

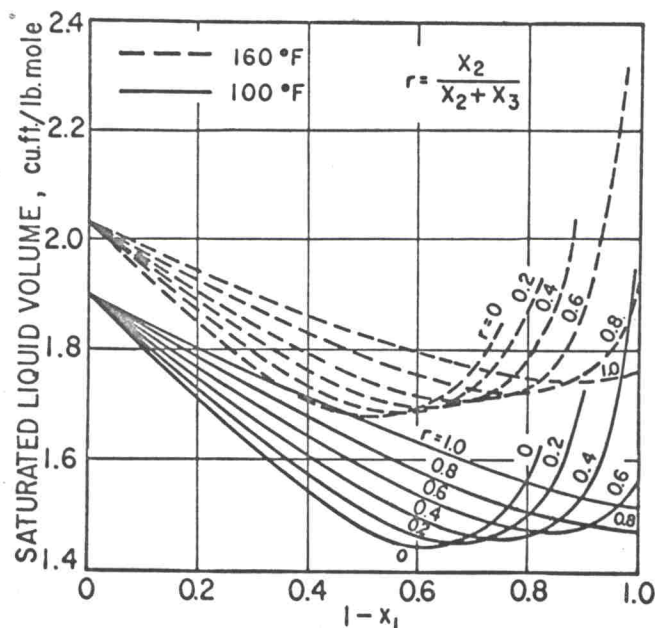


Fig. 6. Calculated saturated liquid molar volumes of the *n*-pentane (1)-propane (2)-methane (3) system.

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*-butane-carbon 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 Ω_a and Ω_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 in-

*For pentane-propane, $k_{ij} = 0.01$, $v_{ij} = -1.018$ cu. ft./lb.-mole and $\tau_{ij} = 7.0^\circ\text{R}$.

roduce 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

$$T'_{cM} = T_{cM} + (T_{cT} - T_{cM}) \mathcal{D}(T_R) \quad (22)$$

and

$$v'_{cM} = v_{cM} + (v_{cT} - v_{cM}) \mathcal{D}(T_R) \quad (23)$$

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

$$\mathcal{D}(T_R) \rightarrow 0 \text{ for } T_R < 0.93 \quad (24)$$

$$\mathcal{D}(T_R) = 1 \text{ at } T_R = 1.0 \quad (25)$$

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:

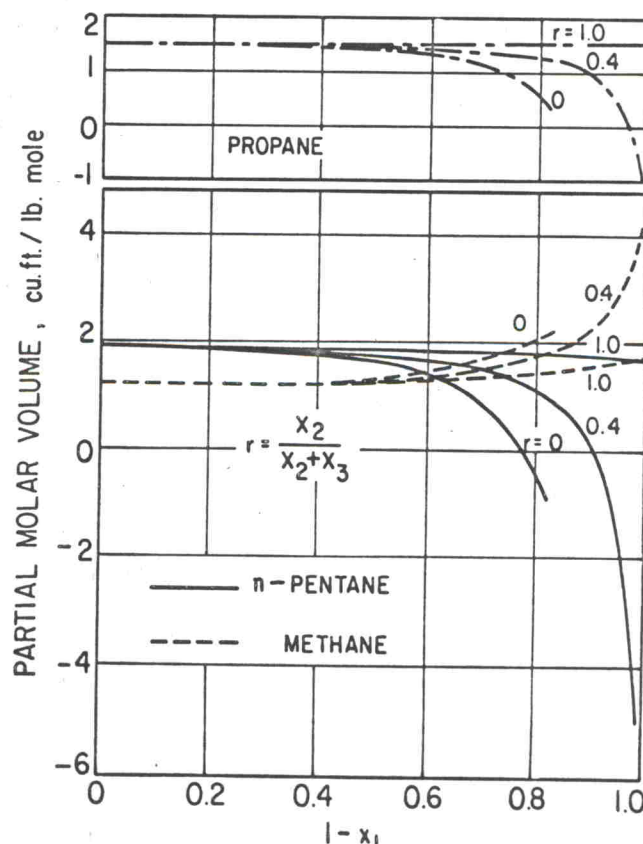


Fig. 7. Calculated partial molar volumes in the saturated liquid phase of the *n*-pentane (1)-propane (2)-methane (3) system at 100°F.