NOTATION

B_x, B_y = magnetic flux density components
$\mathbf{B}$ = magnetic flux vector
D_{AB} = binary diffusion coefficient
H_T = total enthalpy
$\mathbf{J}$ = current density vector
M_x, M_y = mass flux components
N_A, N_B = number density of ionized and neutral constituents respectively
p = total pressure
$(V_x = U_1, V_y = v)$ = bulk velocity components
u_A, u_B = diffusive velocities of ionized and neutral constituents respectively
w_A, w_B = mass fractions of ionized and neutral species respectively
q_c, q_r = conductive and radiative fluxes
ρ = mass density
ω = mole fraction
Φ = dissipative energy source term
σ = gas conductivity
μ = viscosity

LITERATURE CITED

1. Cowling, T. G., *Magnetohydrodynamics*, Academic Press, New York (1957).
2. Rosa, R. J., *Magnetohydrodynamic Energy Conversion*, McGraw-Hill, New York (1968).
3. Hirschfelder, J. O., C. F. Curtiss, and R. B. Bird, *Molecular Theory of Gases and Liquids*, Wiley, New York (1954).
4. Chang, D. B., J. E. Drummond, D. W. Mahaffey, "Method and Apparatus for Reducing Matter to Constituent Elements and Separating One of the Elements from the Other Elements," Patent Pending, Boeing Company. Patent Appl. Ser. No. 269,634 filed July 7, 1972.

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The Prediction of Azeotropic Behavior and Saturated Liquid Densities in the Carbon Dioxide-Ethane System

A. S. TEJA
Department of Chemical Engineering
University of Technology,
Loughborough, Leicestershire LE11 3 TU, England

Gugnoni et al. (1974) have recently discussed the applicability of the Benedict-Webb-Rubin equation to the calculation of vapor-liquid equilibria, including azeotropic behavior, in the carbon dioxide-ethane system. In order to correlate their data, they modified the mixing rule for one of the constants of the equation of state by means of a temperature-dependent binary interaction coefficient. A similar temperature dependent coefficient was required by Hamam and Lu (1974) for correlating carbon dioxide-ethane vapor-liquid equilibria using a modified Redlich-Kwong equation. Thus the equation of state method is not simple to use, especially for predictive purposes, as the interaction coefficient must first be obtained as a function of temperature for each particular case.

The purpose of this note is to alert readers to another technique, described in detail elsewhere, which can be used to correlate and predict the behavior of the carbon dioxide-ethane system. This technique makes use of the extended form of the corresponding states principle as described by Rowlinson and Watson (1969). The method has been used successfully for the calculation of vapor-liquid equilibria (Watson and Rowlinson, 1969; Gunning and Rowlinson, 1973) and critical and azeotropic states (Teja and Rowlinson, 1973, Teja and Kropholler, 1975). Here, after a brief outline of the method, predicted azeotropic states and densities in the carbon dioxide-ethane system are presented and compared with the experimental results of Gugnoni et al. (1974).

CORRESPONDING STATES METHOD

Two pure substances α and 0 are defined to be in corresponding states if the configurational Helmholtz free energy of substance α at density ρ and temperature T may be obtained from the configurational Helmholtz free energy of the reference substance 0 at density $\rho h_{\alpha\alpha,0}$ and temperature $T/f_{\alpha\alpha,0}$ as follows: (The subscripts $\alpha\alpha$,0 signify a property of α relative to substance 0).

$$A_\alpha[\rho, T] = f_{\alpha\alpha,0}\, A_0[\rho h_{\alpha\alpha,0}, T/f_{\alpha\alpha,0}] - RT \ln h_{\alpha\alpha,0} \tag{1}$$

If an analytic expression for the configurational Helmholtz free energy of the reference substance is available as a function of ρ and T (and this may be obtained, for instance, from an accurate equation of state using standard thermodynamic relationships), then an analytic expression for the configurational Helmholtz free energy of substance α may be obtained from that of the reference simply by replacing ρ by $\rho h_{\alpha\alpha,0}$ and T by $T/f_{\alpha\alpha,0}$ and using Equation (1). The parameters $h_{\alpha\alpha,0}$ and $f_{\alpha\alpha,0}$ are related to the critical constants of α and 0 by

$$f_{\alpha\alpha,0} = (T_{\alpha\alpha}{}^{c}/T_0{}^{c})\,\Theta_{\alpha\alpha,0} \tag{2}$$

$$h_{\alpha\alpha,0} = (V_{\alpha\alpha}{}^{c}/V_0{}^{c})\,\Phi_{\alpha\alpha,0} \tag{3}$$

where the shape factors Θ and Φ are slowly varying functions of density and temperature. Analytical expressions for the shape factors are given elsewhere by Leach (1967) and Leland and Chappelear (1968). These expressions are of the form:

$$\Theta_{\alpha\alpha,0} = 1 + (\omega_{\alpha\alpha} - \omega_0)\,k_1 \tag{4}$$

$$\Phi_{\alpha\alpha,0} = 1 + (\omega_{\alpha\alpha} - \omega_0)\,k_2 \tag{5}$$

that is, $(\Theta - 1)$ and $(\Phi - 1)$ are proportional to the difference in Pitzer's acentric factor of the two substances α and 0. The proportionality constants, however, depend on temperature and slightly on density. Given the analytical expressions for shape factors of Leach (1967), the prediction of the thermodynamic properties of substance α requires only a knowledge of an accurate equation of state for the reference substance and three parameters, $T_{\alpha\alpha}{}^{c}$, $V_{\alpha\alpha}{}^{c}$ (or $P_{\alpha\alpha}{}^{c}$) and $\omega_{\alpha\alpha}$.

Equation (1) may be extended to mixtures by assuming that the configurational Helmholtz free energy of the mixture, after subtraction of an ideal free energy of mixing, is equal to that of a single (hypothetical) equivalent substance. Thus

$$A_{\text{mixture}}[\rho, T, \mathbf{x}] = A[\rho, T, \mathbf{x}] + RT \sum_{\alpha} x_\alpha \ln x_\alpha \tag{6}$$

The configurational Helmholtz free energy of the equivalent substance $A[\rho, T, \mathbf{x}]$ may then be obtained from that of the reference using Equation (1) or

$$A[\rho, T, \mathbf{x}] = f\,A_0[\rho h, T/f] - RT \ln h \tag{7}$$

The parameters h and f for the equivalent substance are related to composition by the van der Waals one-fluid model for the mixture:

$$h = \sum_{\alpha}\sum_{\beta} x_\alpha x_\beta h_{\alpha\beta} \tag{8}$$

$$fh = \sum_{\alpha}\sum_{\beta} x_\alpha x_\beta h_{\alpha\beta} f_{\alpha\beta} \tag{9}$$

The like terms are obtained from Equations (2) to (5) and the cross terms $(\alpha \neq \beta)$ from

$$f_{\alpha\beta} = \xi_{\alpha\beta}\,(f_{\alpha\alpha} f_{\beta\beta})^{1/2} \tag{10}$$

$$h_{\alpha\beta}{}^{1/3} = (h_{\alpha\alpha}{}^{1/3} + h_{\beta\beta}{}^{1/3})/2 \tag{11}$$

These are the familiar Lorentz-Berthelot mixing rules when $\xi_{\alpha\beta} = 1$. The parameter $\xi_{\alpha\beta}$ is close to unity and must be obtained from experimental data. However, it is shown below that $\xi_{\alpha\beta}$ calculated from one set of data (for example, by obtaining a best fit to critical states) may be used successfully to predict other data (for example, densities and azeotropic states).

The calculation of azeotropes in mixtures requires only derivatives of Equations (6) and (7) and is described elsewhere (Teja and Rowlinson, 1973). Densities at any given pressure, temperature, and composition may be calculated simply by solving the pressure equation which results when the configurational Helmholtz free energy is differentiated with respect to density.

RESULTS

Methane is used here as the reference since accurate analytical equations of state are available for this substance. The shape factor equations of Leach (1967) for the n-alkanes are also used. Their extension to a mixture containing carbon dioxide has not resulted in any apparent disadvantages. A value of 0.9 for the parameter $\xi_{\alpha\beta}$ has been used for the carbon dioxide-ethane system. This value was obtained in a separate study of critical states in carbon dioxide-ethane mixtures (Teja, 1971; Teja and Rowlinson, 1973) and is in agreement with a value of 0.92 obtained by Chueh and Prausnitz (1967) using a completely different method. No attempt has been made to vary $\xi_{\alpha\beta}$ to obtain a best fit to the experimental results for densities or azeotropic points. Thus the method has been tested for its predictive capabilities.

In the density calculations, the reference equation of state used is that of Bender (1971). The twenty-constant Bender equation is relatively easy to manipulate mathematically and has the advantage that it accurately represents experimental data for methane throughout the temperature and pressure range where such data is available (including the two-phase region). The azeotropic states calculations are those of Teja (1971) and utilized the twenty-six constant Vennix and Kobayashi (1969) equation for methane. The predicted results are compared here with the experimental data of Gugnoni et al. (1974). Were the calculations to be carried out again, the Bender

TABLE 1. PHYSICAL CONSTANTS REQUIRED IN THE CALCULATIONS

Substance	T^c, K	P^c, bar	V^c, m^3/kg mole	ω
Methane (reference)	190.77	46.27	0.099	0.0109
Carbon dioxide	304.16	73.76	0.094	0.223
Ethane	305.42	48.84	0.1462	0.1025

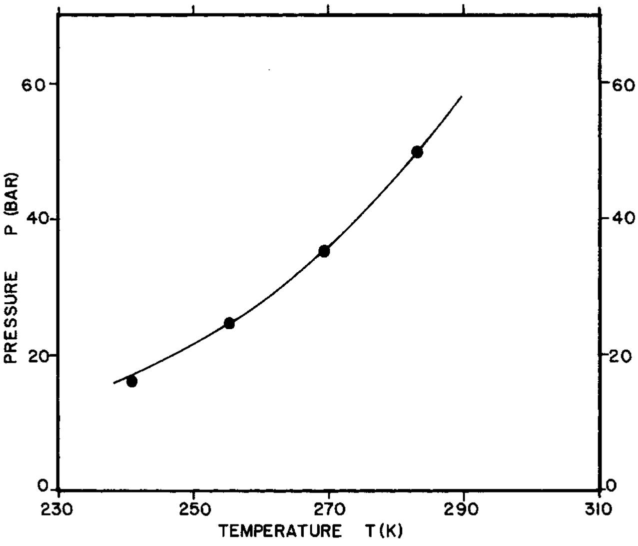

Fig. 1. Calculated and experimental azeotropic locus in the carbon dioxide-ethane system. The experimental results are those of Gugnoni et al. (1974).

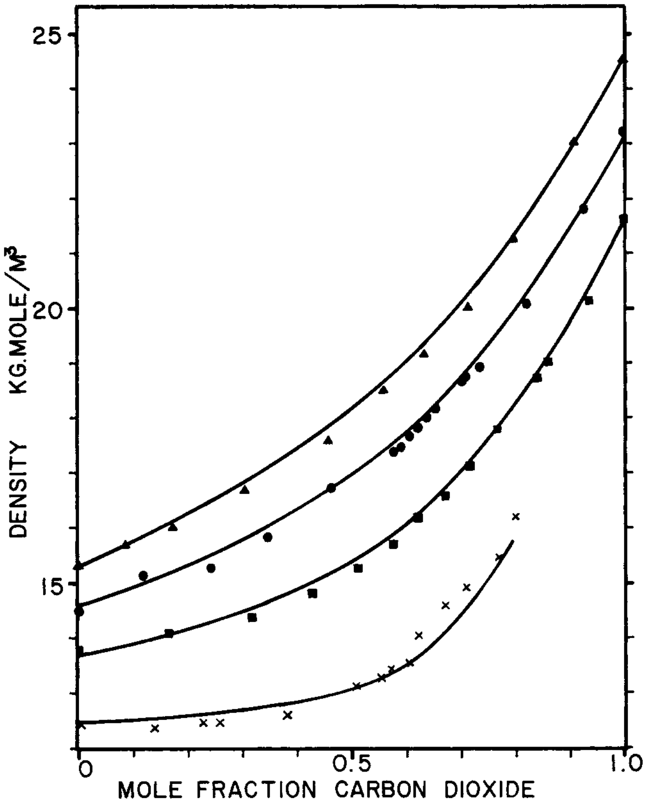

Fig. 2. Calculated and experimental saturated liquid densities in the carbon dioxide-ethane system. The experimental results are those of Gugnoni et al. (1974) at the following temperatures:

▲ 241.45 K
● 255.35 K
■ 269.25 K
× 283.15 K

TABLE 2. COMPARISON OF CALCULATED AND EXPERIMENTAL (GUGNONI ET AL., 1974) LIQUID DENSITIES. THE DEVIATION IS DEFINED AS $(\rho_{\text{calc.}} - \rho_{\text{exptl.}})/\rho_{\text{exptl.}}$

Temperature, K	No. of data points	Avg. absolute deviation, %	Max. deviation, %
241.45	11	0.70	−1.54
255.35	17	0.75	1.74
269.25	15	0.68	1.27
283.15	14	1.4	3.13

equation would be used because of the advantages noted.

Calculated and experimental azeotropic states in the carbon dioxide-ethane system are shown in Figure 1, and densities are shown in Figure 2. Agreement between prediction and experiment is excellent. The density results are summarized in Table 2. The relatively large maximum deviation for the 283.15K isotherm has not been explained.

In conclusion, the corresponding states principle with shape factors has been applied successfully to the prediction of azeotropic behavior and densities in the carbon dioxide-ethane system. The advantages of the method have been highlighted. Its major limitation is that shape factor correlations are only available for the *n*-alkanes and for quantum fluids (Leland and Chappelear, 1968). However, the correlations for the *n*-alkanes have been used without any apparent disadvantages for carbon dioxide and for other simple molecules (see also Gunning and Rowlinson, 1973). A single binary interaction constant, independent of temperature and density, is required for the prediction of azeotropes, densities, critical states, and vapor-liquid equilibria using this approach.

NOTATION

A = configurational Helmholtz free energy
f = corresponding states energy parameter
h = corresponding states volume parameter
P = pressure
R = gas constant
T = thermodynamic temperature
x = mole fraction
$\mathbf{x}$ = the composition vector $x_1, x_2 \ldots\ldots x_n$
Θ, Φ = shape factors
ξ = binary interaction constant
ρ = density
ω = Pitzer's acentric factor

Subscripts

calc. = calculated value
exptl. = experimental value
α, β = general components
0 = reference substance

Superscript

c = critical state

LITERATURE CITED

Bender, E., "Zur Aufstellung von Zustandsgleichungen, aus Denen Sich die Sattigungsgrössen Exakt Berechnen Lassen—Gezeigt am Beispiel des Methans," *Kältech. Klimatisierung*, **23**, 258 (1971).

Chueh, P. L., and J. M. Prausnitz, "Vapor-Liquid Equilibria at High Pressures. Vapor-Phase Fugacity Coefficients in Nonpolar and Quantum-Gas Mixtures," *Ind. Eng. Chem. Fundamentals*, **6**, 492 (1967).

Gugnoni, R. J., J. W. Eldridge, V. C. Okay, and T. J. Lee, "Carbon Dioxide-Ethane Phase Equilibrium and Densities from Experimental Measurements and the B-W-R Equation," *AIChE J.*, **20**, 357 (1974).

Gunning, A. J., and J. S. Rowlinson, "The prediction of the thermodynamic properties of fluids and fluid mixtures—III. Applications," *Chem. Eng. Sci.*, **28**, 521 (1973).

Hamam, S.E.M., and B.C.-Y. Lu, "Vapor-Liquid Equilibrium in the Ethane-Carbon Dioxide System," *Can. J. Chem. Eng.*, **52**, 283 (1974).

Leach, J. W., "Molecular Structure Corrections for Application of the Theory of Corresponding States to Non-spherical Pure Fluids and Mixtures," Ph.D. thesis, Rice University, Houston, Texas (1967).

Leland, T. W., and P. S. Chappelear, "The Corresponding States Principle," *Ind. Eng. Chem.*, **60**(7), 15 (1968).

Rowlinson, J. S., and I. D. Watson, "The prediction of the thermodynamic properties of fluids and fluid mixtures—I. The principle of corresponding states and its extensions," *Chem. Eng. Sci.*, **24**, 1565 (1969).

Teja, A. S., "The Prediction of Phase Equilibria in Hydrocarbon Mixtures," Ph.D. thesis, Univ. London, England (1971).

———., and J. S. Rowlinson, "The prediction of the thermodynamic properties of fluids and fluid mixtures—IV. Critical and Azeotropic States," *Chem. Eng. Sci.*, **28**, 529 (1973).

Teja, A. S., and H. W. Kropholler, "Critical States of Mixtures in which Azeotropic Behaviour Persists in the Critical Region," *Chem. Eng. Sci.*, **30**, 435 (1975).

Vennix, A. J., and R. Kobayashi, "An Equation of State for Methane in the Gas and Liquid Phases," *AIChE J.*, **15**, 926 (1969).

Watson, I. D., and J. S. Rowlinson, "The prediction of the thermodynamic properties of fluids and fluid mixtures—II. Liquid-vapour equilibrium in the system argon+nitrogen+oxygen," *Chem. Eng. Sci.*, **24**, 1575 (1969).

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