TABLE 3. ACENTRIC FACTORS AND DIMENSIONLESS CONSTANTS IN THE REDLICH AND KWONG EQUATION OF STATE FOR SATURATED LIQUIDS

	ω	Ω_a	Ω_b
Methane	0.013	0.4546	0.0872
Nitrogen	0.040	0.4540	0.0875
Ethylene	0.085	0.4290	0.0815
Hydrogen sulfide	0.100	0.4220	0.0823
Ethane	0.105	0.4347	0.0827
Propylene	0.139	0.4130	0.0803
Propane	0.152	0.4138	0.0802
iso-Butane	0.187	0.4100	0.0790
Acetylene	0.190	0.4230	0.0802
1-Butene	0.190	0.4000	0.0780
n-Butane	0.200	0.4184	0.0794
Cyclohexane	0.209	0.4060	0.0787
Benzene	0.211	0.4100	0.0787
iso-Pentane	0.215	0.3970	0.0758
Carbon dioxide	0.225	0.4184	0.0794
n-Pentane	0.252	0.3928	0.0767
n-Hexane	0.298	0.3910	0.0752
n-Heptane	0.349	0.3900	0.0740
n-Nonane	0.447	0.3910	0.0738

ditions at the critical point $\left[\left(\frac{\partial P}{\partial v}\right)_{T_c} = 0 \text{ and } \left(\frac{\partial^2 P}{\partial v^2}\right)_{T_c} = 0\right]$ 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 experimental results 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 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 (*12* to *15*) have shown that the theorem of corresponding state requires a third parameter in order 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 in Table 3 for nineteen common liquids. They differ slightly from the universal values, and show a trend with respect to acentric factor.

For application of Equation (13) to mixtures, we propose the following mixing rules:

$$a = \sum_i \sum_j x_i x_j a_{ij} \quad [a_{ij} \neq (a_i a_j)^{1/2}] \tag{16}$$

$$b = \sum_i x_i b_i \tag{17}$$

where

$$a_{ii} = \frac{\Omega_{a_i} R^2 T_{c_i}^{2.5}}{P_{c_i}} \tag{18}$$

$$b_i = \frac{\Omega_{b_i} R T_{c_i}}{P_{c_i}} \tag{19}$$

$$a_{ij} = \frac{\frac{1}{4}(\Omega_{a_i} + \Omega_{a_j}) R T_{c_{ij}}^{1.5} (v_{c_i} + v_{c_j})}{0.291 - 0.04(\omega_i + \omega_j)} \tag{20}$$

PARTIAL MOLAR VOLUMES

The partial molar volume can be obtained from Equation (13) and the mixing rules, Equations (16) and (17), after performing the partial differentiation indicated in Equation (4):

$$\bar{v}_k = \frac{\frac{RT}{v-b}\left(1 + \frac{b_k}{v-b}\right) - \frac{2\left(\sum_i x_i a_{ki}\right) - a b_k/(v+b)}{v(v+b)T^{1/2}}}{\frac{RT}{(v-b)^2} - \frac{a}{T^{1/2}}\left[\frac{2v+b}{v^2(v+b)^2}\right]} \tag{21}$$

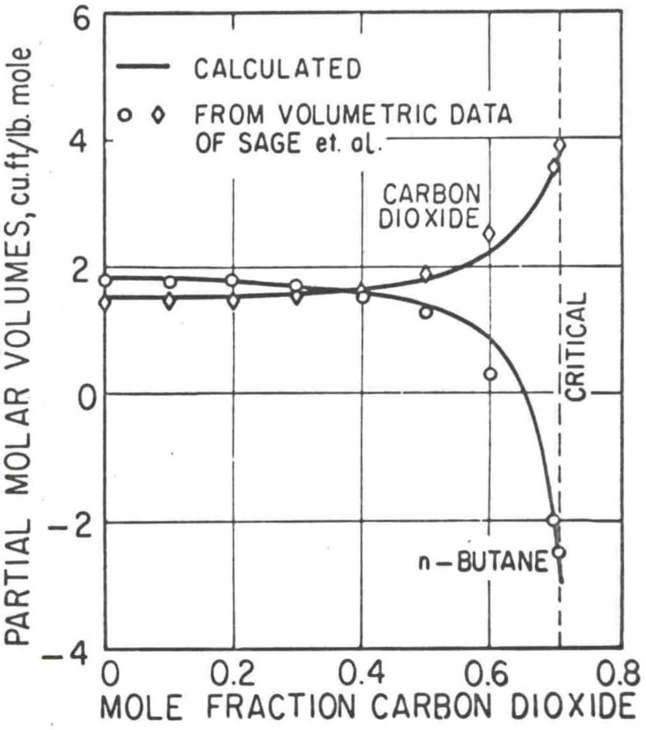

Fig. 4. Partial molar volumes in the saturated liquid phase of the *n*-butane–carbon dioxide system at 160°F.

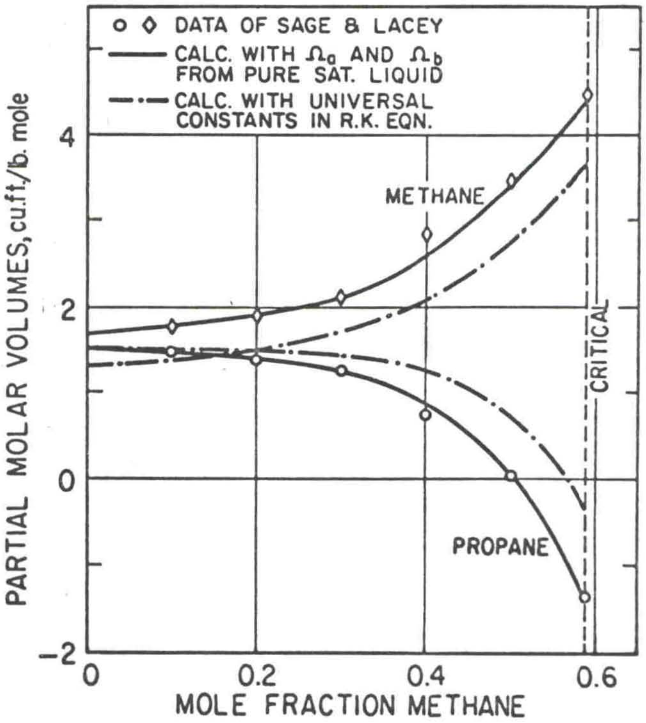

Fig. 5. Partial molar volumes in the saturated liquid phase of the propane-methane system at 100°F.