Efficient High-Pressure State Equations

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A method is presented for a relatively accurate, noniterative, computationally efficient calculation of high-pressure fluid-mixture equations of state, especially targeted to gas turbines and rocket engines. Pressures above 1 bar and temperatures above 100 K are addressed. The method is based on curve fitting an effective reference state relative to departure functions formed using the Peng-Robinson cubic state equation. Fit parameters for H_2, O_2, N_2, propane, methane, n-heptane, and methanol are given.

Introduction

It is desired that realistic and computationally efficient state equations for fuel/oxidant mixtures be available for design studies of the next generation of gas turbines and rocket engines. In such studies, the state equation plays an important basic, if only partial, role in calculations, where it is used a very large number of times. The equation of state not only provides component partial molar volumes and enthalpies for given pressure, temperature, and mass fractions but also information needed for calculating terms in expressions for mole flux and heat flux vectors. The pressures of interest are high ($p \geq 1$ MPa or 10 bar, up to 100 MPa) and temperatures noncryogenic ($T \geq 100$ K). Since the critical locus is a function of mole fractions, subcritical and supercritical regions may exist simultaneously and must be handled. Accuracy of the mixture Gibbs function must be sufficient to provide adequate higher order thermodynamic properties such as isentropic compressibility and thermal expansivity, which have an important effect, direct or indirect, on the fluid mechanical aspect of any design study.

Accurate nonpolar pure substance equations of state (EOS) are frequently based on the Benedict–Webb–Rubin (BWR) form or its modification by Lee and Kesler (Reid et al., 1987) or on the Helmholtz function (McCarty and Arp, 1991; Muller et al., 1996). Databases from the National Institute of Standards and Technology (NIST) are based mostly on a modified BWR form, with mixtures using an extended corresponding states algorithm (Friend and Huber, 1994). BWR-type equations are not computationally efficient since they have relatively complex nonlinear forms, requiring iteration (sometimes extensive) to calculate molar volume values (Reid et al., 1987). This aspect is particularly inconvenient when the EOS is used in transient, multiphase, multicomponent, and multidimensional fluid-dynamics codes where the thermodynamics should play a computationally limited, yet conceptually essential role. Also, application limits may apply; an EOS should generally not be used outside tested P or T ranges (Reid et al., 1987). For oxygen and hydrogen, such available EOSs have maximum temperature limits that are below the temperatures prevailing in engines. On the other hand, the much simpler cubic state equations (Peng–Robinson or Soave–Redlich–Kwong), while qualitatively correct, do not give accurate volume values (Reid et al., 1987). For hydrocarbon mixtures, a simple and accurate form based on an extension of the Redlich–Kwong EOS is available (Riazi and Mansoori, 1993). However, it is not clear that this form may be used for mixtures with nonhydrocarbons, particularly oxygen and hydrogen.

In this article, an accurate and relatively simple noniterative method is described using departure functions based on the Peng-Robinson (PR) state equation. It also allows a reasonable extrapolation from imposed limits to the higher temperatures needed for oxygen and hydrogen. Another advantage is the use of the same functional form for all substances with conventional, coherent mixing rules readily applied to any mixture. This may be done while utilizing the best available form (possibly distinct) for any particular substance to find the parameters the method requires. The mixing rules are treated as given.

Procedure

Departure functions are defined as deviations of thermodynamic functions from a reference state of large molar volume, v_u. For example, for the Helmholtz free energy,

$$F - F^0 = \int_v^{v_u} p(v', T, x_i)\, dv' = F_{PR}. \tag{1}$$

The x_i are mole fractions of species i. The reference state is that of a perfect gas at a relatively low reference pressure p^0, so that $v_u = RT/p^0$. The Gibbs function is obtained by $G - G^0 = F - F^0 + pv - RT$. For a cubic EOS such as PR:

$$p = RT/(v - b_m) - a_m/(v^2 + 2b_m v - b_m^2), \qquad (2)$$

an analytic expression for the pressure integral $F_{PR}(v_{PR}, T, x_i)$ is readily obtained as well as a direct solution for the molar volume function $v_{PR}(T, p, x_i)$. Parameters a_m and b_m follow the conventional mixing rules (Reid et al., 1987; Prausnitz et al., 1986):

$$a_m = \Sigma x_i x_j a_{ij}(T), \qquad (3a)$$

$$b_m = \Sigma x_i b_i. \qquad (3b)$$

The functions $a_{ij}(T)$ and constants b_i are discussed the Appendix. The PR state equation may have a single real volume root or else multiple real roots near saturation conditions. For multiple real roots, the largest and smallest positive roots give gas and liquid volumes, respectively. Although molar volume values thus obtained may not be accurate, the critical pressure and temperature locus of a mixture may be well estimated using determinants of the matrix of second partial derivatives of the PR free energy with respect to mole fractions (Reid et al., 1987). Thus despite the weakness of the PR equation in producing correct volume values, it appears that it may be used as a basis for accurate state equation calculations if a volume correction can be provided.

The method proposed here is to first use the departure function formalism for the pure substances of a mixture, and then to reuse it for the mixture as a whole. This method follows standard practice in dealing with nonideal mixtures by basing mixture properties on well-known, relatively accurate properties of the mixture pure components (standard states) combined with the related concepts of excess Gibbs energy and/or fugacity coefficients. The last are defined using conventional mixing rules. The remaining problem is that of fast, accurate calculation of the pure substance standard states. For this, an accurate calculation is made of the pure substance enthalpy and entropy, H and S (e.g., by a Lee-Kesler calculation, American Petroleum Institute, 1992) in ranges for which correlations are available. In combination with the PR departure functions and using the volume function $v_{PR}(T, p)$, effective pure substance reference states are calculated as

$$H^0(p,T) = H(p,T) - H_{PR}(v_{PR}, T), \qquad (4)$$

$$S^0(p,T) = S(p,T) - S_{PR}(v_{PR}, T), \qquad (5)$$

where

$$H_{PR} = pv_{PR} - RT + (a_m - T\partial a_m/\partial T)\ln[(v_{PR} + (1-\sqrt{2})b_m)/(v_{PR} + (1+\sqrt{2})b_m)]/(2\sqrt{2}b_m) \qquad (6)$$

$$S_{PR} = R\ln[(v_{PR} - b_m)p^0/RT] - \partial a_m/\partial T \ln[(v_{PR} + (1-\sqrt{2})b_m)/(v_{PR} + (1+\sqrt{2})b_m)]/(2\sqrt{2}b_m). \qquad (7)$$

(Here a_m and b_m are pure substance parameters.) With multiple PR roots, the gas volume is selected for pressures below saturation pressure (as a function of T, from Reid et al., 1987). Since the PR state equation is qualitatively correct, the reference state H^0 and S^0 functions are expected to behave similarly to those of a perfect gas. For the substances considered here, this expectation was met. The following form for G^0 is used to produce very good curve fits:

$$G^0(T,p) = RT_C\left(a + b/(2T_R) + eT_R - cT_R \ln T_R + 2d\sqrt{T_R}\right), \qquad (8)$$

which gives reference enthalpy and entropy

$$H^0 = RT_C\left(a + b/T_R + cT_R + d\sqrt{T_R}\right) \qquad (9)$$

$$S^0 = R\left(b/(2T_R^2) - e + c(1 + \ln T_R) - d/\sqrt{T_R}\right), \qquad (10)$$

where the reduced temperature is $T_R \equiv T/T_C$, and a, b, c, d, e are cubic polynomials in reduced pressure $p_R \equiv p/p_C$. The reference pressure is taken $p^0 = 1$ bar, and the volume correction is $v^0 = \partial G^0/\partial p$.

At a given pressure, a set of T values in the available range produces a corresponding set of H^0. A least-squares curve fit then gives a, b, c, and d. Then a set of e values is found from S^0. Consistency requires that e values are independent of T; for the substances considered, this is essentially satisfied and the mean value is used. (Note that the terms from b and d should not be large for the premise of the method to hold.) For oxygen and hydrogen, data are only available up to $T =$ 400 K (McCarty and Arp, 1991); however, for these substances the behavior of the reference enthalpy at larger temperatures is linear, allowing $d \equiv 0$. Figure 1 shows the variation for oxygen. This means that the high-temperature behavior mimics that of an ideal perfect gas allowing for reasonable extrapolation of H^0 (and G^0) to larger temperatures for O_2 or H_2. Temperature fits over a set of pressure values followed by cubic polynomial fits to $a, \ldots, e$ complete the determination of G^0 for the pure-substance standard states of the mixture.

The results indicate that the reference state is essentially that of a perfect gas plus a small correction term. Thus, it is assumed that simple ideal mixing rules apply to the reference state, giving as the mixture Gibbs energy (with $v_{PR}(T, p, x_i)$ from PR equation)

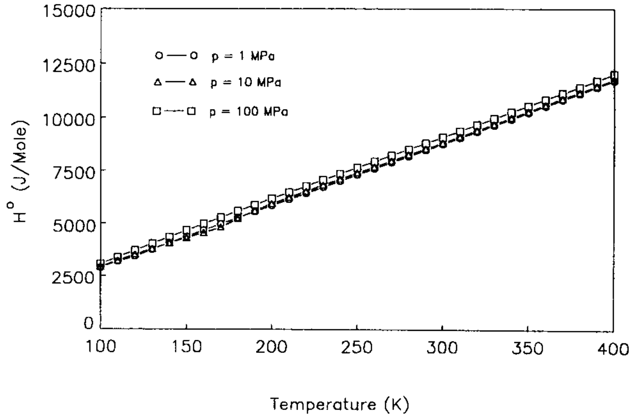

Figure 1. Reference enthalpy for oxygen.

Table 1. Coefficients of Polynomials

n	*a*	*b*	*c*	*d*	*e*
			Hydrogen		
0	−2.2570E+00	9.3200E+00	3.5559E+00	0.0	−4.2756E+00
1	8.9768E−02	−1.8230E−01	−2.0169E−03	0.0	−9.4720E−03
2	−2.0286E−03	4.1623E−03	9.2431E−05	0.0	3.6176E−04
3	1.3241E−05	−2.6840E−05	−6.8674E−07	0.0	−2.6171E−06
			Oxygen		
0	−2.6627E−03	−2.6855E−02	3.5256E+00	0.0	−1.8844E+01
1	−5.5055E−02	3.8370E−02	2.3725E−02	0.0	4.8007E−02
2	1.0802E−02	−5.8455E−03	−4.0817E−03	0.0	−7.9077E−03
3	−3.3882E−04	1.7140E−04	1.3537E−04	0.0	2.5601E−04
			Nitrogen		
0	8.5610E+00	−2.8734E+00	5.2085E+00	−7.3677E+00	−8.8583E+00
1	4.7709E−02	−9.3171E−03	4.9733E−03	−2.8200E−02	2.6602E−02
2	−1.3426E−03	4.4869E−04	−1.4035E−04	9.4103E−04	−7.7410E−04
3	3.8037E−05	−2.1032E−05	2.9341E−06	−2.1826E−05	1.6618E−05
			Propane		
0	2.2709E+01	−1.7434E+00	3.2680E+01	−4.6968E+01	4.4192E+01
1	−2.1505E−01	1.3190E−02	−2.0673E−01	4.1762E−01	−6.2291E−01
2	−1.2160E−02	1.6696E−03	−3.1790E−03	1.3965E−02	−1.6248E−02
3	6.6740E−04	−7.4289E−05	3.5819E−04	−9.6837E−04	1.2999E−03
			Methane		
0	1.4030E+01	−2.2038E+00	1.0979E+01	−1.8812E+01	8.1046E+00
1	−2.9945E+00	5.5502E−01	−1.0712E+00	3.4885E+00	−4.2320E+00
2	8.3379E−01	−1.4803E−01	3.0943E−01	−9.8823E−01	1.2112E+00
3	−6.1095E−02	1.0454E−02	−2.3410E−02	7.3672E−02	−9.1006E−02
			n-Heptane		
0	5.8125E+01	−4.3497E+00	9.0457E+01	−1.2505E+02	1.4930E+02
1	−6.0356E−01	9.9940E−02	−2.3445E−01	7.2965E−01	−8.9921E−01
2	3.0029E−01	−4.9190E−02	1.1821E−01	−3.6738E−01	4.5690E−01
3	−2.0144E−02	3.2149E−03	−8.1978E−03	2.5036E−02	−3.1384E−02
			Methanol		
0	1.5128E+01	−1.7143E+00	2.0654E+01	−2.8922E+01	1.9287E+01
1	−1.9368E−01	4.7942E−02	−3.6714E−02	1.4502E−01	−1.3353E−01
2	6.5346E−02	−1.2544E−02	2.1425E−02	−7.2466E−02	8.6103E−02

$$G(T,p,x_i) = F_{PR}(\upsilon_{PR},T) + p\upsilon_{PR} - RT + \Sigma x_i(G_i^0 + RT\ln x_i), \tag{11}$$

where

$$F_{PR} = a_m \ln[(\upsilon_{PR} + (1-\sqrt{2})b_m)/(\upsilon_{PR} + (1+\sqrt{2})b_m)]/(2\sqrt{2}\,b_m) - RT\ln[(\upsilon_{PR} - b_m)p^0/RT]. \tag{12}$$

This assumption is consistent with the use of F_{PR} to obtain the mixture critical locus independent of the reference state. The fugacity coefficients for the mixture are $\phi_i = \phi_i^0 \times \phi_{PR,i}$ where:

$$\ln \phi_i^0 = [G_i^0(T,p) - G_i^0(T,0)]/RT \tag{13}$$

and

$$\ln \phi_{PR,i} = (2\Sigma x_j a_{ij} - a_m b_i/b_m)\ln[(\upsilon_{PR} + (1-\sqrt{2})b_m)/(\upsilon_{PR} + (1+\sqrt{2})b_m)]/(2\sqrt{2}\,b_m RT) - \ln[p(\upsilon_{PR} - b_m)/RT] + (p\upsilon_{PR}/RT - 1)b_i/b_m. \tag{14}$$

Analytical expressions for mixture and component molar volumes, and enthalpies, along with mixture heat capacities, compressibility, and expansivity can be found by differentiation of G or ϕ_i.

Results

Curve-fit parameters for H_2, O_2, N_2, propane, methane, *n*-heptane, and methanol are given in Table 1. (The last fuel has a dipole moment; fits were made to test usage with polar substances.) EOS inputs for the first five are from McCarty and Arp (1991); the last two use the Lee-Kesler form from the American Petroleum Institute (1992). The program GASPACK is an extension of the previous, widely distributed MIPROPS package from the National Bureau of Standards (NBS) (McCarty, 1986). Accuracy of data from this program is within 2% for enthalpy and entropy (McCarty and Arp, 1991). It should be emphasized that any accurate enthalpy and entropy data may be used for the curve fits; the current choice is illustrative. Good fits for enthalpy and entropy for all substances were obtained. Table 2 gives the rms errors relative to mean values for the temperature fits for H and S, along with the compression factor $p\upsilon/RT$ and e value errors. Table 3 provides the temperature and pressure ranges used in the reference fits. Typically, 50 temperature values and 20 pressure values were used. Except for methanol, compression-factor estimates have an error of approximately 2% or less. Figures 2 and 3 give enthalpy and density input vs. fit comparisons for O_2; similarly, *n*-heptane values are shown in

Table 2. Maximum rms Relative Errors*

Substance	H	S	pv/RT	e
Hydrogen	0.23	0.15	1.0	0.35
Oxygen	1.1	0.2	1.4	0.2
Nitrogen	0.22	0.22	0.7	0.6
Propane	2.9	0.5	2.0	0.3
Methane	0.9	0.3	1.0	1.2
n-Heptane	0.26	0.16	2.2	0.1
Methanol	1.35	1.1	10	1.2

*Percent at fixed pressure.

Table 3. Range of Reference Fits

Substance	T (K)	p (MPa)
Hydrogen	80–400	0.1–100
Oxygen	100–400	0.1–100
Nitrogen	100–2,000	0.1–100
Propane	100–600	0.1–100
Methane	100–600	1–30
n-Heptane	210–1,500	0.1–27
Methanol	210–1,500	1–80

Figures 4 and 5, and methanol values are given in Figures 6 and 7.

A final comparison is made between density calculations for methane using the Bender EOS (Sievers and Schulz, 1980), a BWR-type equation, with calculations of the present method using curve fits to GASPACK data. In Figure 8 the solid curves are the Bender results and the symbols denote results of the present method for pressures of 1, 5 and 10 MPa and temperatures 250–600 K. It is seen that mixture standard states may be well calculated using the proposed Gibbs form for nonpolar components.

Relatively inferior fits to the lower temperature methanol molar volume values were obtained with errors as large as 17% for liquids. (Due to fit inaccuracies, only quadratic polynomials in pressure were used for methanol.) The problem of fit inaccuracy with methanol can be ascribed to the form of its H^0 function. It features a slight "wiggle" in the 200–600 K temperature range, along with definite positive curvature at high temperatures. A good fit would require a more extensive curve-fitting procedure than the one used here, with a function more complex than Eqs. 8 and 9. The present fit, however, is valid for supercritical conditions with $T \geq 500$ K. For lower temperatures, a need for better fit is indicated.

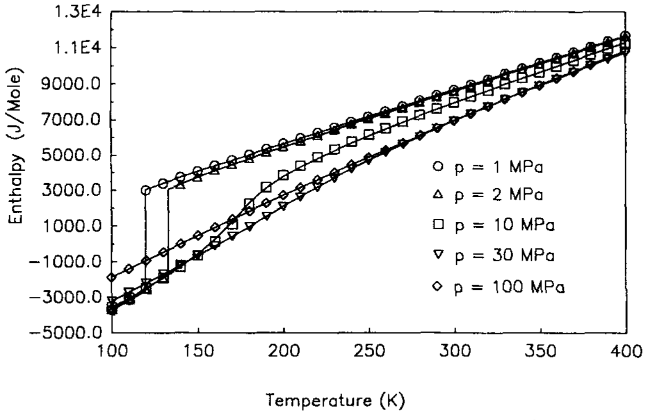

Figure 2. Comparison of input data (symbols) and enthalpy fits for oxygen.

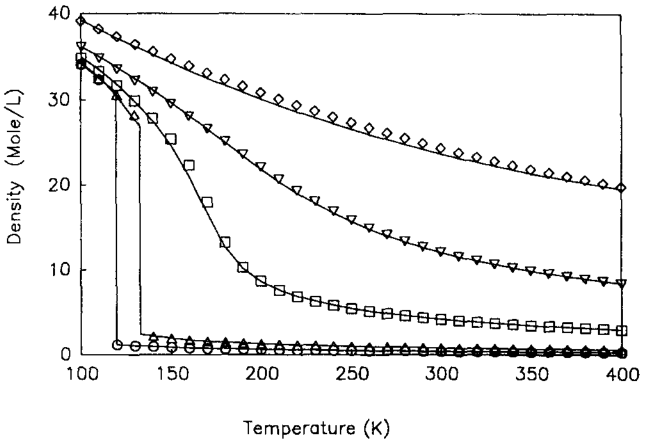

Figure 3. Comparison of input data (symbols) and density fits for oxygen.

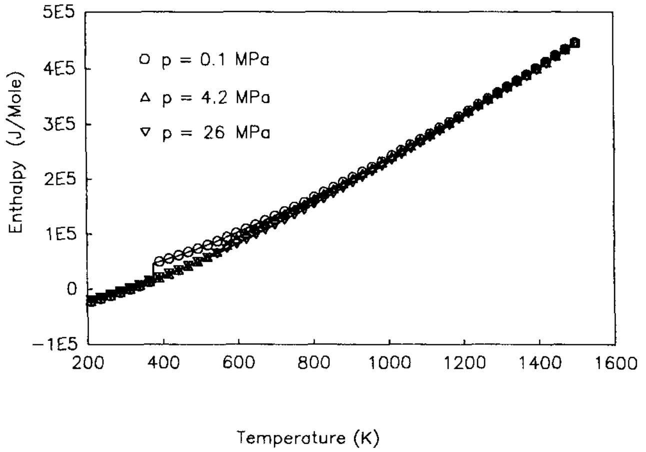

Figure 4. Comparison of input data (symbols) and enthalpy fits for *n*-heptane.

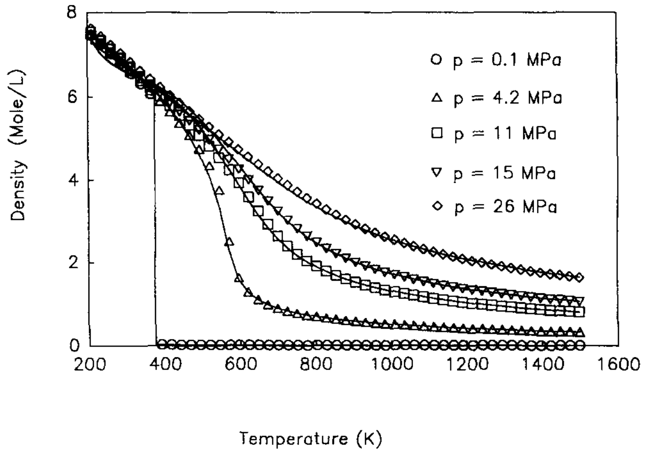

Figure 5. Comparison of input data (symbols) and density fits for *n*-heptane.

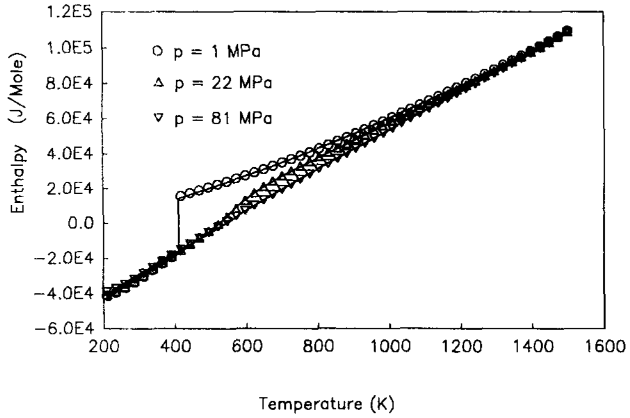

Figure 6. Comparison of input data (symbols) and enthalpy fits for methanol.

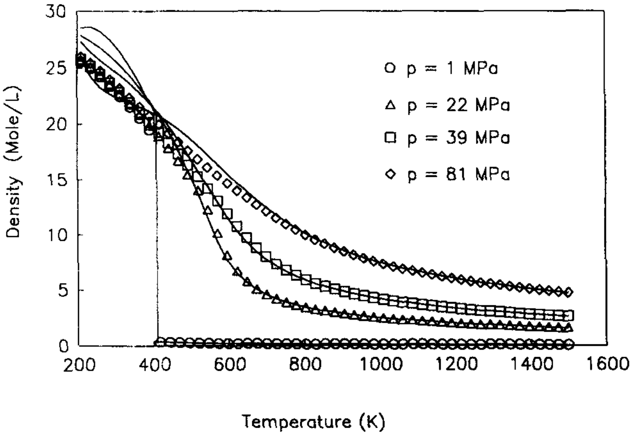

Figure 7. Comparison of input data (symbols) and density fits for methanol.

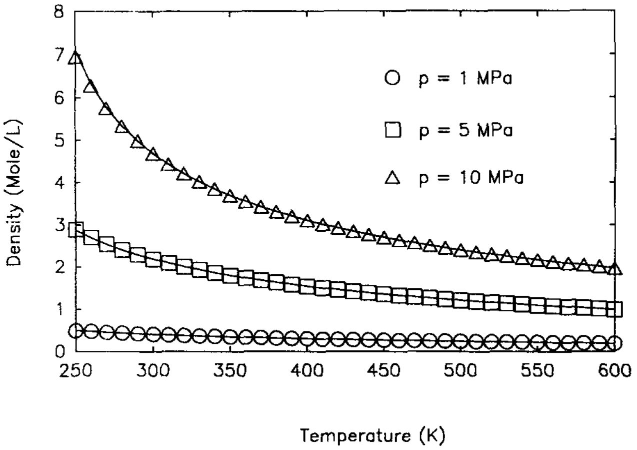

Figure 8. Comparison of density fits (symbols) and Bender's equation for methane.

Summary

The procedure proposed here allows for the use of realistic and computational efficient equation-of-state calculations for high-pressure gas-turbine and rocket engines. It also provides for a reasonable extension to high temperatures of data for H_2 and O_2. The method is based on relatively accurate, noniterative calculations of pure substance properties as standard states of the mixture. Since the same functional form (based on the PR EOS) is used for all substances, conventional mixing rules are readily applied to any set of components.

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Literature Cited

American Petroleum Institute, *Technical Data Book — Petroleum Refining*, Vols. 1 and 2, 5th ed., Washington, DC (1992).

Friend, D. G., and M. L. Huber, "Thermophysical Property Standard Reference Data from NIST," *Int. J. Thermophys.*, **15**, 1279 (1994).

McCarty, R. D., "Interactive FORTRAN Programs for Micro Computers to Calculate the Thermophysical Properties of Twelve Fluids [MIPROPS]," National Bureau of Standards Tech. Note 1097, NBS, Boulder, CO (1986).

McCarty, R. D., and V. Arp, GASPAK Ver. 3 (IBM PC version), Cryodata Inc., Niwot, CO (1991).

Muller, A., J. Winkelmann, and J. Fischer, "Backone Family of Equations of State: 1. Nonpolar and Polar Pure Fluids," *AIChE J.*, **42**, 1116 (1996).

Prausnitz, J. M., R. N. Lichtenthaler, and E. G. de Azevedo, *Molecular Thermodynamics of Fluid-phase Equilibria*, 2nd ed., Prentice Hall, Englewood Cliffs, NJ (1986).

Reid, R. C., J. M. Prausnitz, and B. E. Poling, *The Properties of Gases and Liquids*, 4th ed., McGraw-Hill, New York (1987).

Riazi, M., and G. A. Mansoori, "Simple Equation of State Accurately Predicts Hydrocarbon Densities," *Oil & Gas J.*, **91**, 108 (1993).

Sievers, U., and S. Schulz, "An Equation of State for Methane in the Form of Bender's Equation for Temperatures Between 91 K and 625 K and Pressures up to 500 bar," *Fluid Phase Equilib.*, **5**, 35 (1980).

Appendix: Peng-Robinson State-Equation Parameters

The constants $b_i = 0.077796\, RT_{Ci}/p_{Ci}$ and the diagonal elements of a_{ij} are given by

$$a_{ii}(T) = 0.457236(RT_{Ci})^2\left[1 + c_i\left(1 - \sqrt{T_{Ri}}\right)\right]^2/p_{Ci},$$

where $T_{Ri} \equiv T/T_{Ci}$ and $c_i = 0.37464 + 1.54226\,\omega_i - 0.26992\,\omega_i^2$. Parameter ω_i is the acentric factor for species i. The off-diagonal elements are frequently calculated by (Reid et al., 1987; Prausnitz et al., 1986):

$$a_{ij} = (a_{ii}a_{jj})^{1/2}(1 - k'_{ij}),$$

where k'_{ij} is an empirical binary interaction parameter. The use of the corresponding states principle during calculations of mixture transport properties requires the use of pseudocritical mixture properties. For these, the following is often used (Reid et al., 1987; Prausnitz et al., 1986):

$$v_{Cm} = \Sigma x_i x_j v_{Cij}$$

$$T_{Cm} = \Sigma x_i x_j T_{Cij}(v_{Cij}/v_{Cm})$$

$$Z_{Cm} = 0.2905 - 0.085\omega_m,$$

or

$$Z_{Cm} = \Sigma x_i Z_{Ci}$$

if the Z_{Ci} are known,

$$\omega_m = \Sigma x_i \omega_i$$

$$p_{Cm} = Z_{Cm}(RT_{Cm}/v_{Cm})$$

where

$$T_{Cii} \equiv T_{Ci}, \text{etc.}$$

$$T_{Cij} = (T_{Ci}T_{Cj})^{1/2}(1-k_{ij})$$

$$v_{Cij} = \left[\left(v_{Ci}^{1/3} + v_{Cj}^{1/3}\right)^3\right]/8$$

$$Z_{Cij} = (Z_{Ci} + Z_{Cj})/2$$

$$p_{Cij} = Z_{Cij}(RT_{Cij}/v_{Cij}).$$

Interaction parameters k'_{ij} and k_{ij} are not independent, but are related by compatibility for the second virial coefficient (Reid et al., 1987). Moreover, proper values are important to give the correct mixture fugacity values (Prausnitz et al., 1986), with small changes significantly affecting results. It is convenient to avoid this complication by relying solely on the pseudocritical parameters by calculating off-diagonal $a_{ij}(T)$ using the same expression as for the diagonals, but with T_{Cij}, p_{Cij}, and $\omega_{ij} = (\omega_i + \omega_j)/2$, as was done in Prausnitz et al. (1986, Chap. 5) for the Redlich-Kwong equation.

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