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

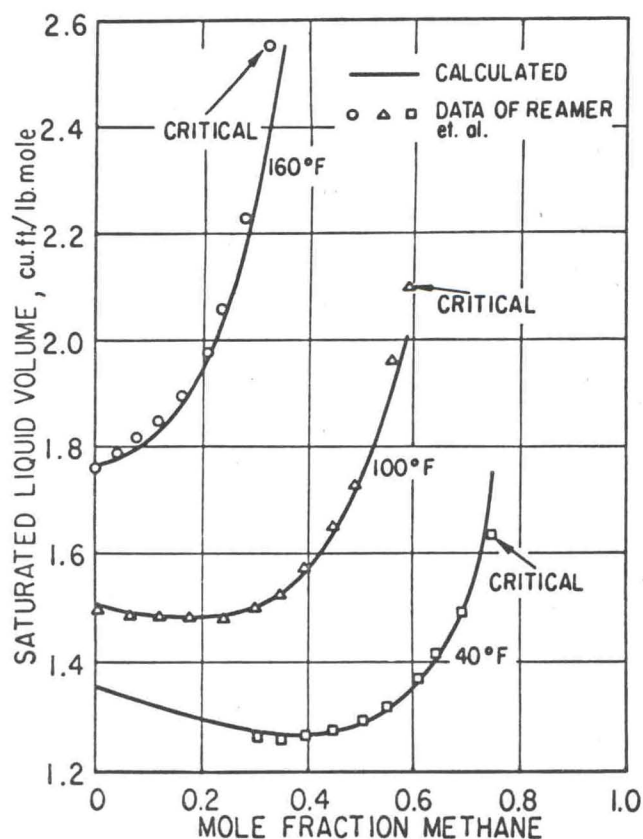Table 2 summarizes the results of calculations for seven binary systems, including those containing carbon dioxide, hydrogen sulfide, and aromatic hydrocarbons. The average deviation and maximum deviation for all twenty-five isotherms are small, and are probably of the same order of magnitude as the uncertainty in the experimental data. The rather good agreement for the system n-pentane-methane (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

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

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

$$a = \frac{\Omega_a R^2 T_c^{2.5}}{P_c} \quad (14)$$

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

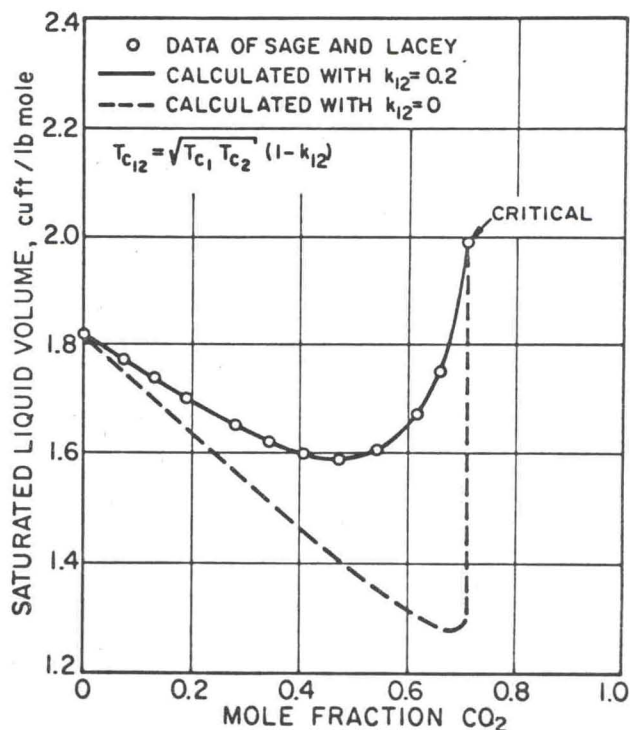where Ω_a and Ω_b are dimensionless constants. If the con-

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

Fig. 3. Saturated liquid molar volume calculated with and without correction to geometric mean for $T_{c_{12}}$ (n-butane–carbon dioxide at 160°F.).