and pressure. The group-contribution method [3] is superior in predicting the critical volume over the PRSV-2 and any other known cubic equation of state. The poor representation of the mixture critical volumes by cubic equations of state is well known and has been widely attributed to the fact that the pure-component critical compressibility calculated from the equation of state is, in general, not equal to the experimental compressibility of most fluids [23]. The above statement is confirmed when one compares the pure-component critical compressibility predicted by the Peng–Robinson equation of state (0.3074) to the range of the experimental compressibilities of the pure compounds used in this study (0.224–0.290).

Since the error between the experimental critical volume and that predicted by any equation of state (including PRSV-2) is so large (see, e.g., Ref. 15), a correction has been introduced in this work to correct for the predicted critical volume. This correction is based on finding the ratio

**Table III.** Standard and Average Deviations in Critical Properties Using the PRSV-2 Equation of State with Critical-Volume Correction ( $v_c = v_p/C_c$ ) and Li-Kiran Work<sup>a</sup>

Mixture	<i>M</i>	$T_c$		$P_c$		$v_c$	
		SD (K)	AD (%)	SD (bar)	AD (%)	SD (ml · mol <sup>-1</sup> )	AD (%)
Ethane-H <sub>2</sub> S	6	0.29	0.07	0.34	0.25	3.13	2.19
		5.91	1.49	7.48	9.57	4.29	2.68
Propane-H <sub>2</sub> S	7	0.68	0.16	1.40	2.07	1.28	0.60
		19.90	4.45	18.60	23.90	6.35	3.64
Heptane-ethylene	8	6.69	1.10	3.50	3.12	17.34	6.76
		15.60	2.87	6.19	5.34	9.85	3.37
Methanol-1-butanol	4	0.19	0.03	5.03	6.05	8.66	3.15
		7.38	1.03	17.70	17.60	11.30	4.81
1-Butanol-diethyl ether	4	0.73	0.11	0.81	1.52	7.79	2.24
		1.18	0.13	1.05	1.82	13.90	3.27
SO <sub>2</sub> -diethyl ether	4	0.41	0.06	2.77	4.17	3.38	1.22
		9.20	1.52	6.65	8.59	15.10	5.60
SO <sub>2</sub> -methyl ethyl ether	5	0.95	0.18	0.39	0.53	2.65	1.14
		1.48	0.24	4.70	6.31	6.81	2.98
Overall average		1.42	0.24	2.03	2.53	6.32	2.47
		8.66	1.68	8.91	10.45	9.66	3.76

<sup>a</sup> First line: PRSV-2 prediction (optimized  $k_{12}$  listed in Table AII) with corrected  $v_c$ . Second line: group-contribution method (Li and Kiran work).

between the predicted critical volume by the PRSV-2 equation of state,  $v_p$ , and the experimental critical volume,  $v_{c, \text{exp}}$ , thus  $C_c = v_p/v_{c, \text{exp}}$ . The calculated values of  $C_c$  are listed in Table AII for reference. When these values have been used to calculate the critical volumes ( $v_c = v_p/C_c$ ) of the systems shown in Tables I and II, the results are as follows. For the non-polar systems listed in Table I, the average SD in critical volumes has fallen from 30.96 ml · mol<sup>-1</sup> before correction to 7.49 ml · mol<sup>-1</sup> after correction, while the average AD has decreased from 12.17 to 3.03%. For the polar systems listed in Table II, the average SD has fallen from 39.50 ml · mol<sup>-1</sup> before correction to 6.24 ml · mol<sup>-1</sup> after correction, while the average AD has decreased from 20.35 to 2.83%. Two representative figures for the percent relative error between predicted and experimental critical volumes versus composition, before and after correction, are presented in Figs. 2 and 3 for the propane-H<sub>2</sub>S and butane-ammonia mixtures, respectively.

For the sake of comparison with the group-contribution method [3], the critical volume correction has been introduced to the systems listed in Table III and the results are superior and even much better than those

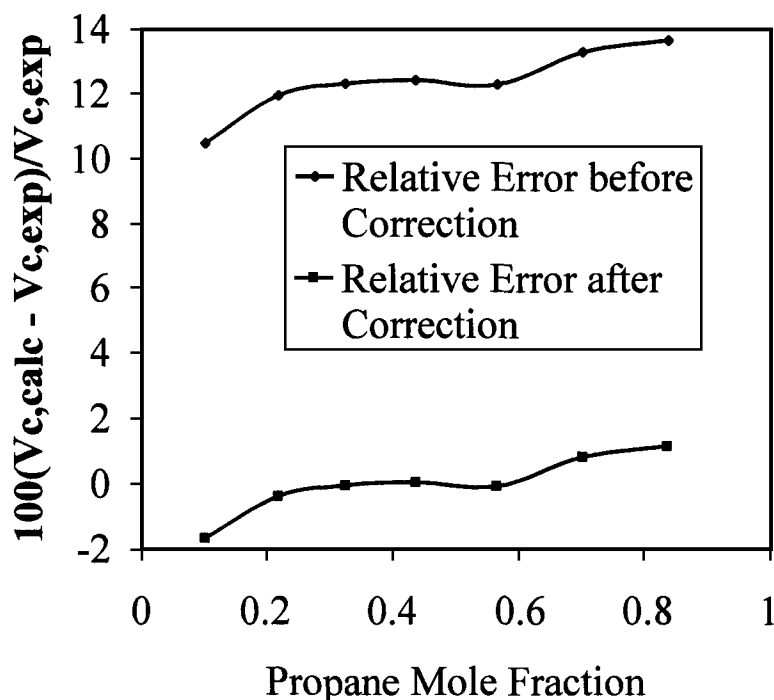


Fig. 2. Percentage relative error between predicted and experimental critical volumes versus composition for the propane(1)-H<sub>2</sub>S(2) mixture.

predicted by the group-contribution method. The respective average values of SD and AD in critical volume before correction were 39.02 ml · mol<sup>-1</sup> and 16.82% [15] and became 6.32 ml · mol<sup>-1</sup> and 2.47% (after correction) compared to 9.66 ml · mol<sup>-1</sup> and 3.76% for Li and Kiran [2].

Finally, for the carbon dioxide-butane system, Table IV shows the point-by-point values of the critical properties using the PRSV-2 equation of state and the values of the critical volume after using the above mentioned correction form. It is clear that the SD and AD for the critical volume have decreased sharply from 21.57 ml · mol<sup>-1</sup> and 11.61% before correction to 5.74 ml · mol<sup>-1</sup> and 3.39% after correction, respectively.

#### 4. CONCLUSIONS

The PRSV-2 equation of state has been used in this work to predict the critical properties of mixtures on the basis of the algorithm adopted by Heidemann and Khalil [10] and explained earlier [15]. The first and second partial derivatives of fugacity with respect to the mole numbers of

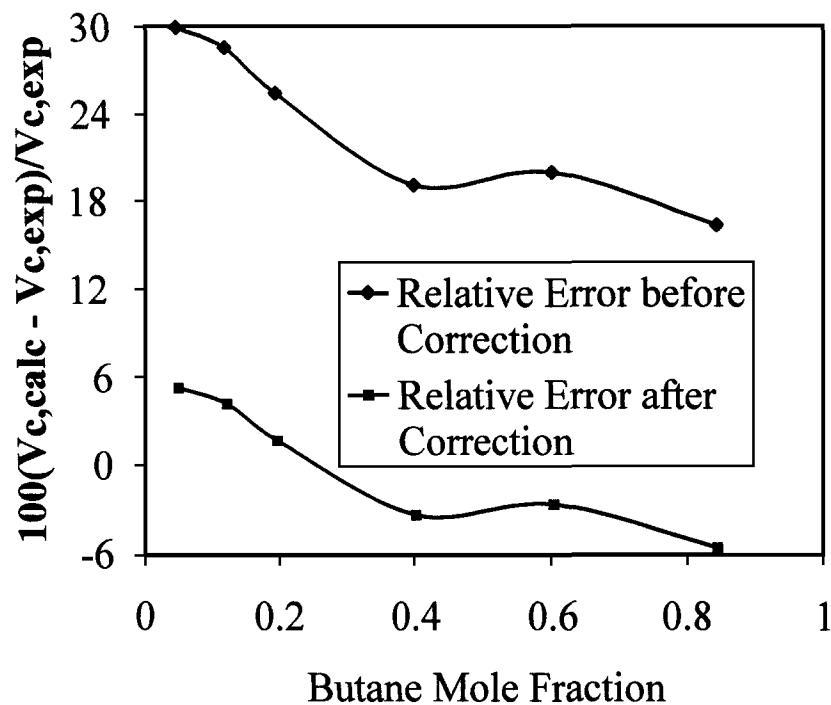


Fig. 3. Percentage relative error between predicted and experimental critical volumes versus composition for the butane(1)-ammonia(2) mixture.

Table IV. Predicted Critical Properties for CO<sub>2</sub>-Butane Using the PRSV-2 Equation of State ( $k_{12}=0.13933$ ) Without and With Critical-Volume Correction

$X_1$	$T_c$ (K)		$P_c$ (bar)		$v_c$ (ml · mol <sup>-1</sup> )		
	Exp.	PRSV-2	Exp.	PRSV-2	Exp.	PRSV-2	PRSV-2 <sup>a</sup>
0.1694	325.93	323.95	79.08	75.76	104.90	125.17	112.15
0.3334	351.71	352.88	81.71	81.15	131.70	143.15	128.25
0.4984	377.21	379.04	75.37	74.91	162.30	173.72	155.65
0.6740	398.76	399.95	62.81	61.94	192.90	211.52	189.51
0.8273	412.26	413.51	51.10	50.10	217.20	246.22	220.61
	SD <sub>T</sub> = 1.70		SD <sub>P</sub> = 1.82		SD <sub>V</sub> = 21.57		SD <sub>V</sub> = 5.74 <sup>a</sup>
	AD <sub>T</sub> = 0.41		AD <sub>P</sub> = 1.77		AD <sub>V</sub> = 11.61		AD <sub>V</sub> = 3.39 <sup>a</sup>

<sup>a</sup> Corrected values using  $v_c = v_p/C_c$ .

the mixture constituents have been evaluated, and the resulting two non-linear equations have been solved simultaneously for the critical temperature and volume. The critical pressure is then calculated from the PRSV-2 equation of state itself. A quasi-Newton technique has been used here to calculate the optimum values of the binary interaction parameters that minimize the deviations between predicted and experimental critical temperatures.

For the 11 nonpolar system and the 10 polar systems listed in Tables I and II, the overall standard deviation using the conventional one-parameter type are, respectively, 2.53 and 1.84 K in the critical temperature and 2.23 and 4.20 bar in the critical pressure. Better predictions are always obtained in both critical temperature and pressure compared to those obtained by the group-contribution method.

The group-contribution method always gives less deviation in the predicted critical volume than any other equation of state. A correction has been introduced in this work to the PRSV-2 predicted critical volume of the form  $v_c = v_p/C_c$ . By using this correction the overall standard deviation, SD, in critical volume for the 21 systems studied in this work has decreased drastically from 35 to 6.9 ml·mol<sup>-1</sup>, while the average of the absolute deviation, AD, has decreased from 16.7 to 2.94%. By using such a correction, the SD and AD for the systems studied by Li and Kiran [2] become very close to or even better than those predicted by the group-contribution method used there.

## APPENDIX A

Table A1. Pure-Component Properties Used in this Work

Compound	$T_c$ (K)	$P_c$ (kPa)	$\omega$	$\kappa_1$	$\kappa_2$	$\kappa_3$	$v_c$ (ml·mol <sup>-1</sup> )
NH <sub>3</sub>	405.6	11289.5	0.25170	0.00100	-0.1265	0.510	72.5
CO <sub>2</sub>	304.2	7382.4	0.22500	0.04285	0.0	0.0	93.9
SO <sub>2</sub>	430.8	7883.1	0.25100	0.03962	NA <sup>a</sup>	NA	122.2
H <sub>2</sub> S	373.2	8940.0	0.10000	0.03160	NA	NA	98.5
H <sub>2</sub> O	647.3	22089.8	0.34380	-0.06635	0.0199	0.443	57.1
Methane	190.6	4595.0	0.01045	-0.00159	0.1521	0.517	99.0
Ethane	305.4	4879.8	0.09781	0.02669	0.1358	0.424	148
Propane	369.8	4249.5	0.15416	0.03136	0.2757	0.447	203
Butane	425.2	3796.6	0.20096	0.03443	0.6767	0.461	255
Heptane	540.1	2735.8	0.35022	0.04648	0.9331	0.496	432

<sup>a</sup> Not Available.

Table AI. (Continued)

Compound	$T_c$ (K)	$P_c$ (kPa)	$\omega$	$\kappa_1$	$\kappa_2$	$\kappa_3$	$v_c$ (ml · mol <sup>-1</sup> )
Octane	568.8	2486.5	0.39822	0.04464	0.6214	0.509	492
Ethylene	282.4	5042.0	0.08652	0.04191	NA	NA	130
Benzene	562.2	4898.0	0.20929	0.07019	0.7939	0.523	259
Methanol	512.6	8095.8	0.56533	-0.16816	-1.3400	0.588	118
Ethanol	513.9	6148.0	0.64439	-0.03374	-2.6846	0.592	167
1-Butanol	563.0	4412.7	0.59020	0.33431	-1.1743	0.642	274
Acetic acid	592.7	5786.0	0.45940	-0.19724	0.8136	0.541	171
Chloroform	536.6	5471.6	0.21600	0.02899	NA	NA	239
Diethyl ether	466.7	3640.0	0.28100	0.05004	NA	NA	280
Dimethyl ether	400.1	5240.0	0.18909	0.05717	-0.1211	0.481	178
Methyl ethyl ether	437.8	4410.0	0.23479	0.16948	0.0515	0.768	221

Table AII. Values of Optimized Conventional Binary Interaction Parameter,  $k_{12}$ , and Critical-Volume Correction Constant,  $C_c$ 

Mixture	$k_{12}$	$C_c = v_p/v_{c, \text{exp}}$
CO <sub>2</sub> -H <sub>2</sub> S	0.115592(8)	1.08743
CO <sub>2</sub> -Propane	0.134531(5)	1.08163
Methane-H <sub>2</sub> S <sup>a</sup>	0.047723(6)	1.07754
	-0.005386(13)	
Ethane-H <sub>2</sub> S	0.094116(6)	1.11445
Ethane-butane	0.033767(12)	1.14211
Ethane-heptane <sup>a</sup>	0.05(10)	1.10329
Propane-H <sub>2</sub> S	0.063486(7)	1.12370
Propane-octane <sup>a</sup>	0.029111(7)	1.11791
Butane-CO <sub>2</sub>	0.139330(5)	1.11614
Butane-heptane <sup>a</sup>	0.022619(5)	1.21450
	0.018492(14)	
Butane-ammonia	0.147287(6)	1.23318
Heptane-ethylene <sup>a</sup>	0.059211(8)	1.13437
Benzene-methanol	0.086253(8)	1.25359
Benzene-ethanol <sup>a</sup>	0.086272(7)	1.24826
Methanol-1-butanol	-0.009107(4)	1.28257
Water-acetic acid	-0.15469(8)	1.54540
Ethylene-chloroform <sup>a</sup>	-0.002443(4)	1.08163
1-Butanol-diethyl ether	0.050966(4)	1.18366
SO <sub>2</sub> -dimethyl ether	-0.111223(4)	1.17530
SO <sub>2</sub> -diethyl ether	-0.038320(4)	1.17021
SO <sub>2</sub> -methyl ethyl ether	-0.080425(5)	1.16016

<sup>a</sup> Oscillatory convergence.

## APPENDIX B

Expressions for First and Second Derivatives of Fugacity of Component  $m$  with Respect to Number of Moles of Species  $l$  and  $k$ 

$$n_T \partial(\ln f_m) / \partial n_l = C_1 - C_2 - C_3 \{ C_4 / C_5 - C_6 / C_5^2 \} - C_7 + C_8 + C_9 \\ + C_{10} C_{15} \{ C_{11} + C_{12} - C_{13} - C_{14} \} \\ + C_{10} (C_{16} - C_{17}) (C_{18} - C_{19})$$

where

$$C_1 = b_m v / b(v - b)$$

$$C_2 = b_m b_l v(v - 2b) / [b(v - b)]^2$$

$$C_3 = b_m v / RT$$

$$C_4 = \sum_j^N x_j (a_{ji} + a_{ij})$$

$$C_5 = b(v^2 + 2vb - b^2)$$

$$C_6 = ab_l(v^2 + 4vb - 3b^2)$$

$$C_7 = b_m / b - b_m b_l / b^2$$

$$C_8 = \delta_{ml} / x_m, \quad \delta = 1.0 \text{ for } m = l, \quad \delta = 0 \text{ for } m \neq l$$

$$C_9 = b_l / (v - b)$$

$$C_{10} = 1/2 \sqrt{2} RT$$

$$C_{11} = C_4 b_m / b^2$$

$$C_{12} = b_l \sum_j^N x_j (a_{jm} + a_{mj}) / b^2$$

$$C_{13} = 2ab_m b_l / b^3$$

$$C_{14} = (a_{lm} + a_{ml}) / b$$

$$C_{15} = \ln \{ (v + (1 + \sqrt{2})b) / (v + (1 - \sqrt{2})b) \}$$

$$C_{16} = a C_{10} b_m / b^2$$

$$C_{17} = C_{10} \sum_j^N x_j (a_{mj} + a_{jm}) / b$$

$$C_{18} = (1 + \sqrt{2}) b_l / (v + (1 + \sqrt{2})b)$$

$$C_{19} = (1 - \sqrt{2}) b_l / (v + (1 - \sqrt{2})b)$$

$$\begin{aligned}
& n_T^2 \partial^2 (\ln f_m) / \partial n_l \partial n_k \\
& = [-D_1 - D_2 + D_3 - D_4 + D_6 + D_9 - D_{10} + D_{11} + D_{12} - D_{13} + D_{14}] \\
& \quad + C_{10} C_{15} \{D_{15} - D_{16} + D_{17} - D_{18} - D_{20} + D_{21} + D_{22}\} \\
& \quad + D_{23} \{D_{24} + D_{25} - D_{26} - D_{27}\} + D_{28} \{D_{29} - D_{30} - D_{31} + D_{32}\} \\
& \quad + D_{33} \{D_{34} - D_{35}\}
\end{aligned}$$

where

$$\begin{aligned}
D_1 &= b_m b_k v(v-2b)/[b(v-b)]^2, \\
D_2 &= b_m b_l v(v-2b-2b_k)/[b(v-b)]^2 \\
D_3 &= 2b_m b_l b_k v(v-2b)^2/[b(v-b)]^3, & D_4 &= b_m v(a_{kl} + a_{lk})/(RTC_5) \\
D_5 &= v^2 + 4bv - 3b^2, & D_6 &= b_m b_k v C_4 D_5 / [RTC_5^2] \\
D_7 &= v D_5 \sum_j^N x_j (a_{jk} + a_{kj}), & D_8 &= ab_k v(4v-6b) \\
D_9 &= b_m b_l (D_7 + D_8) / [RTC_5^2] \\
D_{10} &= 2ab_m b_l b_k v(D_5^2) / [RTC_5^3], & D_{11} &= b_m b_k / b^2 \\
D_{12} &= b_m b_l / b^2 - 2b_m b_l b_k / b^3, & D_{13} &= \delta_{mlk} / x_m^2
\end{aligned}$$

where  $\delta = 1.0$  for  $m = l = k$ , and  $\delta = 0$  for  $m \neq l \neq k$ .

$$\begin{aligned}
D_{14} &= b_l b_k / (v-b)^2, & D_{15} &= b_m (a_{kl} + a_{lk}) / b^2 \\
D_{16} &= 2b_m b_k \sum_j^N x_j (a_{jl} + a_{lj}) / b^3, & D_{17} &= b_l (a_{mk} + a_{km}) / b^2 \\
D_{18} &= 2b_l b_k \sum_j^N x_j (a_{jm} + a_{mj}) / b^3 \\
D_{20} &= 2b_m b_l \sum_j^N x_j (a_{jk} + a_{kj}) / b^3, & D_{21} &= 6ab_m b_l b_k / b^4 \\
D_{22} &= b_k (a_{ml} + a_{lm}) / b^2, & D_{23} &= C_{10} (C_{18} - C_{19}) b_k / b_l \\
D_{24} &= b_m \sum_j^N x_j (a_{jl} + a_{lj}) / b^2, & D_{25} &= b_l \sum_j^N x_j (a_{jm} + a_{mj}) / b^2 \\
D_{26} &= 2ab_m b_l / b^3, & D_{27} &= (a_{lm} + a_{ml}) / b
\end{aligned}$$



$$D_{28} = C_{10}(C_{18} - C_{19}), \quad D_{29} = b_m \sum_j^N x_j (a_{jk} + a_{kj})/b^2$$

$$D_{30} = 2ab_m b_k/b^3, \quad D_{31} = (a_{mk} + a_{km})/b$$

$$D_{32} = b_k \sum_j^N x_j (a_{jm} + a_{mj})/b^2, \quad D_{33} = C_{10}(C_{19}^2 - C_{18}^2) b_k/b_l$$

$$D_{34} = ab_m/b^2, \quad D_{35} = \sum_j^N x_j (a_{jm} + a_{mj})/b$$

## NOMENCLATURE

<i>a</i>	Attraction parameter in the Peng–Robinson equation of state
<i>A</i>	$aP/(RT)^2$
<i>A</i>	Helmholtz free energy
AD	Average of the absolute relative deviations defined by Eq. (19)
<i>b</i>	Repulsion parameter in the Peng–Robinson equation of state
<i>B</i>	$bP/RT$
<i>C</i>	Cubic term defined in Eq. (18)
<i>C<sub>c</sub></i>	Correction constant for critical volume
<i>C'</i>	Derivative of the cubic term, <i>C</i>
det	Determinant
<i>f</i>	Fugacity
<i>k</i>	Binary interaction parameter
<i>M</i>	Number of data points
<i>n</i>	Number of moles
<i>N</i>	Number of components
<i>P</i>	Pressure (bar)
<b>Q</b>	Matrix in the quadratic terms defined in Eq. (17)
<i>Q'</i>	Derivative of the <b>Q</b> matrix
<i>q</i>	Elements of the <b>Q</b> matrix defined by Eq. (16)
<i>R</i>	Universal gas constant
SD	Standard deviation defined by Eq. (20)
<i>T</i>	Absolute temperature (K)
<i>V</i>	Volume (ml)
<i>v</i>	Molar volume (ml · mol <sup>-1</sup> )
<i>x</i>	Mole fraction
<i>Z</i>	Compressibility factor

**Greek Letters**

$\Delta$	Difference in property
$\varepsilon$	Error tolerance
$\kappa$	Function of reduced temperature and acentric factor, Eq. (5)
$\kappa_0$	Function of acentric factor, Eq. (6)
$\kappa_1, \kappa_2, \kappa_3$	Pure-compound parameters in PRSV-2 equation of state
$\omega$	Acentric factor

**Subscripts**

c	Critical property
exp	Experimental
$i, j, k, l, m, n$	Component number
$m$	Mixture property
$o$	Initial state
p	Predicted
r	Reduced property
$T$	Total property

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