

TABLE 2. COMPARISON OF CALCULATED AND EXPERIMENTAL SATURATED MOLAR LIQUID VOLUMES OF BINARY MIXTURES AT HIGH PRESSURES

		(Reduced temperature <0.93)					
System*		k_{12}	T , °F.	Pressure range, lb./sq. in. abs.	x_2 ($T_R \approx 0.93$)	% Deviation	
(1)	(2)					Avg.	Max.
<i>n</i> -Butane-carbon dioxide	0.20	100	51.5 to 800	0.68	0.7	1.0	
		160	120.6 to 900	0.45	0.2	0.5	
		220	241.2 to 600	0.17	0.2	0.5	
Propane-methane	0.20	40	79 to 1,200	0.52	0.6	1.6	
		100	189 to 950	0.29	0.7	1.2	
<i>n</i> -Butane-methane	0.04	100	51.5 to 1,700	0.55	0.7	1.6	
		130	80.6 to 1,600	0.47	1.2	2.4	
		160	120.6 to 1,400	0.38	1.2	2.1	
		190	174.4 to 1,100	0.27	1.2	2.1	
		220	241.2 to 800	0.16	0.8	1.1	
<i>n</i> -Pentane-methane	0.06	100	15.7 to 2,300	0.68	0.1	0.3	
		160	42.5 to 2,100	0.57	0.7	1.9	
		220	94.9 to 1,600	0.41	1.2	2.3	
		280	185.6 to 900	0.20	1.2	1.8	
Propylene-ethane†	0.02	10	58 to 255	—	0.5	0.9	
		40	96.4 to 385	—	0.4	0.8	
		100	227.3 to 470	0.50	0.5	0.8	
Benzene-propane‡	0.03	100	3.2 to 189	—	0.5	1.2	
		160	11.1 to 384	1.0	0.8	1.1	
		220	29.2 to 520	0.81	0.4	0.7	
		280	64.7 to 630	0.64	0.4	1.3	
		340	126.0 to 710	0.44	0.5	1.2	
Hydrogen sulfide-methane	0.04	400	222.1 to 630	0.26	0.5	0.9	
		40	169 to 1,770	0.36	1.0	2.3	
		100	394 to 1,500	0.18	1.3	1.7	

*Critical constants for pure components taken from the compilation of Kobe and Lynn (9) unless otherwise noted. Experimental data of binary systems are taken from Sage et al. (24, 25).

†Critical volume of ethane is 2.27 cu. ft./lb.-mole as reported by Din (5).

‡Critical volume of benzene is 4.06 cu. ft./lb.-mole as reported by Bender et al. (1).

terminated k_{ij} 's are in good agreement with the semitheoretical relation

$$k_{ij} = 1 - \left[\frac{\sqrt{v_{ci}^{1/3} v_{cj}^{1/3}}}{(v_{ci}^{1/3} + v_{cj}^{1/3})/2} \right]^n \quad (12)$$

Equation (12) follows from London's theory of dispersion forces, neglecting small differences in ionization potentials. In agreement with Reid and Leland (23), we found that $n = 3$ gives better results than the theoretical value $n = 6$. Equation (12), however, is useful only for mixtures of paraffins; for other systems it may lead to large errors.

The saturated liquid volume of a multicomponent mixture may be calculated with Equations (5) and (6) and Equations (7) through (11). The pseudocritical rules, Equations (7) and (8), were found to give good predictions for $T_R \leq 0.93$. For larger T_R (critical region) a modification of the pseudocritical rules is required, as indicated later.

Figures 1 and 2 show calculated saturated liquid volumes for two systems, *n*-butane-carbon dioxide and propane-methane, each at three different temperatures; the calculated results are compared with experimental data of Sage and Lacey (21, 24, 25). These figures include the calculations in the critical region to be discussed later. The agreements are quantitative over the relatively wide temperature range.

At 160°F. *n*-butane is subcritical. As the mole fraction of carbon dioxide rises, the molar volume of the liquid mixture decreases at first, primarily because of the introduction of the smaller molecules of carbon dioxide and partly because of the increase in pressure; meanwhile, the re-

duced temperature increases due to the lower critical temperature of carbon dioxide. At an intermediate composition, the effect of increasing reduced temperature dominates the effect of smaller molecular size and higher pressure, and the molar volume of the mixture increases sharply toward its critical value. At high concentrations, the supercritical carbon dioxide expands or dilates the subcritical *n*-butane. This dilative effect becomes particularly pronounced in the critical region; it has been discussed previously in our development of a modified van Laar equation suitable for high-pressure vapor-liquid equilibria (3).

At a lower temperature, say 100°F., carbon dioxide is only slightly supercritical, whereas *n*-butane is well below its critical temperature. At 100°F. the effect of dilation therefore does not become important until very near the critical composition. On the other hand, at a higher temperature (220°F.) the heavier component, *n*-butane, is already close to its critical temperature and therefore is much more sensitive to the dilative effect of the supercritical carbon dioxide. At 220°F. the molar volume of the mixture increases soon after the introduction of carbon dioxide. Similar behavior is observed in the propane-methane system.

The characteristic parameter k_{ij} is very important in these calculations. To illustrate, Figure 3 shows the saturated liquid volumes for *n*-butane-carbon dioxide mixtures, calculated with and without correction to the geometric-mean for T_{c12} . For this system, the geometric-mean assumption is a poor one as was noted previously by Joffe and Zudkevitch (7).