Redlich's original rule gives a value for a_{ij} slightly smaller than that given by the proposed rule with $k_{ij} = 0$. For example, for the methane–n-pentane system, Redlich's original rule gives $a_{ij} = 5.80 \times 10^5$ (p.s.i.a.) (° R.)$^{0.5}$ (cu. ft./lb. mole)^2, whereas the proposed rule gives 6.26×10^5 with $k_{ij} = 0$, and 5.70×10^5 with the recommended k_{ij} of 0.06. For this particular case, Redlich's original rule gives a value of a_{ij} close to that of the proposed rule with the recommended k_{ij} (as obtained from second virial cross coefficients). On the other hand, for the system ethane-acetylene, for which v_{c_i}/v_{c_j} is nearly unity, Redlich's original rule gives an a_{ij} which is essentially equal to that given by the proposed rule with $k_{ij} = 0$; such a_{ij} is 12% too large as compared to the a_{ij} given by the proposed rule with a recommended k_{ij} of 0.08. Finally, for the system carbon dioxide–n-butane, a_{ij} from Redlich's original rule corresponds to that of the proposed rule with $k_{ij} = 0.04$, as compared to a k_{ij} of 0.18 obtained from second virial cross coefficients. This may explain why Redlich's original rule often works well for paraffin-paraffin systems but not for systems containing chemically dissimilar components.

Fugacity Coefficients from Revised Redlich-Kwong Equation

By substituting Equation 5 and the mixing rules, Equations 8 to 16, into Equation 3, the fugacity coefficient of component k in the mixture becomes

$$\ln \varphi_k = \ln \frac{v}{v-b} + \frac{b_k}{v-b} - \frac{2 \sum_{i=1}^{N} y_i a_{ik}}{RT^{3/2} b} \ln \frac{v+b}{v} + \frac{a b_k}{RT^{3/2}\, b^2}\left[\ln \frac{v+b}{v} - \frac{b}{v+b}\right] - \ln \frac{Pv}{RT} \tag{17}$$

The molar volume, v, is that of the gas mixture; it is obtained by solving Equation 5 (which is cubic in v) and taking the largest real root for v.

Figure 1 shows experimental and calculated compressibility factors for three mixtures of nitrogen and n-butane at 310° F. (Evans and Watson, 1956). The values of Ω_a and Ω_b used are those for the pure saturated vapors, although the gas mixtures at this temperature are actually supercritical. The calculated compressibility factors for the gas mixture are in good agreement with the experimental data up to a pressure as high as 9000 p.s.i.a.

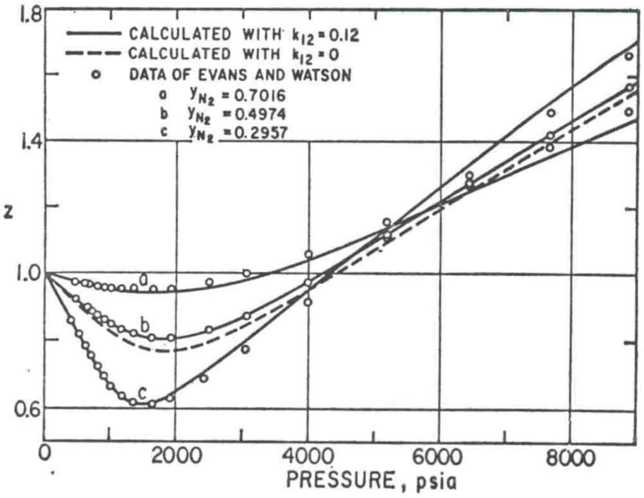

Figure 1. Compressibility factors of nitrogen–n-butane mixtures at 310° F.

$k_{12} = 0.12$ obtained from second virial coefficient data

Figure 2 shows experimental and calculated fugacity coefficients of carbon dioxide in a mixture containing 85 mole % n-butane at 340° F. The experimental fugacity coefficients of carbon dioxide are obtained from the volumetric data of Olds *et al.* (1949) by performing graphically the differentiation and integration indicated in Equation 2. The test is a rather stringent one, since the mole fraction of carbon dioxide is small and the gas mixture is near its critical temperature. The fugacity coefficient of carbon dioxide shows an unusual pressure dependence, going through two inflections and a sharp maximum. The agreement is good considering the uncertainty involved in the numerical differentiation of the experimental data. Also indicated is the poor result obtained when the geometric mean assumption is used for $T_{c_{12}}$. The Lewis fugacity rule fails badly at all pressures, since the mole fraction of carbon dioxide is small.

Figure 3 shows experimental and calculated fugacity coefficients of ethane in an equimolar mixture with methane. The experimental fugacity coefficients of ethane are those reported by Sage and Lacey (1950). Figures 4, 5, and 6 show experimental and calculated compressibility factors for saturated vapor mixtures of three binary systems: propane-methane (Reamer *et al.*, 1950), n-pentane–methane (Sage *et al.*, 1942), and n-pentane–hydrogen sulfide (Reamer *et al.*, 1953). Compressibility factors of the saturated vapors of the first two binary systems first increase with rising methane concentration but soon decrease because of the effect of high pressure. The calculated compressibility factors reproduce this behavior. The agreement is good except for the n-pentane–methane system near the critical.

For the n-pentane–hydrogen sulfide system at 160° F., both components are subcritical and the experimental and calculated compressibility factors are in good agreement over the entire composition range, from pure n-pentane to pure hydrogen sulfide. Calculations based on Redlich's original mixing rules (Redlich and Kwong, 1949) show less satisfactory agreement with experimental data. Also shown are the calculated fugacity coefficients for the heavy components; the fugacity coefficients of propane and n-pentane at high pressure and low

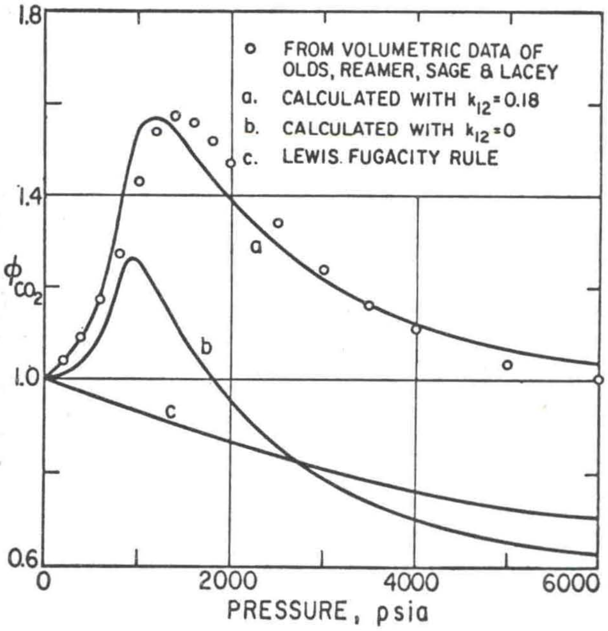

Figure 2. Fugacity coefficients of carbon dioxide in a mixture containing 85 mole % n-butane at 340° F.

$k_{12} = 0.18$ obtained from second virial coefficient data