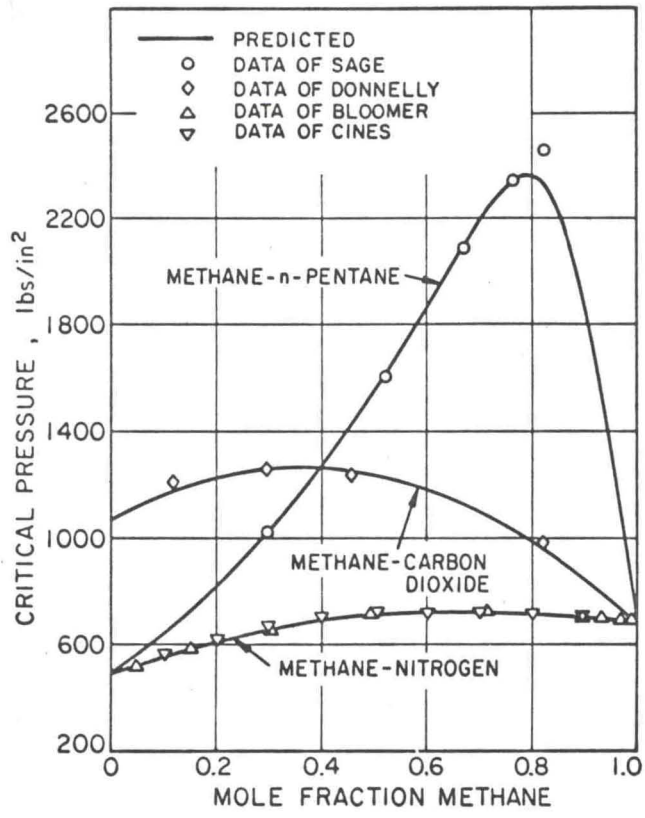

Fig. 6. Critical pressures of three binay systems containing methane.

$$T_{c\,ij} = \sqrt{T_{c\,ii}\,T_{c\,jj}}\,(1 - k_{ij}) \tag{15}$$

The constant k_{ij} is a small number (usually positive and of the order 10^{-2} or 10^{-1}) which is characteristic of the i-j interaction. To a good approximation, it is independent of temperature, density, and composition; it can be determined from a variety of experimental data for the i-j mixture in-

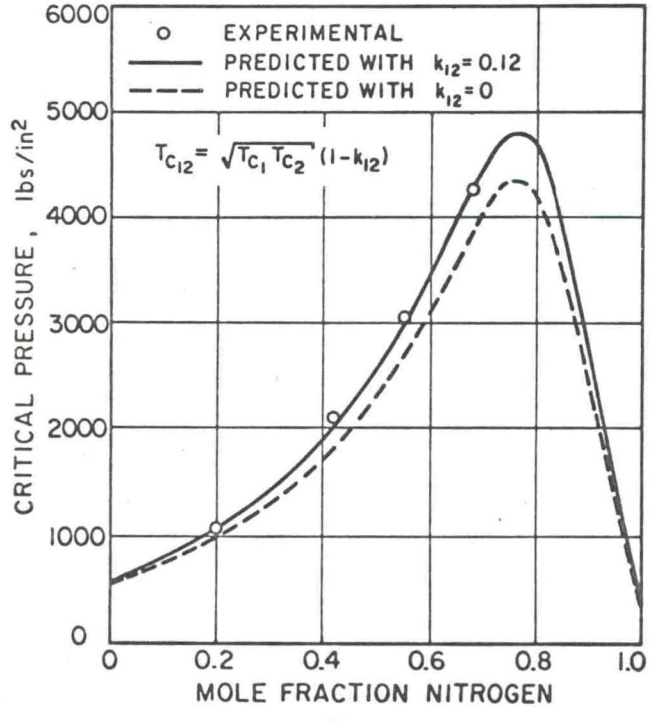

Fig. 7. Effect of correction to geometric mean on predicted critical pressures of the nitrogen–*n*-butane system. (k_{12} obtained from second virial coefficient data.)

cluding second virial coefficients and liquid-phase properties (*8*, *9*, *16*, *49*). Table 1 gives k_{ij} for thirty-six systems as determined from i-j mixture data. (Critical properties of mixtures were not used.)

Using the equation of Redlich and Kwong together with the previously established correlations for critical temperatures and critical volumes, we calculated critical pressures and compared them with experimental results for the thirty-six systems listed in Table 1. The mean of the average deviations is 3.6%. In these calculations, critical temperatures and volumes of mixtures were calculated from Equations (3) and (4); experimental critical temperatures and volumes of mixtures were not used directly in the Redlich-Kwong equation.

Typical results are shown in Figure 5 for three binary systems containing ethane and in Figure 6 for three binary systems containing methane. The system ethane–hydrogen sulfide is unusual, because, unlike the behavior of most systems, the critical pressures fall below a straight line joining the pure component critical pressures.

To illustrate the importance of k_{ij}, Figure 7 gives critical pressures for the *n*-butane–nitrogen system. Experimental results are compared with two sets of calculations; in one set k_{ij} was zero and in the other it was 0.12 as found from second virial coefficient data (*49*). Figure 6 shows that marked improvements can be obtained when small corrections are applied to the (rough) rule that the temperature characteristic of the 1–2 interaction is given by the geometric mean of the pure-component critical temperatures.

MULTICOMPONENT SYSTEMS

Equations (3) and (4) are readily generalized to mixtures containing any number of components. The generalized equations are

$$T_{cT} = \sum_i \theta_i T_{c_i} + \sum_i \sum_j \theta_i \theta_j \tau_{ij} \tag{16}$$

$$v_{cT} = \sum_i \theta_i v_{c_i} + \sum_i \sum_j \theta_i \theta_j v_{ij} \tag{17}$$

where $\tau_{ii} = v_{ii} = 0$.

The critical pressure of a multicomponent mixture is found from the equation of state, Equation (5), with the mixing rules given by Equations (10) to (15).

For systems containing more than two components, directly measured critical temperatures and critical pressures are scarce, and directly measured critical volumes have not been reported at all. Critical constants obtained by extrapolation of vapor-liquid equilibrium (K factor) data are generally not reliable and in some cases may lead to large error, as pointed out by Sutton (*64*). With only directly measured experimental results, calculated and observed critical temperatures and critical pressures have been compared for six ternary systems (*12*, *18*, *19*, *40*), two quaternary systems (*19*), and two quinary systems (*19*). The average deviation for the critical temperature was 0.4% and that for the critical pressure, 4.3%. It appears therefore that the accuracy for calculating critical constants of multicomponent systems is very close to that for calculating critical constants of binary mixtures.

CONCLUSION

With the correlations presented in this work, good estimates can be made of the critical properties of a wide variety of mixtures of normal fluids (including paraffins, olefins, acetylene, aromatics, nitrogen, oxygen, carbon dioxide, and hydrogen sulfide) containing any number of components. Such estimates should be useful for technical calculations required in the petroleum, natural gas, and re-