Vapor-Liquid Equilibria at High Pressures: Calculation of Partial Molar Volumes in Nonpolar Liquid Mixtures

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Thermodynamic analysis of high-pressure vapor-liquid equilibria requires information on the effect of pressure on liquid phase fugacities; this information is given by partial molar volumes in the liquid mixture. A method for predicting these partial molar volumes is presented here. First, molar volumes of saturated liquid mixtures are computed by extending to mixtures the corresponding states correlation of Lyckman and Eckert. These mixture volumes are then used to calculate partial molar volumes with an expression based on a modification of the Redlich-Kwong equation. At high pressures partial molar volumes are strong functions of the composition and in the critical region, may be positive or negative. Calculations are sensitive to the characteristic energy between dissimilar molecules; this energy is generally lower than that given by the geometric-mean rule. Calculated results are in good agreement with experimental data for seven systems containing paraffinic and aromatic hydrocarbons, carbon dioxide, and hydrogen sulfide.

To be useful, a thermodynamic treatment of high-pressure vapor-liquid equilibria must describe how the fugacity of each component, in each phase, depends on the temperature, pressure, and composition. In the vapor phase, this dependence is given by the fugacity coefficient which can be found from vapor-phase volumetric properties as given by an equation of state. In the liquid phase it is more convenient to express the fugacity of a component as the product of the mole fraction, an arbitrary standard state fugacity and an activity coefficient; the effect of temperature, pressure, and composition on the fugacity of a component in the liquid phase is determined by the effect of these variables on the activity coefficient. In this work we are concerned with the effect of pressure on the activity coefficient.

At low or moderate pressures, liquid-phase activity coefficients are very weakly dependent on pressure and, as a result, it has been customary to assume that, for practical purposes, activity coefficients depend only on temperature and composition. In many cases this is a good assumption but for phase equilibria at high pressures, especially for those near critical conditions, it can lead to serious error.

When the standard state fugacity is defined at a constant pressure, then for any component *i* the pressure dependence of the activity coefficient  $\gamma_i$  is given exactly by

$$\left(\frac{\partial \ln \gamma_i}{\partial P}\right)_{T,x} = \frac{\overline{\nu}_i}{RT} \tag{1}$$

On the other hand, when the standard state fugacity is defined at the total pressure of the system, Equation (1) must be modified to

$$\left(\frac{\partial \ln \gamma_i}{\partial P}\right)_{T,x} = \frac{\overline{v_i} - v_i^{\circ}}{RT}$$
(1a)

By judicious choice, it is sometimes possible to use a standard state such that  $\overline{v}_i \approx v_i^{\circ}$ , in which case the activity coefficient is very nearly independent of pressure (17). However, since  $\overline{v}_i$  is a function of composition, whereas  $v_i^{\circ}$  is not, such a happy choice of standard state can make the right-hand side of Equation (2) very small over only a narrow range of composition. At high pressures in the critical region,  $\overline{v}_i$  is usually a strong function of composition, especially for heavy components where  $\overline{v}_i$  frequently changes sign as well as magnitude.

Experimental activity coefficients obtained at P, the total pressure of the system, can be corrected to a constant, arbitrary reference pressure  $P^r$  by integration of Equation (1):

$$\gamma_i^{(P^{\tau})} = \gamma_i^{(P)} \exp \int_P^{P^{\tau}} \frac{\overline{v}_i}{RT} dP$$
(2)

Equation (2) defines adjusted, pressure-independent activity coefficients  $y_i^{(P^{T})}$ , which at constant temperature, satisfy the isobaric, isothermal Gibbs-Duhem equation. It is advantageous to use such adjusted activity coefficients since their composition dependence can be expressed by

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simple algebraic functions such as those of Margules, van Laar, etc. Through Equation (2) the effect of pressure is separated from the effect of composition and, as a result, interpretation and correlation of phase equilibrium data are very much facilitated (18).

Experimental data for partial molar volumes are rare for binary systems and for multicomponent systems there are essentially none. Since thermodynamic analysis or prediction of multicomponent high-pressure phase equilibria requires partial molar volumes, we require a reliable method for calculating partial molar volumes from a minimum of experimental information. In the following, we present such a method, applicable up to critical compositions, for calculating partial molar volumes in multicomponent liquid mixtures at saturation.

# PARTIAL MOLAR VOLUME FROM AN EQUATION OF STATE

The partial molar volume of component k in a mixture of N component is defined by

$$\overline{\nu}_{k} = \left(\frac{\partial V}{\partial n_{k}}\right)_{P, T, n_{i}(i\neq k)}$$
(3)

The partial molar volume can be evaluated from a suitable equation of state for the liquid mixture. Since most equations of state are explicit in pressure, rather than in volume, it is convenient to rewrite Equation (3):

$$\overline{v}_{k} = \frac{-\left(\frac{\partial P}{\partial n_{k}}\right)_{T, V, n_{i}(i \neq k)}}{\left(\frac{\partial P}{\partial V}\right)_{T, n_{i}(\text{all } i)}} = f(x, T, v)$$
(4)

With an equation of state, Equation (4) gives  $\bar{v}_k$  as a function of the composition, temperature, and molar volume of the liquid mixture. Pressure does not appear explicitly in Equation (4), but is implicit in the volume which depends on the pressure.

For practical applications in vapor-liquid equilibria, we require partial molar volumes at saturation; therefore, we need the saturated molar volume of the liquid mixture in Equation (4). Before discussing Equation (4) in more detail, we describe a method for calculating the molar volume of a saturated liquid mixture.

# SATURATED MOLAR VOLUME OF LIQUID MIXTURES UP TO A REDUCED TEMPERATURE OF 0.93

Given only the temperature and composition, it is possible, in principle, to calculate the saturated volume of a liquid mixture from an equation of state. Such a calculation, however, requires an equation of state capable of describing accurately both vapor and liquid phases of multicomponent systems. For a wide variety of mixtures, no such equation of state is known. (In fact, the entire problem of phase equilibria at any pressure could be completely solved if such an equation of state were available.) A more realistic and fruitful approach is provided by a corresponding-states correlation specifically developed for saturated liquids. Such a correlation was given by Lyckman and Eckert (11), who slightly revised Pitzer's tables (15) for the saturated liquid volume of pure substances. In this correlation, the reduced saturated volume is given by

$$v_R = v_R^{(0)} + \omega v_R^{(1)} + \omega^2 v_R^{(2)}$$
(5)

where  $\omega$  is the acentric factor (15, 19) and  $v_R^{(0)}$ ,  $v_R^{(1)}$ , and  $v_R^{(2)}$  are functions of reduced temperature which have been tabulated for reduced temperatures from 0.560 to 0.990 (11). To facilitate calculations with an electronic computer, we

# TABLE 1. COEFFICIENTS IN EQUATION (6) FOR REDUCED VOLUMES OF SATURATED LIQUIDS<sup>†</sup>

j	$a^{(j)}$	$b^{(j)}$	$c^{(j)}$	$d^{(j)}$	$e^{(j)}$	$f^{(j)}$
0	0.11917	0.009513	0.21091	-0.06922	0.07480	-0.084476
1	0.98465	-1.60378	1.82484	-0.61432	-0.34546	0.087037
2	-0.55314	-0.15793	-1.01601	0.34095	0.46795	-0.239938

<sup>†</sup>For reduced temperatures from 0.560 to 0.995.

fitted the tabulated values with the following relation:

$$v_R^{(j)} = a^{(j)} + b^{(j)} T_R + c^{(j)} T_R^2 + d^{(j)} T_R^3 + e^{(j)} / T_R + f^{(j)} \ln (1 - T_R)$$
(6)

where  $a^{(j)}$  to  $f^{(j)}$  are coefficients for  $v_R^{(0)}$ ,  $v_R^{(1)}$  and  $v_R^{(2)}$ ; these coefficients are given in Table 1.

The reducing parameters for the reduced volume and the reduced temperature are the critical volume and the critical temperature, respectively. For  $v_R^{(0)}$ , Equation (6) agrees with the originally tabulated values to the fourth significant figure; for  $v_R^{(1)}$  and  $v_R^{(2)}$  it agrees within ±1 in the fourth significant figure. For pure components, Equations (5) and (6) may be used for reduced temperatures from 0.560 to 0.995. For reduced temperatures above 0.995, the reduced volume may be obtained by first calculating the reduced volumes at  $T_R$  of 0.990 and 0.995, and then interpolating to  $T_R = 1.0$ ; by definition  $v_R = 1.0$  at  $T_R = 1.0$ .

Equations (5) and (6) were obtained from pure component data. For application to mixtures, mixing rules for the pseudocritical volume and temperature are necessary. For pseudoreduced temperatures up to 0.93 we suggest the following rules:

$$v_{cM} = \sum_{i} x_i v_{c_i} \tag{7}$$

$$T_{CM} = \sum_{i} \sum_{j} \Phi_{i} \Phi_{j} T_{c_{ij}}$$
(8)

$$\omega_{M} = \sum_{i} \Phi_{i} \omega_{i} \tag{9}$$

where

$$\Phi_{k} = \frac{x_{k} v_{c_{k}}}{\sum x_{i} v_{c_{i}}}$$
(10)

$$T_{c_{ij}} = \sqrt{T_{c_{ii}} T_{c_{jj}}} \quad (1 - k_{ij})$$
 (11)

Because of the small separation between molecules, molecular size is a more important factor in the liquid phase than in the vapor phase. Therefore, in Equations (8) and (9), we use volume fractions rather than mole fractions (or combinations of mole fractions and volume fractions) which were used in previous pseudocritical rules (6, 8, 10, 20, 26).

The constant  $k_{ij}$  has an absolute value much less than unity; it represents the deviation from the geometric-mean rule for the characteristic temperature of the *i*-*j* pair. To a good approximation,  $k_{ij}$  is a constant independent of temperature and density. The binary constant  $k_{ij}$  must be evaluated from some binary data (for example, second virial coefficients or solubility), which give information on the nature of *i*-*j* interactions. Table 2 gives some of the  $k_{ij}$ values used in this work. These values, although obtained from liquid phase measurements, are in good agreement with those obtained by Gunn (20) from second virial cross coefficients, and with those reported by Pitzer and Hultgren (16) from compressibility factors near the critical region. For paraffin-paraffin systems, experimentally de-

## TABLE 2. COMPARISON OF CALCULATED AND EXPERIMENTAL SATURATED MOLAR LIQUID VOLUMES OF BINARY MIXTURES AT HIGH PRESSURES

(Reduced	temperature	< 0.93)
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		Т	Pressure range	Y	% Dev	iation
System*	k <sub>12</sub>	°F.	lb./sq. in. abs.	$(T_R \approx 0.93)$	Avg.	Max.
(1) (2)						
n-Butane-carbon dioxide	0.20	100 160 220	51.5 to 800 120.6 to 900 241.2 to 600	0.68 0.45 0.17	0.7 0.2 0.2	1.0 0.5 0.5
Propane-methane	0.20	40 100	79 to 1,200 189 to 950	0.52 0.29	0.6 0.7	1.6 1.2
n-Butane-methane	0.04	100 130 160 190 220	51.5 to 1,700 80.6 to 1,600 120.6 to 1,400 174.4 to 1,100 241.2 to 800	0.55 0.47 0.38 0.27 0.16	0.7 1.2 1.2 1.2 0.8	1.6 2.4 2.1 2.1 1.1
n-Pentane-methane	0.06	100 160 220 280	15.7 to 2,300 42.5 to 2,100 94.9 to 1,600 185.6 to 900	0.68 0.57 0.41 0.20	0.1 0.7 1.2 1.2	0.3 1.9 2.3 1.8
Propylene-ethane <sup>†</sup>	0.02	10 40 100	58 to 255 96.4 to 385 227.3 to 470	0.50	0.5 0.4 0.5	0.9 0.8 0.8
Benzene-propane‡	0.03	100 160 220 280 340 400	3.2 to 189 11.1 to 384 29.2 to 520 64.7 to 630 126.0 to 710 222.1 to 630	1.0 0.81 0.64 0.44 0.26	0.5 0.8 0.4 0.4 0.5 0.5	1.2 1.1 0.7 1.3 1.2 0.9
Hydrogen sulfide-methane	0.04	40 100	169 to 1,770 394 to 1,500	0.36 0.18	1.0 1.3	2.3 1.7

\*Critical constants for pure components taken from the compilation of Kobe and Lynn (9) unless otherwise noted. Experimental data of binary systems are taken from Sage et al. (24, 25). †Critical volume of ethane is 2.27 cu. ft./lb.-mole as reported by Din (5).

‡Critical volume of benzene is 4.06 cu. ft./lb.-mole as reported by Bender et al. (1).

termined  $k_{ii}$ 's are in good agreement with the semitheoretical relation

$$k_{ij} = 1 - \left[ \frac{\sqrt{v_{c_i}^{\frac{V_j}{V_j}} v_{c_j}^{\frac{V_j}{V_j}}}}{(v_{c_i}^{\frac{V_j}{V_j}} + v_{c_j}^{\frac{V_j}{V_j}})/2} \right]^n$$
(12)

Equation (12) follows from London's theory of dispersion forces, neglecting small differences in ionization potentials. In agreement with Reid and Leland (23), we found that n = 3 gives better results than the theoretical value n = 6. Equation (12), however, is useful only for mixtures of paraffins; for other systems it may lead to large errors.

The saturated liquid volume of a multicomponent mixture may be calculated with Equations (5) and (6) and Equations (7) through (11). The pseudocritical rules, Equations (7) and (8), were found to give good predictions for  $T_R \leq 0.93$ . For larger  $T_R$  (critical region) a modification of the pseudocritical rules is required, as indicated later.

Figures 1 and 2 show calculated saturated liquid volumes for two systems, n-butane-carbon dioxide and propane-methane, each at three different temperatures; the calculated results are compared with experimental data of Sage and Lacey (21, 24, 25). These figures include the calculations in the critical region to be discussed later. The agreements are quantitative over the relatively wide temperature range.

At 160°F. n-butane is subcritical. As the mole fraction of carbon dioxide rises, the molar volume of the liquid mixture decreases at first, primarily because of the introduction of the smaller molecules of carbon dioxide and partly because of the increase in pressure; meanwhile, the reduced temperature increases due to the lower critical temperature of carbon dioxide. At an intermediate composition, the effect of increasing reduced temperature dominates the effect of smaller molecular size and higher pressure, and the molar volume of the mixture increases sharply toward its critical value. At high concentrations, the supercritical carbon dioxide expands or dilates the subcritical n-butane. This dilative effect becomes particularly pronounced in the critical region; it has been discussed previously in our development of a modified van Laar equation suitable for high-pressure vapor-liquid equilibria (3).

At a lower temperature, say 100°F., carbon dioxide is only slightly supercritical, whereas n-butane is well below its critical temperature. At 100°F. the effect of dilation therefore does not become important until very near the critical composition. On the other hand, at a higher temperature (220°F.) the heavier component, n-butane, is already close to its critical temperature and therefore is much more sensitive to the dilative effect of the supercritical carbon dioxide. At 220°F. the molar volume of the mixture increases soon after the introduction of carbon di-Similar behavior is observed in the propaneoxide. methane system.

The characteristic parameter  $k_{ij}$  is very important in these calculations. To illustrate, Figure 3 shows the saturated liquid volumes for n-butane-carbon dioxide mixtures, calculated with and without correction to the geometric-mean for  $T_{c_{12}}$ . For this system, the geometric-mean assumption is a poor one as was noted previously by Joffe and Zudkevitch (7).

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Table 2 summarizes the results of calculations for seven binary systems, including those containing carbon dioxide, hydrogen sulfide, and aromatic hydrocarbons. The average deviation and maximum deviation for all twenty-five isotherms are small, and are probably of the same order of magnitude as the uncertainty in the experimental data. The rather good agreement for the system *n*-pentanemethane (where the ratio of pure component critical volumes is a little more than three) seems to indicate that the difference in molecular sizes can be adequately taken into account by using volume fractions (rather than mole fractions) in the mixing rules, Equations (8) to (10).

With a reliable method for calculating the volumes of saturated liquid mixtures, we proceed now to calculate partial molar volumes with Equation (4) which requires an equation of state for liquid mixtures.

# EQUATION OF STATE FOR LIQUID MIXTURES

For nonpolar liquids, an equation of the van der Waals type provides a reasonable description of volumetric properties. Since the Redlich and Kwong equation (22) represents a useful modification of van der Waals' equation, we propose to use this equation for liquid mixtures with certain alterations. The Redlich and Kwong equation of state is

$$P = \frac{RT}{\nu - b} - \frac{a}{T^{0.5} \ \nu(\nu + b)}$$
(13)

For any pure fluid, the two constants a and b can be related to the critical properties of that fluid by

$$a = \frac{\Omega_a R^2 T_c^{2.5}}{P_c} \tag{14}$$

$$b = \frac{\Omega_b R T_c}{P_c}$$
(15)

where  $\Omega_a$  and  $\Omega_b$  are dimensionless constants. If the con-



Fig. 2. Saturated liquid molar volumes of propane-methane mixtures.





Fig. 1. Saturated liquid molar volumes of *n*-butane-carbon dioxide mixtures.

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TABLE 3. ACENTRIC FACTORS AND DIMENSIONLESS CONSTANTS IN THE REDLICH AND KWONG EQUATION OF STATE FOR SATURATED LIQUIDS

	·ω	$\Omega_a$	$\Omega_{b}$
Methane	0.013	0.4546	0.0872
Nitrogen	0.040	0.4540	0.0875
Ethylene	0.085	0.4290	0.0815
Hydrogen sulfide	0.100	0.4220	0.0823
Ethane	0.105	0.4347	0.0827
Propylene	0.139	0.4130	0.0803
Propane	0.152	0.4138	0.0802
iso-Butane	0.187	0.4100	0.0790
Acetylene	0.190	0,4230	0.0802
1-Butene	0.190	0.4000	0.0780
n-Butane	0.200	0.4184	0.0794
Cyclohexane	0.209	0,4060	0.0787
Benzene	0.211	0.4100	0.0787
iso-Pentane	0.215	0.3970	0.0758
Carbon dioxide	0.225	0.4184	0.0794
n-Pentane	0.252	0.3928	0.0767
n-Hexane	0.298	0.3910	0.0752
n-Heptane	0.349	0.3900	0.0740
n-Nonane	0.447	0.3910	0.0738

ditions at the critical point  $\left[\left(\frac{\partial P}{\partial \nu}\right)_{T_c} = 0 \text{ and } \left(\frac{\partial^2 P}{\partial \nu^2}\right)_{T_c} = 0\right]$ 

are imposed,  $\Omega_a = 0.4278$  and  $\Omega_b = 0.0867$  for all fluids. Adoption of these values is equivalent to fitting the equation of state to experimental results in the critical region which, although the most sensitive, does not provide the best fit over a wide range of conditions. This is particularly true when the equation is applied to the liquid phase. If we accept universal values for  $\Omega_a$  and  $\Omega_b$ , we are, in effect, subscribing to a two-parameter theorem of corresponding states. However, Pitzer and others (12 to 15) have shown that the theorem of corresponding state requires a third parameter in order to be applicable to a wide class of substances. We propose, therefore, for each pure liquid, to fit the Redlich-Kwong equation to the P-V-T data of the saturated liquid and to evaluate the best  $\Omega_a$  and  $\Omega_b$ for each pure component. Fortunately, such data are readily available; results are given in Table 3 for nineteen common liquids. They differ slightly from the universal values, and show a trend with respect to acentric factor.

For application of Equation (13) to mixtures, we propose the following mixing rules:

$$a = \sum_{i} \sum_{j} x_{i} x_{j} a_{ij} \quad [a_{ij} \neq (a_{i} a_{j})^{\frac{1}{2}}]$$
(16)  
$$b = \sum_{i} x_{i} b_{i}$$
(17)

where

$$a_{ii} = \frac{\Omega_{a_i} R^2 T_{c_i}^{2.5}}{P_{c_i}}$$
(18)

$$b_i = \frac{\Omega_{b_i} R T_{c_i}}{P_{c_i}} \tag{1}$$

$$a_{ij} = \frac{\frac{1}{4} (\Omega_{a_i} + \Omega_{a_j}) R T_{c_{ij}}^{1.5} (\nu_{c_i} + \nu_{c_j})}{0.291 - 0.04 (\omega_i + \omega_j)}$$
(20)

# PARTIAL MOLAR VOLUMES

The partial molar volume can be obtained from Equation (13) and the mixing rules, Equations (16) and (17),



Fig. 4. Partial molar volumes in the saturated liquid phase of the *n*-butane-carbon dioxide system at 160°F.

after performing the partial differentiation indicated in Equation (4):

$$\overline{v}_{k} = \frac{\frac{RT}{v-b}\left(1+\frac{b_{k}}{v-b}\right) - \frac{2\left(\sum_{i} x_{i}a_{ki}\right) - ab_{k}/(v+b)}{v(v+b)T^{\frac{1}{2}}}}{\frac{RT}{(v-b)^{2}} - \frac{a}{T^{\frac{1}{2}}}\left[\frac{2v+b}{v^{2}(v+b)^{2}}\right]}$$
(21)





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Fig. 6. Calculated saturated liquid molar volumes of the *n*-pentane (1)-propane (2)-methane (3) system.

Using v, the saturated liquid molar volume of the mixture, calculated previously, and Equations (16) through (20), one can readily calculate the partial molar volume of each component in a multicomponent liquid mixture from Equation (21). A computer program for performing the calculation is available (2).

Figures 4 and 5 show calculated partial molar volumes in the saturated liquid phase of the systems n-butanecarbon dioxide and propane-methane, including the critical region to be discussed later. The calculated values are compared with those computed from the volumetric data of Sage and Lacey (25). Agreement between calculated and experimental values is quantitative for both systems. The partial molar volumes of the lighter component (supercritical in these cases) and the heavier component show very different behavior in the critical region even for a system as simple as propane-methane. The partial molar volume of the lighter component approaches a large positive value, due to its dilative effect, and that of the heavier component approaches a large negative value, due to its condensing effect. As a result, pressure has exactly opposite effects on the activity coefficients of the lighter component and the heavier component, as indicated by Equation (2). The simple approximation of using partial molar volumes at infinite dilution leads to large error near the critical region.

Also shown in Figure 5 are the partial molar volumes calculated with the universal values  $\Omega_a = 0.4278$  and  $\Omega_b = 0.0867$ . The results are much less satisfactory, indicating the need for evaluating  $\Omega_a$  and  $\Omega_b$  for each pure saturated liquid.

In a multicomponent system, the partial molar volume of each component depends on the liquid composition in a complex manner. Figures 6 and 7 show calculated saturated liquid volumes and partial molar volumes for the system n-pentane-propane-methane,\* including the critical region.

### CRITICAL REGION

In applying previously proposed pseudocritical rules to the critical region, it has often been found necessary to introduce an empirical exponent which depends on the proximity to critical conditions (10, 20). In the following, we introduce a general proximity function which corrects the pseudocritical rules of Equations (7) and (8) in the critical region.

By definition,  $T_R = 1.0$  and  $v_R = 1.0$  at the critical point when the true critical constants of the mixture are used as the reducing parameters. Therefore, if the true criticals of a mixture can be calculated, the mixing rules, Equations (7) and (8), can be modified such that they will always converge to  $T_R = 1.0$  and  $v_R = 1.0$  at the critical point. In the following, we use primes to indicate corrected pseudocriticals. Let

$$T_{cM} = T_{cM} + (T_{cT} - T_{cM}) \mathcal{D} (T_R)$$
(22)

and

$$\nu_{cM} = \nu_{cM} + (\nu_{cT} - \nu_{cM}) \mathcal{D} (T_R)$$
(23)

where  $T_{cT}$  and  $v_{cT}$  refer to the true critical temperature and true critical volume of the mixture, respectively. The second terms on the right-hand sides of Equations (22) and (23) correspond to the corrections added to the simple mixing rules, Equations (7) and (8). The function  $\mathcal{D}(T_R)$  represents the proximity of the system to its critical point; it must satisfy the two boundary conditions

$$\mathfrak{D}(T_R) \longrightarrow 0 \quad \text{for} \quad T_R < 0.93 \tag{24}$$

$$\mathfrak{D}(T_P) = 1$$
 at  $T_P = 1.0$  (25)

The first boundary condition ensures that Equations (22) and (23) reduce to the simple mixing rules, Equations (7) and (8), for  $T_R \leq 0.93$ . The second boundary condition ensures that they converge to  $T_{cM} = T_{cT}$  and  $v_{cM} = v_{cT}$  at the critical point. We suggest the following empirical function which satisfies the above boundary conditions:





<sup>\*</sup>For pentane-propane,  $k_{ij}$  = 0.01,  $\nu_{ij}$  = -1.018 cu. ft./lb.-mole and  $\tau_{ij}$  = 7.0°R.

### TABLE 4. COMPARISON OF CALCULATED AND EXPERIMENTAL SATURATED MOLAR LIQUID VOLUMES OF BINARY MIXTURES IN THE CRITICAL REGION

(Reduced temperature 0.93 to 1.00)

	ν	т	T	Pressure range.	Υ.	% Dev	viation
System*	cu. ft./lb. mole	°R.	°F.	lb./sq. in. abs.	(critical)	Avg.	Max.
(1) (2)							
n-Butane-carbon dioxide	-1.25	- 46.4	100 160 220	800 to 1,057 900 to 1,020 600 to 942	0.954 0.713 0.498	2.3 0.7 0.7	4.3 1.4 3.0
Propane-methane	-0.875	89.7	40 100 160	1,200 to 1,474 950 to 1,353 384 to 1,020	0.7459 0.5882 0.3228	1.6 1.0 1.2	7.6 4.9 5.9
n-Butane-methane	-1.96	101.3	100 130 160 190 220 250	1,700 to 1,912 1,600 to 1,876 1,400 to 1,810 1,100 to 1,698 800 to 1,520 327.7 to 1,264	0.7236 0.6718 0.6165 0.5503 0.4722 0.3602	1.6 1.6 2.2 3.4 4.6 3.3	4.5 3.4 2.8 5.1 9.5 10.3
n-Pentane-methane	- 2.35	141.4	100 160 220 280 340	2,300 to 2,455 2,100 to 2,338 1,600 to 2,081 900 to 1,610 330 to 1,025	0.8236 0.7665 0.6705 0.5211 0.2950	2.5 2.6 3.1 2.3 0.9	5.2 3.7 4.7 3.2 2.1
Propylene-ethane	-0.273	-4.7	100 160	470 to 722 455 to 705	0.9300 0.3500	0.8 2.8	2.5 10.5
Benzene-propane	-0.690	22.1	280 340 400	630 to 750 710 to 850 630 to 850	† † †	0.8 1.4 0.7	1.3 1.6 2.8
Hydrogen sulfide-methane	-0.958	29.3	40 100 160	1,770 to 1,949 1,500 to 1,907 779 to 1,660	0.5500 0.3880 0.2090	3.1 2.2 1.6	4.2 5.2 7.3

 $*k_{12}$  given in Table 1. Experimental data of binary systems are taken from Sage et al. (24, 25). No critical composition reported.

(26)

$$D(T_R) = \exp\left[ (T_R - 1) \left( 2901.01 - 5738.92 \ T_R + 2849.85 \ T_R^2 + \frac{1.74127}{1.01 - T_R} \right) \right]$$

Equation (26) was found to be sufficiently general for all systems investigated. The reducing parameter for  $T_R$  in Equation (26) is the corrected pseudocritical temperature  $T_{c'M}$  rather than the true critical temperature which is adequate at the critical point only. As a result  $T_{c'M}$  appears on both sides of Equation (22) and iteration is required to solve for  $T_{c'M}$ . This is best done by rewriting Equation (22):

$$\left[\frac{(T/T_{cM})}{T_R} - 1\right] - \left[\frac{(T/T_{cM})}{(T/T_cT)} - 1\right] \mathcal{D}(T_R) = 0 \qquad (27)$$

Equation (27) has only one unique solution for  $T_R < 1.0$ which can be readily found by a numerical technique (for example, Reguli-falsi iteration with variable pivoting points). The method usually converges in a few iterations. From Equation (23),  $v'_{CM}$  can then be obtained by direct substitution.

Equations (22) and (23) may be considered as more general pseudocritical rules applicable over the whole temperature range up to the critical point. With the corrected pseudocritical constants, the saturated molar volumes of liquid mixtures can be calculated from Equations (5) and (6) in the manner discussed before.

Figure 8 compares reduced temperatures and reduced volumes calculated for the system *n*-butane-carbon dioxide at 100°F., with the corrected pseudocriticals, Equations (22) and (23), and the uncorrected pseudocriticals, Equations (7) and (8). Whereas  $T_R$  and  $v_R$  based on corrected pseudocriticals composition, those based on the uncorrected pseudocriticals at-



Fig. 8. Reduced temperature and reduced volume in the critical region with corrected and uncorrected pseudocritical constants (*n*-butane-carbon dioxide at 160°F.).

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tain unreasonable values before reaching the critical composition. In the critical region, a small error in the reduced temperature produces a very large error in the calculated mixture volume as shown in Figure 8.

The true critical temperature and volume of mixtures, as needed in Equations (22) and (23), can be calculated from a correlation discussed in detail in reference 4. The true critical constants are related to the composition by expressions using the surface fraction  $\theta$ :

$$v_{cT} = \sum_{i} \theta_i v_{ci} + \sum_{i} \sum_{j} \theta_i \theta_j v_{ij}, \quad (v_{ii} = 0)$$
(28)

$$T_{cT} = \sum_{i} \theta_{i} T_{c_{i}} + \sum_{i} \sum_{j} \theta_{i} \theta_{j} \tau_{ij}, \quad (\tau_{ii} = 0)$$
(29)

where

$$_{k} = \frac{x_{k} v_{c_{k}}^{2\prime_{j}}}{\sum_{i} x_{i} v_{c_{i}}^{2\prime_{j}}}$$
(30)

The correlating parameters  $\nu_{ij}$  and  $\tau_{ij}$  are measures of the (small) deviations of the mixture criticals as given by a linear dependence on the  $\theta$  fraction; they are characteristic of the *i*-*j* pair. Table 4 gives  $\nu_{12}$  and  $\tau_{12}$  for the seven systems investigated in this work. More extensive compilations of these parameters are given in the following paper (4).

θ

Table 4 also summarizes calculations of saturated liquid volumes in the critical region for seven systems and twenty-five isotherms. In the critical region, deviations are larger than those found in the region where  $T_R < 0.93$ . Most of the largest deviations occur in the immediate vicinity of the critical point where experimental results are most likely to be in error. For example, Reamer et al. (21) reported that the accuracy of their liquid-phase mole fractions was about 0.013 mole fraction. If the critical mole fraction is known within  $\pm 0.013$ , this uncertainty causes an error of about 5% in the critical volume.

In the critical region the calculations are strongly dependent on the accuracy of the calculated true critical temperature. An error of 0.5% in the calculated true critical temperature may cause an error of more than 5% in the calculated volume. The reduced volume is a very sensitive function of reduced temperature in the critical region; for a simple fluid ( $\omega = 0$ ), the reduced volume at  $T_R = 0.99$  is 0.7327, whereas at  $T_R = 1.00$ ,  $v_R = 1.0$  by definition. Thus, near the critical point, a 1% change in reduced temperature causes a change in reduced volume of about 30%. This extreme sensitivity of volumetric properties to small changes in temperature or composition is an inherent nature of the critical state and cannot easily be eliminated, neither by experiment nor by calculation.

Once the saturated liquid volume is known, partial molar volumes can be calculated from Equation (21) in exactly the same manner as that discussed before. Calculated partial molar volumes in the critical region are shown in Figures 4, 5, and 7 for the binary systems *n*-butane-carbon dioxide and propane-methane, and for the ternary system *n*-pentane-propane-methane.

### CONCLUSION

This work presents a method for predicting partial molar volumes in a multicomponent liquid mixture at saturation. Calculated partial molar volumes depend strongly on the liquid composition, especially in the critical region where the partial molar volume of the heavier component may change sign. Calculated results are in quantitative agreement with the limited experimental data now available.

The calculations are sensitive to the characteristic energy between two dissimilar molecules which, in general, is lower than that given by the geometric mean. These characteristic energies have been determined for a number of systems from several binary data sources, such as second virial cross coefficients and binary saturated liquid volumes. For a given binary system, characteristic energies found from different sources generally agree well with each other.

With partial molar volumes, the effect of pressure on liquid-phase activity coefficients can be taken into account. By separating the effect of pressure from that of composition, one can subject experimental liquid phase activity coefficients to rigorous thermodynamic analysis. Such analysis permits meaningful interpretation and correlation of binary, high-pressure, vapor-liquid equilibrium data and facilitates prediction of multicomponent phase behavior.

### ACKNOWLEDGMENT

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## NOTATION

- a, b = constants in Redlich and Kwong equation of state
- $k_{ij}$  = characteristic constant for *i*-*j* interaction
- $n_k$  = number of moles of component k in the mixture
- P = total pressure
- $P_c$  = critical pressure
- R = gas constant
- T = temperature
- $T_c$  = critical temperature
- $T_{CM}$  = pseudocritical temperature of a mixture
- $T'_{cM}$  = corrected pseudocritical temperature of a mixture
- $T_{cT}$  = true critical temperature of a mixture
- $T_R$  = reduced temperature
- V =total volume of a liquid mixture
- v = molar volume of liquid or liquid mixture
- $\overline{v}_k$  = partial molar volume of component k in the liquid phase
- $v_{cM}$  = pseudocritical volume of a mixture
- $v'_{CM}$  = corrected pseudocritical volume of a mixture
- $v_{cT}$  = true critical volume of a mixture
- $v_R$  = reduced volume
- \$\nu\_R^{(j)}\$ = generalized reduced molar-volume function of saturated liquid, as defined by Equation (6)
   \$x\$ = mole fraction in liquid phase
- $\gamma_k^{(P)}$  = activity coefficient of component k at pressure P
- $\gamma_k^{(P^{\tau})}$  = activity coefficient of component k at some constant reference pressure
  - $\theta$  = surface fraction as defined by Equation (30)
  - $\nu_{ij}$  = correlating parameter for true critical volume of *i-j* binary
  - $\tau_{ij}$  = correlating parameter for true critical temperature of *i*-*j* binary
  - $\Phi$  = volume fraction as defined by Equation (10)
- $\Omega_a, \Omega_b$  = dimensionless constants in Redlich and Kwong parameters as defined by Equations (14) and (15)  $\omega$  = acentric factor

### Subscripts

- c = critical
- i, ii = component i

j, jj = component j

- *ij = i-j* pair
- M = mixture
- R =reduced quantity
- Superscript
- 0 = standard state

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# Vapor-Liquid Equilibria at High **Pressures: Calculation of Critical** Temperatures, Volumes, and **Pressures of Nonpolar Mixtures**

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An analysis of critical data for a large number of binary mixtures of normal fluids shows that the critical temperature and the critical volume can each be expressed as quadratic functions of the surface fraction. Each of these functions requires one adjustable parameter characteristic of the binary pair; for any family of chemical components, these parameters, upon suitable reduction, follow definite trends. It was shown that the surface fraction gives much better correlation than any other size-weighted variable. For the critical pressure, however, no quadratic function was adequate. To calculate critical pressures, the correlations for critical temperature and critical volume were used in conjunction with a slightly altered version of the Redlich-Kwong equation.

Generalizations to systems containing more than two components follow without additional assumptions. The methods presented in this paper provide good estimates for critical constants of multicomponent mixtures. These are particularly useful for analyzing and correlating vapor-liquid equilibria in the critical region.

The critical properties of pure fluids have received much attention and as a result of much experimental work, dating back nearly 100 years (3, 6), as well as semiempirical correlations (56), it is now possible to make good estimates of the critical temperature, pressure, and volume of most pure fluids encountered in typical chemical engineering

work. The critical properties of mixtures, however, are not known nearly as well, although experimental data are available for a surprisingly large number of binary mixtures (58).

Critical properties of mixtures are required in petroleum and natural gas engineering and for rational design of separation equipment and chemical reactors at high pressures.

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The rising use of high pressures in chemical technology calls for increased knowledge of fluid phase behavior in the critical region. Since our primary aim is to establish thermodynamic methods for calculating vapor-liquid equilibria at high pressures, including the critical region (see preceding paper), it is essential to have available methods for estimating the critical conditions wherein the vapor phase and the liquid phase become identical.

In this work we present correlations for the critical temperatures and volumes of binary mixtures, and we present an equation-of-state method for calculating critical pressures using critical temperatures and volumes. In a very straightforward way, we generalize our results for estimating critical properties of mixtures containing any number of components. Our attention is restricted to normal fluids [as defined by Pitzer (47)]; that is to molecules which have zero (or small) dipole moments, no tendency to associate by hydrogen bonding or similar chemical forces, and which have sufficiently large mass to permit neglect of quantum corrections.

Several authors (1, 14, 17, 19, 21, 22, 34, 36, 44, 45, 63, 64) have reported correlations of the critical temperature or critical pressure of mixtures but these, by and large, have been confined to a particular chemical class of substances (usually paraffins). Very little work has been reported on the correlation of critical volumes of mixtures (22). While the critical volume seldom enters directly into engineering calculations, it is of more fundamental significance than the critical pressure, and it is needed to provide estimates of the very large effect of pressure on liquid phase activity coefficients in the critical region.

### CRITICAL TEMPERATURES

Rowlinson (58) has shown that for a binary mixture of components 1 and 2, the critical temperature of the mixture is, to a good approximation, a simple quadratic function of the mole fraction, provided components 1 and 2 consist of simple, spherically symmetric molecules of nearly the same size. Rowlinson writes



Fig. 1. Critical temperatures of the methane-*n*-pentane system as a function of mole fraction and of surface fraction.

$$T_{cT} = x_1 T_{c_1} + x_2 T_{c_2} + 2x_1 x_2 \Delta T_{12}$$
(1)

where  $\Delta T_{12}$  is a known function of  $T_{c_1}$ ,  $T_{c_2}$ ,  $\nu_{c_1}$  and  $\nu_{c_2}$ , and a parameter which depends on the two exponents used in the potential function for describing the intermolecular forces. In addition,  $\Delta T_{12}$  depends on the energy characteristic of the 1-2 interaction; it is common to assume that this characteristic energy is given by the geometric mean of the pure-component characteristic energies, but this assumption, unfortunately, can often lead to appreciable error. The important simplifying element of Rowlinson's treatment lies in his assumption of pairwise additivity of intermolecular energies; the potential energy of a multibody assembly is given by the sum of the potential energies of all nearest neighbor pairs. As a result, the critical temperature of the mixture is a quadratic function of the mole fractions. Rowlinson's treatment is not useful for mixtures whose components differ appreciably in molecular size. For such mixtures, the thermodynamic properties are quadratic functions of the mole fraction only at moderate densities (second virial coefficients); at liquid-like densities, it has been common practice to express the thermodynamic properties of such mixtures in terms of volume fractions. The critical density is intermediate between that of liquids and that wherein the second virial coefficient gives a sufficiently good approximation. We propose, therefore, to correlate experimentally determined critical temperatures as a quadratic function of the surface fraction  $\theta$  defined by

$$\theta_{i} = \frac{x_{i} v_{c_{i}}^{2_{j}}}{\sum_{i} x_{i} v_{c_{i}}^{2_{j}}}$$
(2)

For a binary mixture, the critical temperature is given by

 $T_{cT} = \theta_1 T_{c_1} + \theta_2 T_{c_2} + 2\theta_1\theta_2 \tau_{12}$ (3)

where  $\tau_{12}$  is a parameter characteristic of the 1-2 interaction. Equation (3) is a one-parameter equation. By expressing the mixture's critical temperature as a function of surface fraction, we find that the quadratic term  $2\theta_1\theta_2\tau_{12}$ makes a comparatively small contribution. For mixtures whose components differ very much in molecular size, the contribution of the quadratic term is smaller when surface fractions are used; it is significantly larger if the critical temperature is expressed by quadratic functions in mole fraction. To illustrate, Figure 1 shows that the critical temperatures of the methane-n-pentane system are more nearly linear and symmetric when plotted against surface fraction rather than mole fraction. As a result, the correlating parameter  $\tau_{12}$  in Equation (3) is smaller than  $\Delta T_{12}$ in Equation (1); uncertainties in  $T_{12}$ , therefore, lead to smaller error than comparable uncertainties in  $\Delta T_{12}$ . For the methane-n-pentane system the experimental data (62) are correlated by Equation (3) (using  $\tau_{12} = 78.8^{\circ}$ K.) with an average error of 0.73%. On the other hand, the optimum fit of the data with Equation (1) (using  $\Delta T_{12} = 127.8^{\circ}$ K.) produces an average error of 4.08%.

Equation (3) has been used to correlate the critical temperatures of sixty-five binary systems; Table 1 gives the parameters  $\tau_{12}$  in reduced form for these systems. The average deviation of all experimental and fitted critical temperatures is 0.4%.

For a given family of chemical systems, the reduced parameters follow a trend which can form the basis for interpolation and cautious extrapolation. For example, for paraffin-paraffin systems (for which experimental data are most plentiful) the reduced parameter is a smooth function of the absolute value of  $(T_{c_1} - T_{c_2})/(T_{c_1} + T_{c_2})$  as illustrated in Figure 2. Paraffin-olefin systems follow the same

# TABLE 1. CALCULATED AND EXPERIMENTAL CRITICAL TEMPERATURES, VOLUMES, AND PRESSURES OF BINARY SYSTEMS

(Critical pressures are calculated from revised Redlich-Kwong equation)

a there		Ava Dev		2τ.,	Aug Dev	22,2		Ave Dev t	
4	Suctom	in T m		$\frac{12}{T + T}$	in Var %	1/- + 1/-	k*	in P-T %	Ref.
-1	System	m rcT,	0	1 <sub>C1</sub> + 1 <sub>C2</sub>	III VCI, 10	C1 C2	12	c1, 10	
	Methane-argon	0.05		0.0044				10.00 CT	24
7	Methane-nitrogen	0.33		0.0198	T T	-0.07	0.03	1.4, 1.7	24, 5, 11
)	Methane-oxygen	0.51		-0.0400					24
7	Methane-propane	1.39		0.1237		0.04.50			1a
1	Methane-propane	0.28		0.1410	1.9	-0.3653	0.00	10	61
1	Methane-propane	0.39		0.1775			0.02	4.9	50
the second	Methane-n-butane	0.81		0.1826	1.4	-0.6975	0.04	5.5	59
2	Methane-iso-butane	0.45		0.1444	0.3	-0.6503	0.05	3.1	43
1	Methane-n-pentane	0.73		0.2378	3.4	-0.7153	0.06	2.3	62
	Methane-iso-pentane	0.02		0.1953	1		0.07	3.7	2
1	Methane-n-heptane	3.39		0.2773	5.9	-0.9808	0.10	6.8	54
1	Acetylene-ethane	0.20		-0.0866			0.08	1.8	33
2	Acetylene-ethylene	0.84		-0.0545			0.06	2.4**	10
J.	Acetylene-propane	0.62		-0.0468			0.09	5.2**	38
	Acetylene-propylene	0.17		-0.0304			0.07	5.6**	38
1	Ethane-propane	0.13	-	0.0211			0	3.7**	35
1	Ethane-propylene	0.24		-0.0078	0.4	-0.1057	0	1.3	39
F	Ethane-n-butane	0.13		0.0267	0.8	-0.2753	0.01	1.7	26
E	Ethane-n-pentane	0.73	-	0.0438	1.0	-0.5250	0.02	3.6**	55
E	Ethane-cyclohexane	0.47		0.0695	2.9	-0.5931	0.03	3.2**	29
k	Ethane-n-heptane	0.61		0.0743	3.9	-0.6826	0.04	6.0	25
1	Ethylene-ethane	0.17		0.0006					37
h	Ethylene-propylene	0.14		0.0241					23
10th	Ethylene-n-heptane	0.69		0.0799	4.8	-0.8327	0.04	10.9	28
F	Propane-n-butane	0.12		0.0144	1.3	-0.0061	0	1.1	41
1	Propane-n-pentane	0.14		0.0092			0.01	1.1**	60
1	Propane-iso-pentane	0.06		0.0088	1.1	-0.2991	0	1.4	65
2	n-Butane-nitrogen	1.80		0.3500	\$	-0.95	0.12	4.0	57
ě.	n-Butane-n-heptane	0.03		0.0192	1.9	-0.3042	0	1.1	27
1	n-Pentane-neo-pentane	0.02		0.0038					. 46
5	n-Pentane-n-hexane	0.06		0.0031					. 46
k	n-Pentane-cyclohexane	0.03		0.0201					46
8	n-Pentane-n-heptane	0.05		0.0076		×.	0	1.4	13
1	neo-Pentane-n-bexane	0.09		0.0064					46
	neo-Pentane-cyclohexane	0.05		0.0047					46
1	n-Harane-cyclohexane	0.03		0.0013					46
5	Banzana-athana	0.82		0.0526	3.8	-0.5588	0.03	2.6**	31
E.	Benzene-propana	1 16		0.0264			0.02	2.0	20
E	Benzene-propane	0.71		-0.0066			0.01		46
T.	Benzene-neo-pentane	0.44		-0.0258					46
1	Banzana-n-bexane	0.14	1. a.	-0.0182					46
t	Benzene-evelohexane	0.01		-0.0128					46
F.	Banzana-toluana	0.03	· .	0.0008					46
1	Toluana_r_pentane	0.14		-0.0302					46
E	Toluene " beyane	0.09		-0.0028	0.0	-0.1141			46.66
1	Toluene evolobaxane	0.04		-0.0061	- 010	011111			46
	Carbon diaxida-mathana	1 61		0.0472			0.07	2.4	15
2	Carbon dioxide-athane	0.10		-0.0911			0.07		33
1	Carbon dioxide-ethane	0.10		-0.0573			0.10	6.5	48
4.	Carbon dioxide-propane	0.99		-0.0693	3.0	-0.3418	0.10	015	52
13	Carbon dioxide - propane	0.01		-0.0313	510	010 120			48
1	Carbon dioxide - n-butane	0.74		-0.0707	1.0	-0 4513	0.18	7.0	42
10	Carbon dioxide - n-butane	2 42		0.0156	1.0	-0.4515	0.10		48
2	Carbon monovide_argon	0.13		-0.0015					24
6	Carbon monoxide avugan	0.13		-0.0015					. 24
	Carbon monovide nitrogen	0.07		-0.0054					24
2	Carbon monoxide methons	0.00		0.0220					24
	Carbon monoxide methane	0.10		0.3560					67
5	Under an autide propane	0.20		0.5500	27	-0.6063	0.06	16	51
57	Hydrogen sulfidemethane	0.84		-0.0693	2.1	-0.1279	0.06	1.7	30
5	lludragen sulfide	0.30		-0.0085	1.0	-0.12/9	0.00	1.2	22
r	Hydrogen sulfide-propane	0.04		-0.0748	1.0	-0.1740	0.00	0 1	52
R .	hydrogen sulfide-n-pentane	1.75		-0.0168¶	2.1	-0.5050	0.10	2 1	33
1	hydrogen sullide-carbon dioxide	0.14		-0.0000	0.8	-0.0700	0.08	2.1	24
2 9	Nitrogen-argon	0.08		0.0098					24
2	Nurogen-oxygen	0.05		0.0103					24
	Argon-oxygen	0.03		-0.0090					24

\*Values of  $k_{12}$  are obtained from second virial coefficient ( $B_{12}$ ) data or saturated liquid volume data of binary mixtures.

<sup>†</sup>In calculating  $\nu_{cT}$  and  $T_{cT}$  values of  $\tau_{12}$  and  $\nu_{12}$  were taken from this table unless otherwise noted. <sup>‡</sup>No critical volumes of mixtures available for these systems. Values of  $\nu_{12}$  are back-calculated from critical pressure of mixture. \*\*Value of  $v_{12}$  for these systems were taken from the smoothed curves of Figure 4.

This parameter does not follow the trend of other hydrogen sulfide-paraffin systems shown in Figure 2.

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eracexon of  $\theta_2 \tau_{12}$ tures , the rface tical mole tical more rface cor- $\Delta T_{12}$ id to For (62) th an m fit protems the The tical

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trend as paraffin-paraffin systems. Systems containing acetylene with a paraffin (or olefin), however, do not follow the paraffin-paraffin curve (see Table 1), due to the large quadrupole moment of acetylene. Figure 3 gives plots for paraffin-aromatic, paraffin-carbon dioxide, and paraffinhydrogen sulfide systems.

The uncertainties in  $\tau_{12}$  follow, in part, from experimental uncertainties. For example, three different investigators have reported critical temperatures for the system methanepropane. When fitted to Equation (3), we obtain  $2\tau_{12}/(T_{c_1} + T_{c_2})$  equal to 0.1775 from reference 50, 0.1410 from reference 61, and 0.1237 from reference 1a. When compared with experimental results for other paraffin-paraffin systems (Figure 2), it appears that the data of reference 1a are the most reliable.

# CRITICAL VOLUMES

If we utilize the simplifying assumption that the configurational thermodynamic properties of a dense system



Fig. 3. Correlating parameter  $\tau_{12}$  for critical temperatures of some binary systems: I. aromatic paraffin II. Carbon dioxide-paraffin III. Hydrogen sulfide-paraffin.

## TABLE 2. AVERAGE PERCENT DEVIATIONS IN CORRELATING CRITICAL VOLUMES OF BINARY MIXTURES WITH DIFFERENT WEIGHTING OF MOLECULAR SIZE\*

	Type of weighting					
System	Mole fract.	Diameter fract.	Surface fract.	Volume fract.		
Methane-n-heptane	24.27	16.79	5.89	8.06		
Methane-n-pentane	7.50	5.09	3.43	4.86		
Methane-n-butane	2.70	0.94	1.41	4.14		
Methane-iso-butane	4.27	2.36	0.34	2.59		
Ethane-benzene	6.09	5.01	3.81	3.39		
Ethane-n-heptane	6.16	4.33	3.91	6.54		
Ethane-n-pentane	3.34	1.70	0.97	2.97		
Ethane-n-butane	1.56	1.03	0.80	0.89		
Hydrogen sulfide-n-pentane	2.60	1.79	2.09	5.30		
Carbon dioxide-n-butane	2.96	1.99	1.00	2.96		

i)

\*In each case a one-parameter quadratic function is used for correlation.

are due to two-body, nearest-neighbor interactions, we can express the critical volume of a mixture as a quadratic function of the composition. However, the composition can be specified in many ways and for components of significantly different molecular size, the mole fraction is inadequate. As for the critical temperature, we have found that the surface fraction [Equation (2)] provides the most useful measure of composition. Table 2 presents average deviations for the critical 'volumes of ten systems when experimental data are fitted to quadratic functions of four measures of composition: mole fraction, diameter fraction,\* surface fraction, and volume fraction. The surface fraction gives the minimum deviation. The critical volume of a binary mixture therefore is written as

$$v_{CT} = \theta_1 v_{C_1} + \theta_2 v_{C_2} + 2\theta_1 \theta_2 v_{12} \tag{4}$$

where  $v_{12}$  is a correlating parameter characteristic of the 1, 2 binary. Experimental data for critical volumes of binary mixtures are not nearly as plentiful as those for critical temperatures nor, because of experimental difficulties, are they as accurate. Table 1 gives the parameter  $v_{12}$  in reduced form as determined from experimental data for twenty-five systems. For these systems, Equation (4) correlated the data with an overall average deviation of 1.9%. Since accurate experimental determination of critical volumes is not simple, this deviation in many cases is of the same order as the experimental uncertainty.

Figure 4 presents the reduced correlating parameter as a function of the absolute value of  $(v_{c_1}^{2'_3} - v_{c_2}^{2'_3})/(v_{c_1}^{2'_3} + v_{c_2}^{2'_3})$ . Definite trends can be observed for different chemical families; Figure 4, therefore, should be useful for estimating critical volumes of systems where experimental data are lacking. The paraffin-paraffin curve for  $v_{12}$  may be used for systems consisting of paraffins, olefins, and acetylenes.

# CRITICAL PRESSURES

Having correlated critical temperatures and critical volumes with quadratic functions of the surface fraction, one is tempted to try a similar correlation for the critical pressure. Such a correlation was tried and failed. Previous workers (64) have noted that the dependence of the critical pressure on composition is much more strongly nonlinear

\*Diameter fraction weights the mole fraction of component i with  $\nu_{c_i}^{1/2}$ .



4. Correlating parameter  $v_{12}$  for critical volumes of some binary systems.

than that of the critical temperature and the critical volume; in many systems a plot of critical pressure vs. mole fraction shows a sharp maximum and a point of inflection. The more complicated behavior of the critical pressure follows from its nonfundamental nature; subject to welldefined assumptions, both critical temperatures and critical volumes can be related directly to the intermolecular potential, but the critical pressure can be related to the intermolecular potential only indirectly through the critical temperature and critical volume.

To express the critical pressure as a function of composition, we propose to use our correlations for critical temperature and critical volume coupled with an equation of We have adopted the Redlich-Kwong equation of state. state (1) with certain alterations. The Redlich-Kwong equation is

$$P = \frac{RT}{v - b} - \frac{a}{T^{\frac{1}{2}}v(v + b)}$$
(5)

For a pure component, the constants a and b are related to the critical temperature and pressure of that component by

$$a = \frac{\Omega_a R^2 T_c^{23}}{P_c}$$
(6)  
$$b = \frac{\Omega_b R T_c}{P_c}$$
(7)

The dimensionless constants  $\Omega_a$  and  $\Omega_b$  may be found (as is commonly done) by equating to zero the first two isothermal derivatives of pressure with respect to volume at the critical point. This procedure gives  $\Omega_a = 0.4278$ and  $\Omega_b = 0.0867$ . To do so, however, puts a severe strain on the equation of state, leading to a value of  $z_c$  which is too large. Since any two-parameter equation of state is necessarily approximate when applied to a wide range of

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temperature and density, it is best to determine the dimensionless parameters  $\Omega_a$  and  $\Omega_b$  from experimental data available in the region of temperature and density where the equation of state is to be used. Toward that end, we have previously (7, 9) evaluated the parameter  $\Omega_b$  for a variety of fluids from pure-component volumetric data, once for saturated liquids and once for saturated vapors. For our present purpose, we use for  $\Omega_b$  for each substance the arithmetic mean of the two values obtained from saturated liquid and saturated vapor volumes. For a variety of normal fluids, this  $\Omega_b$  may be represented by a function of the acentric factor  $\omega$  (47, 9):

$$\Omega_b = 0.0867 - 0.0125 \ \omega + 0.011 \ \omega^2 \quad (0 \le \omega < 0.6) \tag{8}$$

To force agreement for each pure component at the critical point,  $\Omega_a$  is determined by the experimental critical temperature, pressure, and volume of that component according to

$$\Omega_{a} = \left(\frac{RT_{c}}{v_{c} - b} - P_{c}\right) \frac{P_{c} v_{c} (v_{c} + b)}{(RT_{c})^{2}}$$
(9)

where b is given by Equations (7) and (8).

To apply Equation (5) to mixtures, we require mixing rules for a and b. We propose, as before (9), to use

$$a = \sum_{i} \sum_{j} x_{i} x_{j} a_{ij} \quad (a_{ij} \neq \sqrt{a_{ii} a_{jj}})$$
(10)

$$b = \sum_{i} x_i b_i \tag{11}$$

where

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$$ii = \frac{\Omega_{a_i} R^2 T_{c_i}^{2.5}}{P_{c_i}}$$
(12)

$$_{i} = \frac{\Omega_{b_{i}} R T_{c_{i}}}{P_{c_{i}}}$$
(13)

$$a_{ij} = \frac{\frac{1}{4} \left(\Omega_{a_i} + \Omega_{a_j}\right) R T_{c\,ij}^{1.5} \left(v_{c_i} + v_{c_j}\right)}{0.291 - 0.04 \left(\sigma_i + \omega_j\right)} \tag{14}$$





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Fig. 6. Critical pressures of three binay systems containing methane.

$$T_{c_{ij}} = \sqrt{T_{c_{ii}} T_{c_{jj}}} (1 - k_{ij})$$
(15)

The constant  $k_{ij}$  is a small number (usually positive and of the order  $10^{-2}$  or  $10^{-1}$ ) which is characteristic of the *i*-*j* interaction. To a good approximation, it is independent of temperature, density, and composition; it can be determined from a variety of experimental data for the *i*-*j* mixture in-



Fig. 7. Effect of correction to geometric mean on predicted critical pressures of the nitrogen—n-butane system. (k<sub>12</sub> obtained from second virial coefficient data.)

cluding second virial coefficients and liquid-phase properties (8, 9, 16, 49). Table 1 gives  $k_{ij}$  for thirty-six systems as determined from *i*-*j* mixture data. (Critical properties of mixtures were not used.)

Using the equation of Redlich and Kwong together with the previously established correlations for critical temperatures and critical volumes, we calculated critical pressures and compared them with experimental results for the thirty-six systems listed in Table 1. The mean of the average deviations is 3.6%. In these calculations, critical temperatures and volumes of mixtures were calculated from Equations (3) and (4); experimental critical temperatures and volumes of mixtures were not used directly in the Redlich-Kwong equation.

Typical results are shown in Figure 5 for three binary systems containing ethane and in Figure 6 for three binary systems containing methane. The system ethane-hydrogen sulfide is unusual, because, unlike the behavior of most systems, the critical pressures fall below a straight line joining the pure component critical pressures.

To illustrate the importance of  $k_{ij}$ , Figure 7 gives critical pressures for the *n*-butane-nitrogen system. Experimental results are compared with two sets of calculations; in one set  $k_{ij}$  was zero and in the other it was 0.12 as found from second virial coefficient data (49). Figure 6 shows that marked improvements can be obtained when small corrections are applied to the (rough) rule that the temperature characteristic of the 1-2 interaction is given by the geometric mean of the pure-component critical temperatures.

# MULTICOMPONENT SYSTEMS

Equations (3) and (4) are readily generalized to mixtures containing any number of components. The generalized equations are

$$T_{cT} = \sum_{i} \theta_{i} T_{c_{i}} + \sum_{i} \sum_{j} \theta_{i} \theta_{j} \tau_{ij}$$
(16)

$$v_{cT} = \sum_{i} \theta_{i} v_{c_{i}} + \sum_{i} \sum_{j} \theta_{i} \theta_{j} v_{ij}$$
(17)

where  $\tau_{ii} = \nu_{ii} = 0$ .

The critical pressure of a multicomponent mixture is found from the equation of state, Equation (5), with the mixing rules given by Equations (10) to (15).

For systems containing more than two components, directly measured critical temperatures and critical pressures are scarce, and directly measured critical volumes have not been reported at all. Critical constants obtained by extrapolation of vapor-liquid equilibrium (K factor) data are generally not reliable and in some cases may lead to large error, as pointed out by Sutton (64). With only directly measured experimental results, calculated and observed critical temperatures and critical pressures have been compared for six ternary systems (12, 18, 19, 40), two quaternary systems (19), and two quinary systems (19). The average deviation for the critical temperature was 0.4% and that for the critical pressure, 4.3%. It appears therefore that the accuracy for calculating critical constants of multicomponent systems is very close to that for calculating critical constants of binary mixtures.

### CONCLUSION

With the correlations presented in this work, good estimates can be made of the critical properties of a wide variety of mixtures of normal fluids (including paraffins, olefins, acetylene, aromatics, nitrogen, oxygen, carbon dioxide, and hydrogen sulfide) containing any number of components. Such estimates should be useful for technical calculations required in the petroleum, natural gas, and re-

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lated industries. Since the correlations are in analytical form, they can easily be implemented in an electronic computer. Critical temperatures and critical volumes are of particular interest in establishing techniques for analyzing and correlating high-pressure vapor-liquid equilibria in the critical region, as discussed in the previous paper.

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# NOTATION

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- a, b = constants in Redlich-Kwong equation of state
- $k_{ii}$  = characteristic constant for *i*-*j* interaction
- P = pressure

 $P_{c_i}$  = critical pressure of component *i* 

- $P_{cT}$  = critical pressure of a mixture
  - R = gas constant
  - T = temperature
- $T_{c_i}$  = critical temperature of component *i*
- $T_{c_{ii}}$  = characteristic temperature of *i*-*j* interaction
- $T_{cT}$  = critical temperature of a mixture
  - v = molar volume
- $v_{c_i}$  = critical volume of component *i*
- $v_{CT}$  = critical volume of a mixture
  - x = mole fraction

# **Greek Letters**

- $\theta = surface fraction$
- $\tau_{ii}$  = correlating parameter for critical temperature
- $v_{ii}$  = correlating parameter for critical volume

 $\omega$  = acentric factor

 $\Omega_a, \Omega_b$  = dimensionless constants in Redlich-Kwong equation, as given by Equations (9) and (8)

#### Subscripts

- c = critical
- i, ii = pure component i
  - ij = i j pair
  - M = mixture

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