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 θ:

$$v_{cT} = \sum_i \theta_i v_{c_i} + \sum_i \sum_j \theta_i \theta_j \nu_{ij}, \quad (\nu_{ii} = 0) \tag{28}$$

$$T_{cT} = \sum_i \theta_i T_{c_i} + \sum_i \sum_j \theta_i \theta_j \tau_{ij}, \quad (\tau_{ii} = 0) \tag{29}$$

where

$$\theta_k = \frac{x_k \, v_{c_k}^{2/3}}{\sum_i x_i \, v_{c_i}^{2/3}} \tag{30}$$

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

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 ±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.

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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
$\bar{v}_k$ = 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
$v_R^{(j)}$ = 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
$\gamma_k^{(P^r)}$ = activity coefficient of component k at some constant reference pressure
θ = surface fraction as defined by Equation (30)
ν_{ij} = correlating parameter for true critical volume of *i-j* binary
τ_{ij} = correlating parameter for true critical temperature of *i-j* binary
Φ = volume fraction as defined by Equation (10)
Ω_a, Ω_b = dimensionless constants in Redlich and Kwong parameters as defined by Equations (14) and (15)
ω = 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