

Vapor-Liquid Equilibria at High Pressures: Calculation of Partial Molar Volumes in Nonpolar Liquid Mixtures

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Thermodynamic analysis of high-pressure vapor-liquid equilibria requires information on the effect of pressure on liquid phase fugacities; this information is given by partial molar volumes in the liquid mixture. A method for predicting these partial molar volumes is presented here. First, molar volumes of saturated liquid mixtures are computed by extending to mixtures the corresponding states correlation of Lyckman and Eckert. These mixture volumes are then used to calculate partial molar volumes with an expression based on a modification of the Redlich-Kwong equation. At high pressures partial molar volumes are strong functions of the composition and in the critical region, may be positive or negative. Calculations are sensitive to the characteristic energy between dissimilar molecules; this energy is generally lower than that given by the geometric-mean rule. Calculated results are in good agreement with experimental data for seven systems containing paraffinic and aromatic hydrocarbons, carbon dioxide, and hydrogen sulfide.

To be useful, a thermodynamic treatment of high-pressure vapor-liquid equilibria must describe how the fugacity of each component, in each phase, depends on the temperature, pressure, and composition. In the vapor phase, this dependence is given by the fugacity coefficient which can be found from vapor-phase volumetric properties as given by an equation of state. In the liquid phase it is more convenient to express the fugacity of a component as the product of the mole fraction, an arbitrary standard state fugacity and an activity coefficient; the effect of temperature, pressure, and composition on the fugacity of a component in the liquid phase is determined by the effect of these variables on the activity coefficient. In this work we are concerned with the effect of pressure on the activity coefficient.

At low or moderate pressures, liquid-phase activity coefficients are very weakly dependent on pressure and, as a result, it has been customary to assume that, for practical purposes, activity coefficients depend only on temperature and composition. In many cases this is a good assumption but for phase equilibria at high pressures, especially for those near critical conditions, it can lead to serious error.

When the standard state fugacity is defined at a constant pressure, then for any component i the pressure dependence of the activity coefficient γ_i is given exactly by

$$\left(\frac{\partial \ln \gamma_i}{\partial P}\right)_{T,x} = \frac{\bar{v}_i}{RT} \quad (1)$$

On the other hand, when the standard state fugacity is defined at the total pressure of the system, Equation (1) must be modified to

$$\left(\frac{\partial \ln \gamma_i}{\partial P}\right)_{T,x} = \frac{\bar{v}_i - v_i^0}{RT} \quad (1a)$$

By judicious choice, it is sometimes possible to use a standard state such that $\bar{v}_i \approx v_i^0$, in which case the activity coefficient is very nearly independent of pressure (17). However, since $\bar{v}_i$ is a function of composition, whereas v_i^0 is not, such a happy choice of standard state can make the right-hand side of Equation (2) very small over only a narrow range of composition. At high pressures in the critical region, $\bar{v}_i$ is usually a strong function of composition, especially for heavy components where $\bar{v}_i$ frequently changes sign as well as magnitude.

Experimental activity coefficients obtained at P , the total pressure of the system, can be corrected to a constant, arbitrary reference pressure P^r by integration of Equation (1):

$$\gamma_i^{(P^r)} = \gamma_i^{(P)} \exp \int_P^{P^r} \frac{\bar{v}_i}{RT} dP \quad (2)$$

Equation (2) defines adjusted, pressure-independent activity coefficients $\gamma_i^{(P^r)}$, which at constant temperature, satisfy the isobaric, isothermal Gibbs-Duhem equation. It is advantageous to use such adjusted activity coefficients since their composition dependence can be expressed by