

The fundamental equation of vapor-liquid equilibrium is conveniently written in terms of fugacities; for each component i the fugacity in the vapor f_i^V is equal to that in the liquid, f_i^L :

$$f_i^V = f_i^L \quad (1)$$

To facilitate thermodynamic analysis, we introduce two auxiliary functions: the vapor-phase fugacity coefficient ϕ_i and the liquid-phase activity coefficient γ_i :

$$f_i^V = \phi_i y_i P \quad (2)$$

$$f_i^L = \gamma_i x_i f_i^o \quad (3)$$

where y and x are, respectively, mole fractions in the vapor and in the liquid, P is the total pressure, and f_i^o is the standard-state fugacity of component i . Each of these auxiliary functions is discussed separately; Section A considers the fugacity coefficient while Sections B and C consider the activity coefficient. Finally, in Section D we synthesize the analysis of the other sections and compare with experiment some predicted results for several multicomponent systems.

A. Vapor-Phase Fugacity Coefficients

In this section we are concerned with a reliable technique for calculating vapor-phase fugacity coefficients in nonpolar mixtures, including those contain-

ing one of the quantum gases. To that end we propose to use the Redlich-Kwong equation with certain modifications.

The Redlich-Kwong equation (32) is now nearly 20 years old; recently it has been discussed by several authors (2, 12, 36, 41), and it is generally regarded as the best two-parameter equation now available (40). For mixtures, however, it often gives poor results, as does the recent modification given by Redlich and co-workers (37). The failure of the equation to give consistently good results for mixtures is due to the inflexible mixing rules for the composition dependence of the equation-of-state constants. We propose a modified mixing rule for the constant a ; this modification incorporates one characteristic binary constant, and such constants have been reported for 115 binary systems (8). Extension to multicomponent systems follows without further assumptions and with no ternary (or higher) constants. A somewhat similar treatment, restricted to paraffin-carbon dioxide mixtures, has been suggested by Joffe and Zudkevitch (16). Other modifications of the Redlich-Kwong equation have been reported by Wilson (41), Esters and Tully (12), Robinson and Jacoby (36), and by Barner, Pigford, and Schreiner (2).

The Redlich-Kwong equation is:

$$P = \frac{RT}{v - b} - \frac{a}{T^{0.5}v(v + b)} \quad (4)$$

where

$$a = \frac{\Omega_a R^2 T_{c_i}^{2.5}}{P_{c_i}} \quad (5)$$

$$b = \frac{\Omega_b R T_{c_i}}{P_{c_i}} \quad (6)$$

The dimensionless constants Ω_a and Ω_b are, respectively, 0.4278 and 0.0867 if the first and second isothermal derivatives of pressure with respect to volume are set equal to zero at the critical point. In vapor-liquid equilibria, however, we are interested in the volumetric behavior of saturated vapors over a relatively wide range of temperature, rather than in the critical region only. We propose, therefore, to evaluate Ω_a and Ω_b for each pure component by fitting Equation 4 to the volumetric data of the saturated vapor. The temperature range used is that from the normal boiling point to the critical temperature. A list of Ω_a and Ω_b for the saturated vapors of 19 pure substances most often encountered in high pressure vapor-liquid equilibria has been given (8).

To apply Equation 4 to mixtures, we need a mixing rule. We propose:

$$b = \sum_{i=1}^N y_i b_i \quad (7)$$

where

$$b_i = \frac{\Omega_b R T_{c_i}}{P_{c_i}} \quad (8)$$

and

$$a = \sum_{i=1}^N \sum_{j=1}^N y_i y_j a_{ij} \quad (a_{ij} \neq \sqrt{a_{ii} a_{jj}}) \quad (9)$$

where

$$a_{ii} = \frac{\Omega_{ai} R^2 T_{ci}^{2.5}}{P_{ci}} \quad (10)$$

$$a_{ij} = \frac{(\Omega_{ai} + \Omega_{aj}) R^2 T_{cij}^{2.5}}{2 P_{cij}} \quad (11)$$

$$P_{cij} = \frac{z_{cij} R T_{cij}}{v_{cij}} \quad (12)$$

$$v_{cij}^{1/3} = \frac{1}{2} (v_{ci}^{1/3} + v_{cj}^{1/3}) \quad (13)$$

$$z_{cij} = 0.291 - 0.08 \left(\frac{\omega_i + \omega_j}{2} \right) \quad (14)$$

$$T_{cij} = \sqrt{T_{cii} T_{cjj}} (1 - k_{ij}) \quad (15)$$

The binary constant k_{ij} represents the deviation from the geometric mean for T_{cij} . It is a constant characteristic of the i - j interaction; to a good approximation k_{ij} is independent of the temperature, density, and composition. In general, k_{ij} must be obtained from some experimental information about the binary interaction. Good sources of this information are provided by second virial cross coefficients (28). Best estimates of k_{ij} have been reported for 115 binary systems (8).

Fugacity coefficient. The fugacity of a component i in a gas mixture is related to the total pressure P and its mole fraction y_i through the fugacity coefficient ϕ_i as shown in Equation 2 of the preceding section.

The fugacity coefficient is a function of pressure, temperature, and gas composition; it is related to the volumetric properties of the gas mixture by the exact relation (3, 24):

$$RT \ln \phi_i = \int_V^\infty \left[\left(\frac{\partial P}{\partial n_i} \right)_{T,V,n_j} - \frac{RT}{V} \right] dV - RT \ln z \quad (16)$$

where V is the total volume of the gas mixture, and z is the compressibility of the gas mixture at T and P .

By substituting Equation 4 and the mixing rules, Equations 7 to 15, into 16, the fugacity coefficient of component k in the mixture becomes:

$$\ln \phi_k = \ln \frac{v}{v-b} + \frac{b_k}{v-b} - \frac{2 \sum_{i=1}^N y_i a_{ik}}{RT^{3/2} b} \ln \frac{v+b}{v} + \frac{ab_k}{RT^{3/2} b^2} \left[\ln \frac{v+b}{v} - \frac{b}{v+b} \right] - \ln \frac{Pv}{RT} \quad (17)$$

The molar volume, v , is that of the gas mixture; it is obtained by solving Equation 4 (which is cubic in v) and taking the largest real root for v .

Figure 1 shows experimental and calculated fugacity coefficients of carbon dioxide in a mixture containing

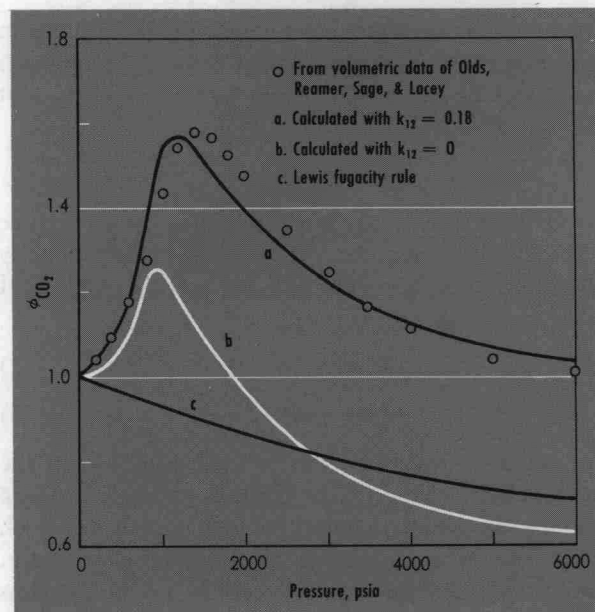


Figure 1. Fugacity coefficients of carbon dioxide in a mixture containing 85 mole per cent n -butane at 340° F. ($k_{12} = 0.18$ obtained from second virial coefficient data)

85 mole per cent n -butane at 340° F. The experimental fugacity coefficients of carbon dioxide are obtained from the volumetric data of Olds *et al.* (22). The comparison 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. Agreement is good considering the uncertainty involved in the numerical differentiation of the experimental data. Also indicated is the poor result obtained when the geometrical mean assumption is used for T_{cij} . The Lewis fugacity rule fails badly at all pressures, since the mole fraction of carbon dioxide is small.

The configurational properties of low-molecular-weight gases (hydrogen, helium, neon) are described by quantum, rather than classical, statistical mechanics. As a result, the properties of these gases cannot be given by the same corresponding-states treatment (Equations 8, 10–15) as that used for classical gases when the true critical constants are used as the reducing parameters. It is possible, however, to define temperature-dependent effective critical constants with which the properties of quantum gases can be made to coincide with those for classical gases (13).

Figure 2 shows experimental and calculated fugacity coefficients of methane in a mixture with hydrogen at equilibrium with solid methane (14). Good agreement at these low temperatures and high pressures suggests that the revised Redlich-Kwong equation can be successfully applied to mixtures of nonpolar and quantum gases. Other examples for fugacity coefficients and for compressibility factors of vapor mixtures have also been reported (8).