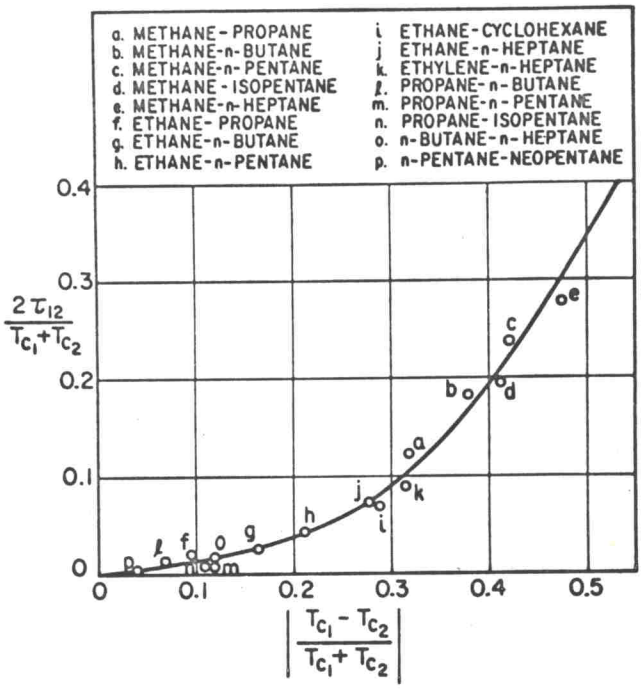

Fig. 2. Correlating parameter τ_{12} for critical temperatures of some binary systems containing satuated hydocarbons.

trend as paraffin-paraffin systems. Systems containing acetylene with a paraffin (or olefin), however, do not follow the paraffin-paraffin curve (see Table 1), due to the large quadrupole moment of acetylene. Figure 3 gives plots for paraffin-aromatic, paraffin-carbon dioxide, and paraffin-hydrogen sulfide systems.

The uncertainties in τ_{12} follow, in part, from experimental uncertainties. For example, three different investigators have reported critical temperatures for the system methane-propane. When fitted to Equation (3), we obtain $2\tau_{12}/(T_{c_1}+T_{c_2})$ equal to 0.1775 from reference *50*, 0.1410 from reference *61*, and 0.1237 from reference *1a*. When compared with experimental results for other paraffin-paraffin systems (Figure 2), it appears that the data of reference *1a* are the most reliable.

CRITICAL VOLUMES

If we utilize the simplifying assumption that the configurational thermodynamic properties of a dense system

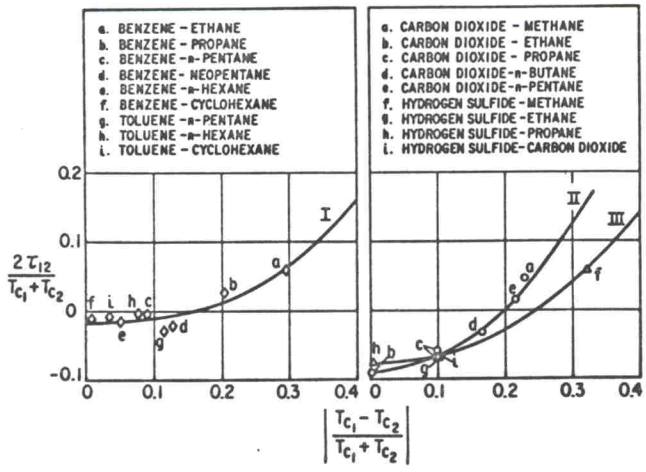

Fig. 3. Correlating parameter τ_{12} for critical temperatures of some binary systems: I. aromatic paraffin II. Carbon dioxide-paraffin III. Hydrogen sulfide-paraffin.

TABLE 2. AVERAGE PERCENT DEVIATIONS IN CORRELATING CRITICAL VOLUMES OF BINARY MIXTURES WITH DIFFERENT WEIGHTING OF MOLECULAR SIZE*

System	Type of weighting: Mole fract.	Diameter fract.	Surface fract.	Volume fract.
Methane–*n*-heptane	24.27	16.79	5.89	8.06
Methane–*n*-pentane	7.50	5.09	3.43	4.86
Methane–*n*-butane	2.70	0.94	1.41	4.14
Methane–iso-butane	4.27	2.36	0.34	2.59
Ethane–benzene	6.09	5.01	3.81	3.39
Ethane–*n*-heptane	6.16	4.33	3.91	6.54
Ethane–*n*-pentane	3.34	1.70	0.97	2.97
Ethane–*n*-butane	1.56	1.03	0.80	0.89
Hydrogen sulfide–*n*-pentane	2.60	1.79	2.09	5.30
Carbon dioxide–*n*-butane	2.96	1.99	1.00	2.96

*In each case a one-parameter quadratic function is used for correlation.

are due to two-body, nearest-neighbor interactions, we can express the critical volume of a mixture as a quadratic function of the composition. However, the composition can be specified in many ways and for components of significantly different molecular size, the mole fraction is inadequate. As for the critical temperature, we have found that the surface fraction [Equation (2)] provides the most useful measure of composition. Table 2 presents average deviations for the critical volumes of ten systems when experimental data are fitted to quadratic functions of four measures of composition: mole fraction, diameter fraction,* surface fraction, and volume fraction. The surface fraction gives the minimum deviation. The critical volume of a binary mixture therefore is written as

$$v_{cT} = \theta_1 v_{c_1} + \theta_2 v_{c_2} + 2\theta_1\theta_2 v_{12} \tag{4}$$

where v_{12} is a correlating parameter characteristic of the 1, 2 binary. Experimental data for critical volumes of binary mixtures are not nearly as plentiful as those for critical temperatures nor, because of experimental difficulties, are they as accurate. Table 1 gives the parameter v_{12} in reduced form as determined from experimental data for twenty-five systems. For these systems, Equation (4) correlated the data with an overall average deviation of 1.9%. Since accurate experimental determination of critical volumes is not simple, this deviation in many cases is of the same order as the experimental uncertainty.

Figure 4 presents the reduced correlating parameter as a function of the absolute value of $(v_{c_1}^{2/3} - v_{c_2}^{2/3})/(v_{c_1}^{2/3} + v_{c_2}^{2/3})$. Definite trends can be observed for different chemical families; Figure 4, therefore, should be useful for estimating critical volumes of systems where experimental data are lacking. The paraffin-paraffin curve for v_{12} may be used for systems consisting of paraffins, olefins, and acetylenes.

CRITICAL PRESSURES

Having correlated critical temperatures and critical volumes with quadratic functions of the surface fraction, one is tempted to try a similar correlation for the critical pressure. Such a correlation was tried and failed. Previous workers (*64*) have noted that the dependence of the critical pressure on composition is much more strongly nonlinear

*Diameter fraction weights the mole fraction of component i with $v_{c_i}^{1/3}$.