

somewhat similar study, restricted to paraffin-carbon dioxide mixtures, has recently been published by Joffe and Zudkevitch (1966). Other modifications of the Redlich-Kwong equation have been reported by Wilson (1964), Estes and Tully (1967), Robinson and Jacoby (1965), and Barner, Pigford, and Shreiner (1966).

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 :

$$f_i = \varphi_i y_i P \quad (1)$$

The fugacity coefficient is a function of pressure, temperature, and gas composition; it is related to the volumetric properties of the gas mixture by either of the two exact relations (Beattie, 1949; Prausnitz, 1959):

$$RT \ln \varphi_i = \int_0^P \left[\left(\frac{\partial V}{\partial n_i} \right)_{T,P,n_j} - \frac{RT}{P} \right] dP \quad (2)$$

$$RT \ln \varphi_i = \int_V^\infty \left[\left(\frac{\partial P}{\partial n_i} \right)_{T,V,n_j} - \frac{RT}{V} \right] dV - RT \ln z \quad (3)$$

where V is the total volume of the gas mixture, and z is the compressibility factor of the gas mixture at T and P . Since most equations of state are explicit in pressure, Equation 3 is more convenient to use.

For a mixture of ideal gases $\varphi_i = 1$ for all i . For a gas mixture that follows Amagat's assumption ($\bar{v}_i = v_{\text{pure } i}$ at the same T and P for the entire pressure range from zero to P), Equation 2 gives the Lewis fugacity rule (Lewis and Randall, 1923) which says

$$\varphi_i = \varphi_{\text{pure } i} \quad (\text{at same } T \text{ and } P) \quad (4)$$

This simplifying assumption, however, may lead to large error, especially for components present in small concentrations. The Lewis fugacity rule becomes exact (at any pressure) only in the limit $y_i \rightarrow 1$.

The fugacity coefficient of component i in a gas mixture can be calculated from Equations 2 and 3 if sufficient volumetric data are available for the gas mixture. Since such data are not usually available, especially for multicomponent systems, fugacity coefficients are most often calculated by an extension of the theorem of corresponding states or with an equation of state. The method based on corresponding states has been discussed (Joffe, 1948; Leland *et al.*, 1962). In the following we discuss a method based on an equation of state which is more convenient to use than the corresponding-states method.

Equation of State

Only the virial equation has a sound theoretical foundation for representing the properties of pure and mixed gases. When truncated after the third term, the virial equation is useful up to a density nearly corresponding to the critical density. A method for estimating the third virial coefficient of mixtures is given elsewhere (Chueh and Prausnitz, 1967a,b; Orentlicher and Prausnitz, 1967). For application at higher densities, an empirical equation of state such as the Redlich-Kwong equation (1949) is more reliable. For vapor-phase fugacity coefficients we use the Redlich-Kwong equation throughout the entire range of density.

The Redlich-Kwong equation is

$$P = \frac{RT}{v-b} - \frac{a}{T^{0.5}v(v+b)} \quad (5)$$

where

$$a = \frac{\Omega_a R^2 T_{ci}^{2.5}}{P_{ci}} \quad (6)$$

$$b = \frac{\Omega_b R T_{ci}}{P_{ci}} \quad (7)$$

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 5 to the volumetric data of the saturated vapor. The temperature range used is that from the normal boiling point to the critical temperature. Table I lists Ω_a and Ω_b for the saturated vapors of 19 pure substances most often encountered in high pressure vapor-liquid equilibria.

To apply Equation 5 to mixtures, we need a mixing rule. We propose

$$b = \sum_{i=1}^N y_i b_i \quad (8)$$

where

$$b_i = \frac{\Omega_b R T_{ci}}{P_{ci}} \quad (9)$$

and

$$a = \sum_{i=1}^N \sum_{j=1}^N y_i y_j a_{ij} \quad (a_{ij} \neq \sqrt{a_i a_j}) \quad (10)$$

where

$$a_{ii} = \frac{\Omega_a R^2 T_{ci}^{2.5}}{P_{ci}} \quad (11)$$

$$a_{ij} = \frac{(\Omega_a i + \Omega_a j) R^2 T_{cij}^{2.5}}{2 P_{cij}} \quad (12)$$

$$P_{cij} = \frac{z_{cij} R T_{cij}}{v_{cij}} \quad (13)$$

Table I. Acentric Factors and Dimensionless Constants in Redlich-Kwong Equation of State for Saturated Vapors

	ω	Ω_a	Ω_b
Methane	0.013	0.4278	0.0867
Nitrogen	0.040	0.4290	0.0870
Ethylene	0.085	0.4323	0.0876
Hydrogen sulfide	0.100	0.4340	0.0882
Ethane	0.105	0.4340	0.0880
Propylene	0.139	0.4370	0.0889
Propane	0.152	0.4380	0.0889
Isobutane	0.187	0.4420	0.0898
Acetylene	0.190	0.4420	0.0902
1-Butene	0.190	0.4420	0.0902
n-Butane	0.200	0.4450	0.0906
Cyclohexane	0.209	0.4440	0.0903
Benzene	0.211	0.4450	0.0904
Isopentane	0.215	0.4450	0.0906
Carbon dioxide	0.225	0.4470	0.0911
n-Pentane	0.252	0.4510	0.0919
n-Hexane	0.298	0.4590	0.0935
n-Heptane	0.349	0.4680	0.0952
n-Octane	0.398	0.4760	0.0968