

## CALCULATION OF $H_m^E$ FOR BINARY MIXTURES: SOME CONSEQUENCES OF THE CONVERSION OF CUBIC EQUATIONS OF STATE TO HARD-SPHERE VERSIONS \*

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### ABSTRACT

It has been reported by Mosedale and Wormald [1], and by Christensen et al. [2,3], that replacement in cubic equations of state (EOS) of the free volume term,  $1/(V_m - b)$ , with a hard-sphere expression improves the fit to the enthalpies of mixing,  $H_m^E$ , at near critical, constant, temperatures and pressures for binary mixtures. Further improvements can be obtained in some cases with Kreglewski's square-well combining rule for  $a_{12}$  [4], and with a temperature-dependent  $b$  parameter [5]. For mixtures of  $\text{CO}_2$  with a hydrocarbon, the improvements appear to allow estimates of  $H_m^E$  data that are as reliable as correlations with one adjustable interaction parameter. Attempts to use a hard-sphere expression in the Peng–Robinson equation lead to an unacceptable EOS. Singularities can be used to forecast when a hard-sphere version will be unacceptable.

### INTRODUCTION

Large negative and positive  $H_m^E$  values are observed when two substances are mixed at constant temperature and pressure, near and between the critical points of the pure substances [3] due to phase changes below the critical line, and to large changes in density and compressibility above the critical line. An illustration for two components with critical points close together is shown in Fig. 1 [6], and for two components with critical points far apart, in Fig. 2 [7]. Wormald and co-workers [8] have shown how an EOS can be used to calculate  $H_m^E$  data.

In this paper, cubic EOS will be compared with hard-sphere versions and improvements in fits to the  $H_m^E$  data will be shown when a hard-sphere expression is used. The reasons why a hard-sphere Peng–Robinson equation is unacceptable will be discussed.

\* Dedicated to Professor James J. Christensen in memory of his contribution to innovation in calorimetry.

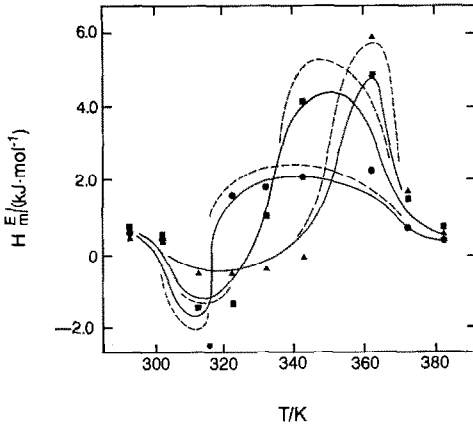


Fig. 1. Plots of  $H_m^E$  against  $T$  at 5.15 MPa for three mole fractions  $x$  for  $x\text{C}_2\text{H}_6 + (1-x)\text{CHF}_2\text{Cl}$ ; interpolated experimental values [6].  $\bullet$ ,  $x = 0.8$ ;  $\blacksquare$ ,  $x = 0.5$ ;  $\blacktriangle$ ,  $x = 0.2$ ; —, SV EOS,  $k_{AB} = 0.917$ ; - - - - -, ASV EOS,  $k_{AB} = 0.938$ . Values for  $T_c$  and  $P_c$  are 305.4 K and 4.88 MPa for  $\text{C}_2\text{H}_6$ , and 369.2 K and 4.98 MPa for  $\text{CHF}_2\text{Cl}$ .

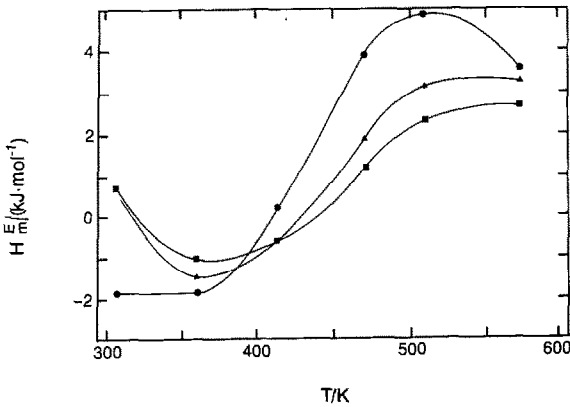


Fig. 2. Plots of  $H_m^E$  against  $T$  at three pressures for mole fraction  $x = 0.5$ , for  $\text{CO}_2 + n\text{-C}_6\text{H}_{14}$  [7]; interpolated experimental values:  $\bullet$ , 7.50 MPa;  $\blacktriangle$ , 10.50 MPa;  $\blacksquare$ , 12.50 MPa. Values for  $T_c$  and  $P_c$  are 304.21 K and 7.38 MPa for  $\text{CO}_2$ , and 507.4 K and 2.97 MPa for  $n\text{-C}_6\text{H}_{14}$ .

## CALCULATIONS

The experimental  $H_m^E$  data used in the calculations were measured at constant temperature and pressure [3]. The calculation of  $H_m^E$  from an EOS [8] proceeded through the residual enthalpies,  $H^*$ , where

$$H^* = \int_{\infty}^V (T(\partial P/\partial T)_V - P) dV + PV - RT \quad (1)$$

Experimental pressures and temperatures were used with each EOS to solve for the volumes.

All calculations, unless otherwise referenced, were conducted on a UNISYS 1100/70 H2 mainframe. The word size was 36 bits and single precision was used. Computer programs were written in Pascal 1100. Using the calculations of  $H_m^E$  for the mixings of  $\text{CO}_2 + n\text{-C}_6\text{H}_{14}$  for 480 data values as an example, the cubic SV EOS with volumes found analytically, and with  $k_{AB} = 0.825$ , required 39 seconds of CPU time to compile and run. The same calculations with the fifth-degree PYSV EOS, with volumes found numerically, and with  $k_{AB} = 0.923$ , required 48 seconds of CPU time. An optimization routine that used a simplex [9] was written to solve for the adjustable parameters of an EOS. The search for the above  $k_{AB}$  values required 29 iterations and 2 minutes of CPU time for the SV EOS, and 28 iterations and 5 minutes 37 seconds of CPU time for the PYSV EOS.

When eqn. (8) was used for a temperature dependent  $b$ , the inclusion of  $\partial b/\partial T$  in the integrand of eqn. (1) resulted in calculated  $H_m^E$  values that differed greatly from the experimental values. While a temperature-dependent  $b$  parameter improves the calculation of  $H_m^E$  by hard-sphere EOS, apparently the temperature derivative of eqn. (8) inadequately reflects the residual enthalpies. Therefore,  $\partial b/\partial T$  was not used in the integrand of eqn. (1) for the calculations of  $H_m^E$ .

#### EQUATIONS OF STATE COMPARED

Cubic EOS can be represented in reduced form as

$$P_R = \frac{(1/Z_c)T_R}{V_R - B} - \frac{(a/Z_c^2)\phi(T_R, \omega)}{V_R^2 + \alpha B V_R + \beta B^2} \quad (2)$$

where  $P_R$ ,  $V_R$ , and  $T_R$  represent the reduced pressure, volume, and temperature, respectively ( $P/P_c$ ,  $V/V_c$ , and  $T/T_c$ , where the subscript  $c$  means the critical point),  $B$  is the reduced excluded volume,  $b/V_c$ , and  $Z_c$  and  $a$  are constants derived from the critical point conditions

$$(\partial P/\partial V)_T = (\partial^2 P/\partial V^2)_T = 0 \quad (3)$$

The values of  $\alpha$  and  $\beta$  and the function  $\phi$  distinguish the various cubic EOS. For example,  $\alpha = \beta = 0$  indicates the van der Waals EOS (VDW). If  $\alpha = 1$  and  $\beta = 0$ , the Soave EOS (SV) [10] is formed. With  $\alpha = 2$  and  $\beta = 1$ , the Peng–Robinson EOS (PR) [11] is expressed. The function  $\phi$  is set to 1 for VDW, is  $1/T^{1/2}$  for the Redlich–Kwong EOS (RK) [12], and has the form  $(1 + M[1 - (T/T_c)^{1/2}])^2$  for SV and PR, and  $M = c_1 + c_2\omega + c_3\omega^2$ , where  $c_1$ ,  $c_2$ , and  $c_3$  are constants correlated with vapor pressure data for a set of non-electrolytes [11,13]. Omega  $\omega$  represents Pitzer's acentric factor [14]. Other restrictions on  $\alpha$ ,  $\beta$  and  $\phi$  can show other EOS.

TABLE 1

Hard-sphere expressions used to replace  $1/(V_R - B)$  in eqn. (2)

EOS	Expression
Percus-Yevick (PY) [15]	$\frac{1}{V_R} \left[ \frac{1 + \eta_R + \eta_R^2}{(1 - \eta_R)^3} \right]$
Carnahan-Starling (CS) [16]	$\frac{1}{V_R} \left[ \frac{1 + \eta_R + \eta_R^2 - \eta_R^3}{(1 - \eta_R)^3} \right]$
Andrews (A) [17]	$\frac{28 \eta_R^2}{B Q} - \frac{4 \ln(1 - \eta_R)}{B}$ $\frac{-14.38 \ln Q}{B} - \frac{47.31 \ln \left[ \frac{1 - 0.7210 \eta_R}{1 - 1.350 \eta_R} \right]}{B}$ $Q = 1 - 2.017 \eta_R + 0.9736 \eta_R^2$ $B = b/V_c$ $\eta_R = B/4V_R$

Hard-sphere versions can be formed by replacement of the free volume term  $1/(V_R - B)$  with an expression whose values agree with computer simulations of hard-sphere fluids. Three are shown in Table 1.

When the critical point conditions of eqn. (3) are applied to an EOS, the excluded volume,  $b$ , and the attraction parameter,  $a$ , can be evaluated. Normally, their values are calculated from experimental  $P_c$  and  $T_c$  data together with the ideal gas value for the gas constant  $R$ . Thus,  $V_c$  and the critical compressibility factor,  $Z_c$ , become fixed and are usually greater than

TABLE 2

Values of  $Z_c$ ,  $a$ , and  $B$  in eqn. (2) for several EOS derived from the critical point condition  $(\partial P/\partial V)_T = (\partial^2 P/\partial V^2)_T = 0$ 

EOS	$Z_c$	$B$	$a$
VDW	0.375	$\frac{1}{3}$	0.4219
PYVDW	0.3599	0.5146	0.49348
CSVVDW <sup>a</sup>	0.3590	0.5217	0.4964
SV	$\frac{1}{3}$	0.2602	0.4275
PYSV	0.3149	0.33217	0.4610
CSSV <sup>b</sup>	0.3157	0.3326	0.4619
PR	0.3074	0.2531	0.4572
PYPR	0.2825	0.3442	0.50994
CSPR <sup>a,b</sup>	0.2763	0.3538	0.51161

<sup>a</sup> Harmens and Jeremiah [18].<sup>b</sup> ASV and APR EOS have been formulated using the same values as CSSV and CSPR.

the experimental values. Table 2 shows the results for  $Z_c$ ,  $B$ , and  $a$  in eqn. (2) for several EOS. Hard-sphere versions have lower  $Z_c$  values than the cubic versions.

#### IMPROVEMENTS WITH A HARD-SPHERE EXPRESSION

Mosedale and Wormald [1] mixed argon and methane in the critical region and found that the  $H_m^E$  were fitted better by CSVDW than by VDW, and by CSRK than by RK. Christensen et al. [2] reported that  $H_m^E$  in the critical region were fitted better by CSRK than by RK, by CSSV then by SV, and by CSSV than by CSRK for mixings of ethane and chlorodifluoromethane (Freon-22). An illustration of the progression [3] can be seen in Fig. 3 for mixings of ethane and chlorodifluoromethane (Freon-22) at 5.15 MPa and 363.15 K.

The correlations in Table 3 can be used to compare standard deviations for the cubic SV with the PYSV hard-sphere version at each temperature and pressure of measurement [7] for the mixings of carbon dioxide and *n*-hexane. The largest values for  $H_m^E$ , which occur at 308.15 K and 7.5 MPa for negative  $H_m^E$  values and at 510.15 K and 7.5 MPa for positive  $H_m^E$  values, are better correlated by the hard-sphere version. The cubic EOS correlation has lower standard deviations at most of the intermediate temperatures. A similar pattern can be seen in Fig. 1 for the mixings of ethane and chlorodifluoromethane. There the solid curves represent the

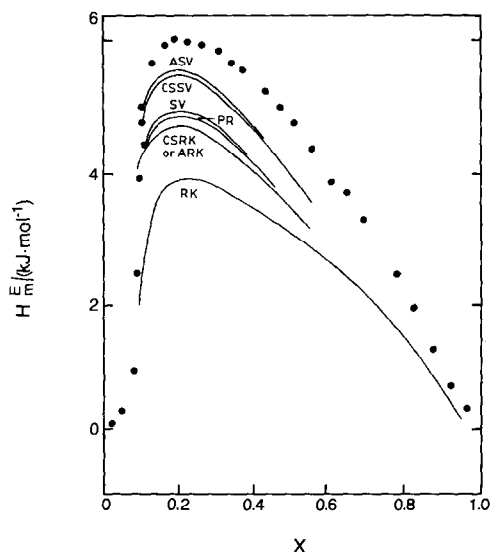


Fig. 3. Plots of  $H_m^E$  against mole fraction  $x$  for  $x\text{C}_2\text{H}_6 + (1-x)\text{Freon-22}$  at 363.15 K and 5.15 MPa: ●, experimental data [6]; —, various EOS [3].

TABLE 3

Comparison of fits of  $H_m^E$  data [7] as a function of temperature and pressure for  $\text{CO}_2 + n\text{-C}_6\text{H}_{14}$ ; standard deviations  $s$  ( $\text{J mol}^{-1}$ )

$T$ (K)	$P$ (MPa)	Max $H_m^E$ ( $\text{kJ mol}^{-1}$ )	Correlations		PYSV predictions <sup>a</sup>	
			SV ( $k_{AB}$ 0.825)	PYSV <sup>a</sup> ( $k_{AB}$ 0.924)	$b \neq f(T)$	$b = f(T)$
308.15	7.5	-3.8	582	427	482	358
	10.5	0.67	318	532	597	390
	12.5	0.85	251	428	492	300
358.15	7.5	-1.8	165	207	216	159
	10.5	-1.8	236	192	191	164
	12.5	-1.4	337	257	228	192
413.15	7.5	2.3	143	383	320	240
	10.5	1.4	159	410	306	214
	12.5	0.84	144	326	218	140
470.15	7.5	4.4	57	428	308	185
	10.5	2.8	38	423	279	147
	12.5	2.1	58	400	263	141
510.15	7.5	5.1	394	135	212	265
	10.5	3.3	99	222	119	79
	12.5	2.7	97	216	106	61
573.15	7.5	3.8	288	342	411	291
	10.5	3.5	285	270	356	285
	12.5	2.8	144	134	193	154
All 480 values			248	341	328	229

<sup>a</sup> The Graboski–Daubert expression [13] for  $M$  was replaced by  $M = 0.4343 + 1.2308\omega - 0.2559\omega^2$ .

correlations with the cubic SV. The ASV hard-sphere version, represented by the broken curves, fits better the largest of the minima and maxima [3]. Intermediate temperatures are fitted better by the cubic EOS [3]. The correlations in Table 4 can be used to compare standard deviations for several binary systems over a range of temperatures and pressures in the critical region. For some the correlations of the hard-sphere version are better, for others the cubic EOS is the better fit. The greatest difference occurs for the mixtures of carbon dioxide with pyridine.

In order to obtain correlations with PYSV that were as good as those with SV, the Graboski–Daubert expression [13],  $M = 0.48508 + 1.55171\omega - 0.15613\omega^2$ , used with SV, was replaced by the expression,  $M = 0.4343 + 1.2308\omega - 0.2559\omega^2$ , whenever PYSV was used. The latter expression for  $M$  was obtained by a best fit (an average of 6.6 percent over all the data) to 444 pairs of single-phase residual enthalpies and molar volumes taken from IUPAC [19] that ranged from  $P_R = 0.5$  to 2.7 and  $T_R = 0.7$  to 2.3.

The expression  $V_R - B$  in eqn. (2) can be rationalized as free volume (total volume less excluded volume) if only binary collisions are assumed

TABLE 4

Comparison of overall fits of  $H_m^E$  data [3] for several systems: standard deviations,  $s$ ,  $J\ mol^{-1}$ 

No. of data values $T, P$ range (K, MPa)	Max $H_m^E$ ( $kJ\ mol^{-1}$ )	Correlations		PYSV predictions <sup>a</sup>	
		SV ( $k_{AB}$ )	PYSV <sup>a</sup> ( $k_{AB}$ )	$b \neq f(T)$	$b = f(T)$
$CO_2 + n-C_6H_{14}$					
480 308–573 7.5–12.5	5.1	(0.825) 248	(0.924) 341	328	229
$CO_2 + C_5H_5N$					
286 308–573 7.5–12.5	9.5	(0.900) 208	(0.968) 629	573	432
$CO_2 + C_7H_8$					
483 308–573 7.5–12.5	8.1	(0.840) 341	(0.920) 516	468	404
$CO_2 + n-C_{10}H_{22}$					
322 283–573 7.6, 12.5	4.8	(0.785) 482	(0.914) 417	404	361
$C_2H_6 + CHClF_2$ <sup>b</sup>					
275 293–363 5.15	6.0	(0.917) 433	(0.979, ASV) 319	(ASV) 875	919
$C_3H_8 + CCl_2F_2$					
470 353–398 4.45	3.2	(0.971) 358	(0.979, ASV) 209 <sup>b</sup>	(ASV) 713 <sup>b</sup>	768

<sup>a</sup> The Graboski–Daubert expression [13] for  $M$  was replaced by  $M = 0.4343 + 1.2308\omega - 0.2559\omega^2$ .

<sup>b</sup> Ref. 3.

[20]. The assumption is invalid at critical point densities. The distinction between a binary collision, cubic EOS, and its hard-sphere version can be seen in Fig. 4 where sketches of the reduced critical isotherm are displayed for SV and for PYSV. Changes in singularities when PYSV is formed from SV are marked with arrows. The singularities  $-B$  and zero arise from the

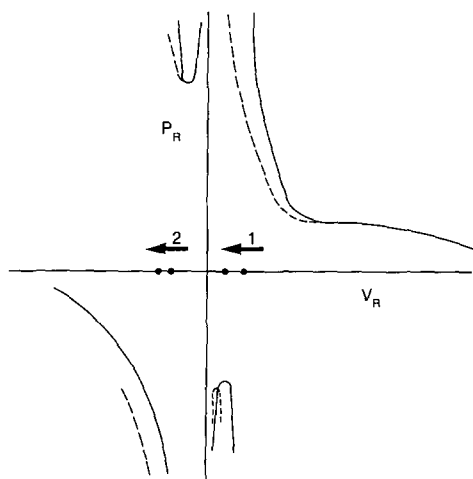


Fig. 4. Reduced critical isotherms  $P_R$  against  $V_R$  for the SV EOS and the PYSV EOS: —, SV EOS; - - - - -, PYSV EOS. Changes in singularities upon forming PYSV from SV:  $\overset{1}{\rightarrow}$ , 0.260 to 0.083 from the collision term;  $\overset{2}{\rightarrow}$ , -0.260 to -0.332 from the attraction term.

attraction term ( $1/V_R(V_R + B)$ ). The positive singularity arises from the collision term, and is equal to  $+B = 0.260$  for SV (from  $1/(V_R - B)$ ) and  $+B/4 = 0.083$  for PYSV (from  $1/(1 - \eta_R)^3$ ). The binary collision, free volume SV EOS is too incompressible. The difference becomes significant at densities greater than critical. The CSSV and ASV equations, as well as isotherms other than  $T_R = 1$ , show the same feature.

When calculations with SV and PYSV are compared with experimental data [19] for carbon dioxide in and near the critical region, calculated volumes are too large, and residual enthalpies are insufficiently negative for SV. With PYSV, calculated volumes are usually smaller than experimental volumes, and residual enthalpies are excessively negative.

All of the results cited used mixing rules that are quadratic in mole fraction for the mixtures

$$a \text{ or } b = \sum_{i=1}^2 \sum_{j=1}^2 x_i x_j a_{ij} \text{ or } b_{ij} \quad (4)$$

an arithmetic mean combining rule for  $b_{12}$

$$b_{12} = (b_{11} + b_{22})/2 \quad (5)$$

and a geometric mean combining rule for  $a_{12}$

$$a_{12} = k_{12}(a_{11}a_{22})^{1/2} \quad (6)$$

where  $k_{12}$ , the interaction parameter, is adjusted until the lowest standard deviation is found between experimental and calculated  $H_m^E$ .

A change in the combining rule for  $a_{12}$ , and the conversion of  $b$  to a temperature-dependent parameter, have been found to improve the hard-



sphere EOS fit to some  $H_m^E$  data in the critical region. These improvements for  $\text{CO}_2 + n\text{-C}_6\text{H}_{14}$  for each temperature and pressure of measurement [7] are shown in Table 3 as PYSV predictions. Kreglewski's square-well combining rule [4]

$$a_{12} = 2\alpha_1\alpha_2a_{11}a_{22}/(\alpha_2^2a_{11} + \alpha_1^2a_{22}) \quad (7)$$

is predictive in that it has no adjustable parameter. When eqn. (7) is used in place of eqn. (6), PYSV predictions,  $b \neq f(T)$ , in Table 3, are better than the PYSV correlations at most of the intermediate temperatures and pressures. An expression for  $b(T)$  attributed to Fermeglia by Skjold-Jorgensen [5]

$$b(T) = b_c\{1.065655[1 - 0.12 \exp(-2T_c/3T)]\}^3 \quad (8)$$

improves the predictions further.

Overall fits for the same changes are compared for several systems in Table 4. It appears that, for mixings of  $\text{CO}_2$  and a hydrocarbon, the use of eqns. (7) and (8) provides a predictive estimate of the enthalpies of mixing to an overall fit of 8% or less of the maximum  $H_m^E$  values. Unfortunately, overall fits are much worsened when the same changes are extended to the mixings of a freon and a hydrocarbon.

#### SINGULARITIES FORECAST AN UNACCEPTABLE EOS

When attempts were made to use the PYPR EOS to calculate  $H_m^E$  for the mixings of  $\text{CO}_2$  and  $n$ -hexane, convergence difficulties were encountered at the low temperatures. At high temperatures, calculated  $H_m^E$  values are negative whereas experimental values are positive. Harmens and Jeremiah [18] reported convergence difficulties with CSPR. They argued that dense phase volumes were too small at very low pressures and at high supercritical pressures. They concluded that a hard-sphere expression cannot be combined with a Peng-Robinson attraction term. The reason why can be seen in Fig. 5. The reduced critical isotherm,  $P_R$  against  $V_R$ , is displayed as the solid curve in Fig. 5 for the PR EOS [21]. The broken curve represents the PYPR critical isotherm. The singularities for the PR EOS occur at  $B = 0.253$  from the binary collision term,  $1/(V_R - B)$ , and  $(-1 \pm \sqrt{2})B$ , or  $+0.105$  and  $-0.611$ , from the attraction term,  $1/(V_R^2 + 2BV_R - B^2)$ . As described by Lawal [21], there can be positive roots less than those valid for the high pressure fluid, or liquid if  $T_R < 1$ , caused by the positive singularity that arises from the attraction term. These roots can be seen in the solid parabola of Fig. 5 at high pressures. Nevertheless, Lawal [21] argues that if the smallest positive root greater than  $B$  is chosen, no difficulties arise with the PR equation because the positive singularity from the attraction term occurs at a volume less than the smallest possible liquid phase root. As can be seen in the broken curves of Fig. 5, these positions are reversed in PYPR.

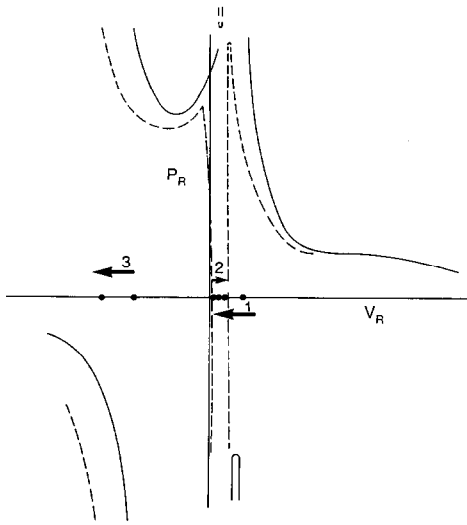


Fig. 5. Reduced critical isotherms  $P_R$  against  $V_R$  for the PR EOS and the PYPR EOS: —, PR EOS [21]; - - - - -, PYPR EOS. Changes in singularities upon forming PYPR from PR:  $\xrightarrow{1}$ , 0.253 to 0.086 from the hard-sphere term;  $\xrightarrow{2}$ , 0.105 to 0.143 from the attraction term;  $\xrightarrow{3}$ , -0.611 to -0.831 from the attraction term.

The positive singularity from the collision term is shifted from  $V_R = B = 0.253$  to  $V_R = B/4 = 0.086$  when PR is changed to PYPR. The positive singularity from the attraction term is shifted from  $V_R = +0.105$  to  $+0.143$ . These shifts are marked with arrows in Fig. 5. Liquid phase volumes may exist that are less than the volume of the attraction term singularity. As a consequence of the shift in singularities, the maximum seen in the broken curve is forced in the PYPR isotherm at high pressures. The maximum occurs at a reduced pressure of 72 for the critical isotherm, 31 when  $T_R$  is 0.9, and -1 when  $T_R$  is 0.8. When  $T_R \leq 0.8$ , there is no liquid phase for the PYPR EOS! The pattern with CSPR and APR is the same. There are still spurious positive roots at very low pressures, and again at very high pressures, as can be seen in the broken curves of Fig. 5, and as observed by Harmens and Jeremiah [18]. The singularities show us when the EOS is unacceptable. On the other hand, the singularities in Fig. 4 predict no difficulties for PYSV.

## CONCLUSIONS

It has been shown that acceptable hard-sphere versions of cubic EOS fit enthalpy of mixing data in the critical region as well as the original cubic EOS. Singularities must be used to decide if a hard-sphere EOS is acceptable. Singularities greater than or equal to  $B/4$  yield EOS with spurious

roots for volumes and compressibilities. Use of Kreglewski's combining rule and a temperature-dependent  $b$  parameter with an acceptable hard-sphere EOS can provide predictive estimates for CO<sub>2</sub> and hydrocarbon mixings, but fail for mixings between a hydrocarbon and a freon.

#### ACKNOWLEDGEMENTS

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