TABLE 4. COMPARISON OF CALCULATED AND EXPERIMENTAL SATURATED MOLAR LIQUID VOLUMES OF BINARY MIXTURES IN THE CRITICAL REGION

(Reduced temperature 0.93 to 1.00)

System* (1) (2)	ν_{12}, cu. ft./lb. mole	τ_{12}, °R.	T, °F.	Pressure range, lb./sq. in. abs.	x_2 (critical)	% Deviation Avg.	% Deviation Max.
			100	800 to 1,057	0.954	2.3	4.3
n-Butane–carbon dioxide	−1.25	−46.4	160	900 to 1,020	0.713	0.7	1.4
			220	600 to 942	0.498	0.7	3.0
			40	1,200 to 1,474	0.7459	1.6	7.6
Propane-methane	−0.875	89.7	100	950 to 1,353	0.5882	1.0	4.9
			160	384 to 1,020	0.3228	1.2	5.9
			100	1,700 to 1,912	0.7236	1.6	4.5
			130	1,600 to 1,876	0.6718	1.6	3.4
			160	1,400 to 1,810	0.6165	2.2	2.8
n-Butane–methane	−1.96	101.3	190	1,100 to 1,698	0.5503	3.4	5.1
			220	800 to 1,520	0.4722	4.6	9.5
			250	327.7 to 1,264	0.3602	3.3	10.3
			100	2,300 to 2,455	0.8236	2.5	5.2
			160	2,100 to 2,338	0.7665	2.6	3.7
n-Pentane–methane	−2.35	141.4	220	1,600 to 2,081	0.6705	3.1	4.7
			280	900 to 1,610	0.5211	2.3	3.2
			340	330 to 1,025	0.2950	0.9	2.1
			100	470 to 722	0.9300	0.8	2.5
Propylene-ethane	−0.273	−4.7	160	455 to 705	0.3500	2.8	10.5
			280	630 to 750	†	0.8	1.3
Benzene-propane	−0.690	22.1	340	710 to 850	†	1.4	1.6
			400	630 to 850	†	0.7	2.8
			40	1,770 to 1,949	0.5500	3.1	4.2
Hydrogen sulfide-methane	−0.958	29.3	100	1,500 to 1,907	0.3880	2.2	5.2
			160	779 to 1,660	0.2090	1.6	7.3

*k_{12} given in Table 1. Experimental data of binary systems are taken from Sage et al. (*24, 25*).
†No critical composition reported.

$$\mathfrak{D}(T_{\dot{R}}) = \exp\left[(T_R - 1)\left(2901.01 - 5738.92\ T_R + 2849.85\ T_R^2 + \frac{1.74127}{1.01 - T_R}\right)\right] \quad (26)$$

Equation (26) was found to be sufficiently general for all systems investigated. The reducing parameter for T_R in Equation (26) is the corrected pseudocritical temperature T'_{cM} rather than the true critical temperature which is adequate at the critical point only. As a result T'_{cM} appears on both sides of Equation (22) and iteration is required to solve for T'_{cM}. This is best done by rewriting Equation (22):

$$\left[\frac{(T/T_{cM})}{T_R} - 1\right] - \left[\frac{(T/T_{cM})}{(T/T_{cT})} - 1\right]\mathfrak{D}(T_R) = 0 \quad (27)$$

Equation (27) has only one unique solution for $T_R < 1.0$ which can be readily found by a numerical technique (for example, Reguli-falsi iteration with variable pivoting points). The method usually converges in a few iterations. From Equation (23), v'_{cM} can then be obtained by direct substitution.

Equations (22) and (23) may be considered as more general pseudocritical rules applicable over the whole temperature range up to the critical point. With the corrected pseudocritical constants, the saturated molar volumes of liquid mixtures can be calculated from Equations (5) and (6) in the manner discussed before.

Figure 8 compares reduced temperatures and reduced volumes calculated for the system *n*-butane–carbon dioxide at 100°F., with the corrected pseudocriticals, Equations (22) and (23), and the uncorrected pseudocriticals, Equations (7) and (8). Whereas T_R and v_R based on corrected pseudocriticals converge to the right limit at the critical composition, those based on the uncorrected pseudocriticals at-

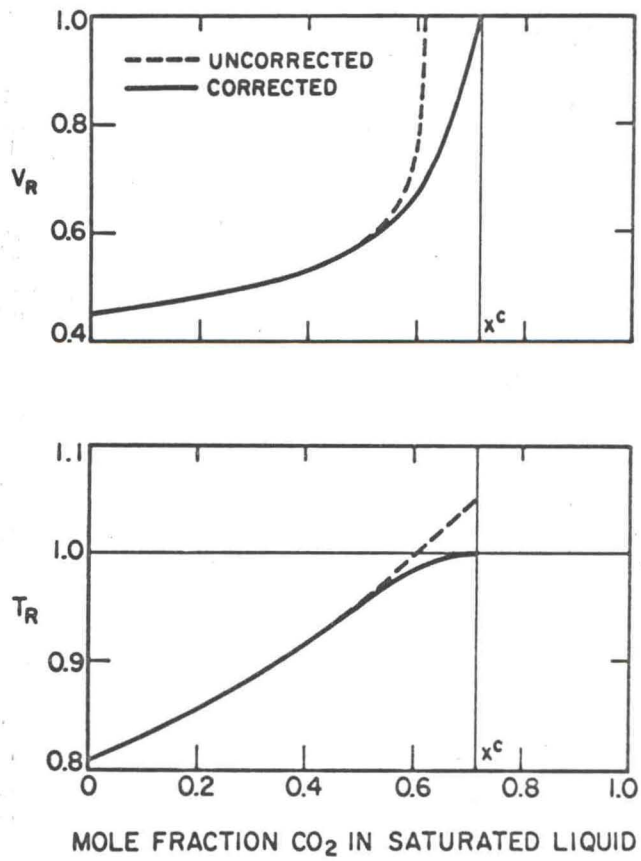

Fig. 8. Reduced temperature and reduced volume in the critical region with corrected and uncorrected pseudocritical constants (*n*-butane–carbon dioxide at 160°F.).