COMMUNICATIONS TO THE EDITOR

Pseudocritical Constants from Volumetric Data for Gas Mixtures

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As a result of recent correlations based on an extended theorem of corresponding states (*2, 3*), it is now possible to estimate the volumetric properties of pure, nonpolar or slightly polar fluids with an accuracy of about 2% or better. In an effort to extend the correlation of Pitzer and co-workers (*3*) for the estimation of the properties of gas mixtures by means of pseudocritical parameters, it became necessary to decide on a suitable method of determining pseudocritical constants from volumetric data. Such a method is described.

There are four pseudocritical parameters for any mixture at constant composition: the pseudocritical temperature, pressure, and volume, and the acentric factor of the mixture. Of these four only three are independent. At reduced temperatures of unity or above, the effect of the acentric factor, is not very large, and it was therefore arbitrarily decided to define the acentric factor of the mixture by the linear relationship

$$\omega_m = \sum_i y_i \omega_i \qquad (1)$$

The pseudocritical temperature and pressure can then be determined conveniently from volumetric data in the following manner. From the generalized compressibility tables (*3*) a table is prepared which gives the value of the minimum compressibility factor with respect to the reduced temperature and the acentric factor. For a given value of the acentric factor the minimum compressibility factor uniquely determines the pseudocritical temperature. From volumetric data the minimum compressibility factor for a mixture at a particular temperature is selected. The reduced temperature corresponding to this minimum compressibility factor and to the acentric factor of the gaseous mixture is found from the table. Both the absolute and the reduced temperatures are known; hence the pseudocritical temperature for the mixture can be found. The minimum compressibility factor is relatively insensitive to the reduced pressure; therefore the pseudocritical pressure is best calculated from an experimental compressibility factor at as high a pressure as possible. At high pressures the compressibility factors are sensitive to the reduced pressure but relatively insensitive to errors in the reduced temperature. Once the pseudocritical temperature is known, the pseudocritical pressure can be calculated from a compressibility factor for the mixture at a high pressure by use of the Pitzer compressibility tables. The same value of the compressibility factor is located in the generalized compressibility-factor tables at the same reduced temperature and acentric factor as those of the mixture, and the reduced pressure corresponding to this compressibility factor is obtained. Once the reduced and absolute pressures are known, the pseudocritical pressure is found.

The pseudocritical temperatures and pressures were determined in the manner described for a number of mixtures, including the systems methane-decane, methane–*n*-heptane, methane–*n*-pentane, propane-benzene, hydrogen sulfide–decane, carbon dioxide–nitrogen, nitrogen-ethane, carbon dioxide–*n*-butane, and carbon dioxide–ethane. With these pseudocritical constants it was possible to calculate the compressibility factors for the respective mixtures to within 2 or 3%, even near the critical region. It was found that the pseudocritical temperature and pressure are complicated functions of the composition which cannot be predicted accurately by simple rules. The pseudocritical volume, however, appears to be a much simpler function of the composition and is calculated from the pseudocritical pressure and temperature by the equation

$$V_{c_m} = \frac{z_{c_m} R T_{c_m}}{P_{c_m}} \qquad (2)$$

According to the Pitzer compressibility tables the compressibility factor at the critical point is related to the acentric factor by a linear relationship; the arbitrary mixing rule for the acentric factor [Equation (1)] implies therefore that

$$z_{c_m} = \sum_i y_i z_{c_i} \qquad (3)$$

For all systems studied it was found that the pseudocritical volume could be predicted by a quadratic function of the mole fractions

$$V_{c_m} = \sum_{ij} y_i y_j V_{c_{ij}} \qquad (4)$$

It was also found that, when the ratio of the critical volumes of the pure components is less than about 3, the pseudocritical volume is a linear function of the composition; this result has also been reported by Haselden and coworkers (*1*). For such cases, therefore, Equation (4) still holds, with the additional relation

$$V_{c_{ij}} = \tfrac{1}{2}(V_{c_i} + V_{c_j}) \qquad (5)$$

In that case Equation (4) becomes

$$V_{c_m} = \sum_i y_i V_{c_i} \qquad (4a)$$

A more detailed discussion of the application of corresponding states theory to mixtures is given elsewhere (*4*).

NOTATION

P = pressure
R = gas constant
T = absolute temperature
V = volume
y = mole fraction
z = compressibility factor
z_c = compressibility factor at critical point
ω = acentric factor

Subscripts

i, j = components
c = critical (or pseudocritical)
m = mixture

LITERATURE CITED

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