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

$$\bar{v}_k = \left(\frac{\partial V}{\partial n_k}\right)_{P,T,n_i(i \neq k)} \tag{3}$$

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):

$$\bar{v}_k = \frac{-\left(\dfrac{\partial P}{\partial n_k}\right)_{T,V,n_i(i \neq k)}}{\left(\dfrac{\partial P}{\partial V}\right)_{T,n_i(\text{all } i)}} = f(x, T, v) \tag{4}$$

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

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

where ω 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 fitted the tabulated values with the following relation:

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

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.

TABLE 1. COEFFICIENTS IN EQUATION (6) FOR REDUCED VOLUMES OF SATURATED LIQUIDS†

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

† For reduced temperatures from 0.560 to 0.995.

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:

$$v_{cM} = \sum_i x_i v_{c_i} \tag{7}$$

$$T_{cM} = \sum_i \sum_j \Phi_i \Phi_j T_{c_{ij}} \tag{8}$$

$$\omega_M = \sum_i \Phi_i \omega_i \tag{9}$$

where

$$\Phi_k = \frac{x_k v_{c_k}}{\sum_i x_i v_{c_i}} \tag{10}$$

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

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-