

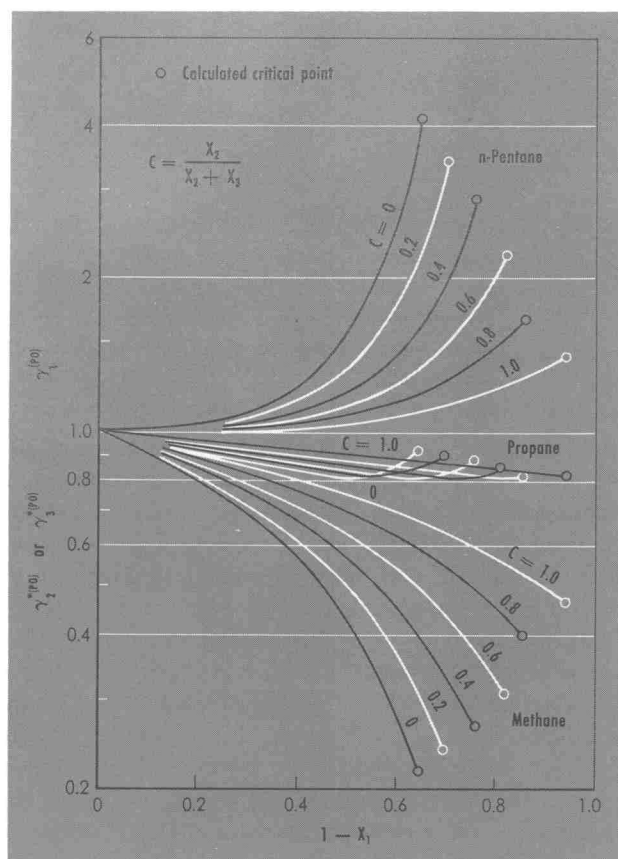


Figure 6. Calculated activity coefficients for the ternary system *n*-pentane(1)-propane(2)-methane(3) at 220° F.

pendence of the activity coefficient γ_i is given exactly by:

$$\left(\frac{\partial \ln \gamma_i}{\partial P}\right)_{T,x} = \frac{\bar{v}_i}{RT} \quad (72)$$

At high pressures in the critical region, $\bar{v}_i$ is usually a strong function of composition, especially for heavy components where $\bar{v}_i$ frequently changes sign as well as magnitude.

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.

Partial molar volume from an equation of state. The partial molal volume of component k in a mixture of N components is defined by

$$\bar{v}_k = \left(\frac{\partial V}{\partial n_k}\right)_{P,T,n_i(i \neq k)} \quad (73)$$

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 73:

$$\bar{v}_k = \frac{-\left(\frac{\partial P}{\partial n_k}\right)_{T,V,n_i(i \neq k)}}{\left(\frac{\partial P}{\partial V}\right)_{T,n_i(\text{all } i)}} = f(x_1, \dots, T, v) \quad (74)$$

With an equation of state, Equation 74 gives $\bar{v}_k$ as a function of the composition, temperature, and molar volume v of the liquid mixture. Pressure does not appear explicitly in Equation 74 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 74. The saturated molar volume of a liquid mixture can be calculated by extending to mixtures the corresponding-states correlation of Lyckman and Eckert (17) who slightly revised Pitzer's tables (23) for the saturated liquid volume of pure substances for the reduced temperature region 0.56–1.00. Pseudocritical rules are required for applications to mixtures. Such rules have been proposed (7) for the region in which the pseudoreduced temperature of the mixture is less than 0.93. In the critical region ($T_R > 0.93$), it has been found necessary to modify the pseudocritical rules in order that they converge to the true critical constants of the mixture at the critical point. To this end, we have developed correlations for true critical temperatures and volumes of mixtures and, also, an equation-of-state method for calculating the true critical pressures of mixtures. For reduced temperatures less than 0.56 other modifications are required. Details and results of these calculations are given elsewhere (7, 26).

In Equation 74, besides the saturated molar volume of the liquid mixture, we need an explicit form of the function f . For this, we need 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-Kwong equation (33) represents a useful modification of the van der Waals equation, we propose to use this equation for liquid mixtures with certain alterations. The Redlich-Kwong equation of state is given by Equation 4, and, for any pure fluid, the two constants a and b can be related to the critical properties of that fluid by Equations 5 and 6. As noted in Section A, if the conditions at the critical point 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 derivatives 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

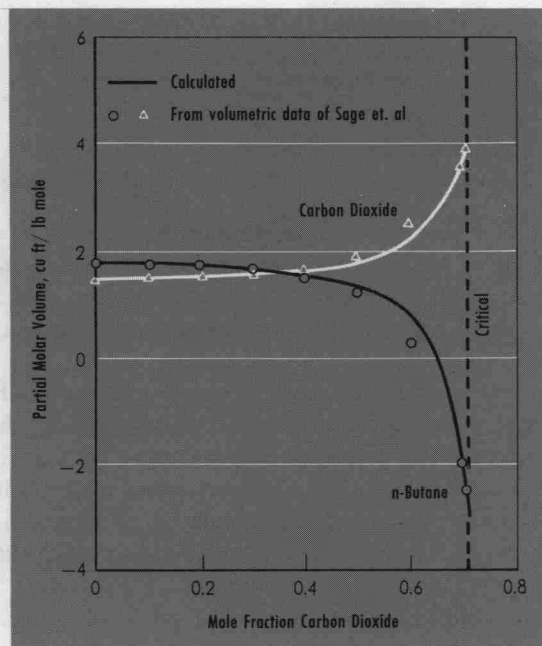


Figure 7. Partial molal volumes in the saturated liquid phase of the *n*-butane-carbon dioxide system at 160° F.

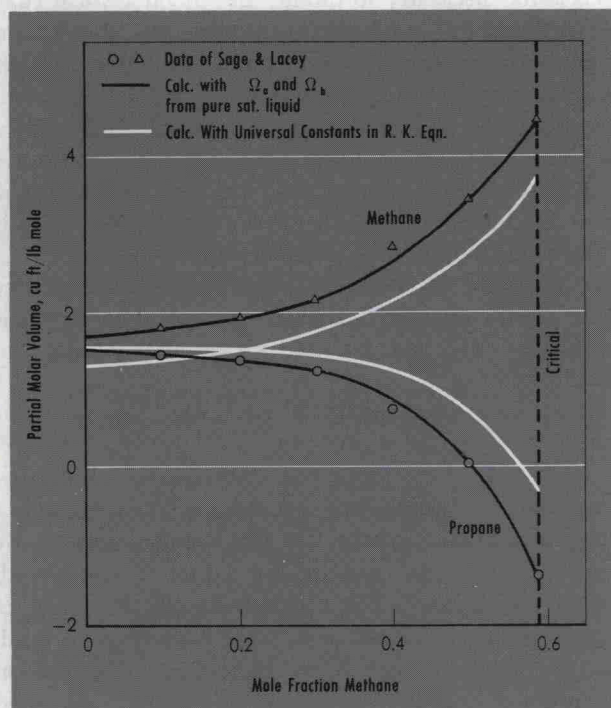


Figure 8. Partial molar volumes in the saturated liquid phase of the propane-methane system at 100° F.

phase. If we accept universal values for Ω_a and Ω_b , we are, in effect, subscribing to a two-parameter theorem of corresponding states. However, Pitzer and others (19, 23, 34, 37) have shown that the theorem of corresponding states requires a third parameter 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 Ω_a and Ω_b for each pure component. Fortunately, such data are readily available; results are given elsewhere (26) for 19 common liquids. They differ slightly from the universal values and show a trend with respect to an acentric factor.

For application to mixtures, we use the same mixing rules as given by Equations 7 through 15, except that the cube-root average for v_{cij} , Equation 13, is replaced by the arithmetic mean of v_{ci} and v_{cj} ; this is done to weight the larger molecule slightly more heavily in the liquid phase. The binary constant k_{ij} , which represents the deviation from the geometric mean for T_{cij} , is the same for both vapor and liquid phases; to a good approximation k_{ij} is independent of the temperature, density, and composition. Special precautions are needed for mixtures containing hydrogen or helium (26).

Partial molar volumes. The partial molar volume can be obtained after performing the partial differentiation indicated in Equation 74:

$$\bar{v}_k = \frac{\frac{RT}{v-b} \left(1 + \frac{b_k}{v-b} \right) - \frac{2 \left(\sum_i^N x_i a_{ki} \right) - \frac{ab_k}{v+b}}{v(v+b)T^{1/2}}}{\frac{RT}{(v-b)^2} - \frac{a}{T^{1/2} \left[\frac{2v+b}{v^2(v+b)^2} \right]}} \quad (75)$$

With v , the saturated liquid molar volume of the mixture, calculated from a corresponding states correlation, the partial molar volume of each component in a multi-component liquid mixture can be readily calculated from Equation 75. A computer program for performing the calculation is given elsewhere (26).

Figures 7 and 8 show calculated partial molar volumes in the saturated liquid phase of the systems *n*-butane-carbon dioxide and propane-methane, including the critical region. The calculated values are compared with those computed from the volumetric data of Sage and Lacey (38); 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