

A Four-Parameter Corresponding-States Method for the Prediction of Thermodynamic Properties of Polar and Nonpolar Fluids¹

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A four-parameter corresponding-states correlation has been developed for the prediction of thermodynamic properties of polar and nonpolar fluids. Required input constants include the critical temperature, the critical pressure, the radius of gyration (to account for geometrical deviations from simple corresponding states), and a liquid density at any known conditions from which a fourth constant (to account for polar and association effects) is calculated. The fluid property is written as a Taylor's series expansion about the simple fluid at the same reduced conditions, thereby separating deviations from simple corresponding states into geometric and polar contributions. Three fixed reference fluids are used to evaluate the deviation terms. Nonpolar results were equivalent to those obtained by the Lee-Kesler three-parameter method; polar results were substantially better than obtainable from any other currently available method. Average errors for calculated compressibility factors of polar fluids were 1.9 and 1.6% for the vapor and liquid phases, respectively, while those for enthalpy departure functions were 250 and 422 J·mol⁻¹, respectively.

KEY WORDS: corresponding states; four parameter; nonpolar; polar; thermodynamic properties.

1. INTRODUCTION

The corresponding-states principle (CSP) is probably the most effective and widely used basis for thermophysical property correlation and

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estimation techniques. While the two-parameter CSP has a rigorous basis for spherical nonpolar fluids, properties of other types of fluids have been effectively correlated by introducing a third and even a fourth parameter. In 1975, Lee and Kesler [1] published a three-parameter CSP method which has proven to be very useful for the prediction of thermodynamic properties of nonpolar and slightly polar fluids. The success of the Lee-Kesler (LK) method is due largely to the use of accurate analytic equations of state which represent the two reference fluids used.

In this paper, an extension of the LK method applicable to polar as well as nonpolar fluids is presented. A third reference fluid is used to approximate the polar effects and two new, but readily calculable, pure component constants are used in conjunction with T_c and P_c to account for geometric and polar effects, separately.

2. FOUR-PARAMETER CSP

At a given reduced temperature and pressure, any dimensionless configurational property of the fluid, J , may be expressed as a Taylor's series expansion about the simple fluid value of J with respect to geometrical and polar effects:

$$J = J_0 + (\partial J / \partial \alpha)_{T_r, P_r, \beta} (\alpha - \alpha_0) + (\partial J / \partial \beta)_{T_r, P_r, \alpha} (\beta - \beta_0) + O(\alpha^2, \beta^2, \alpha\beta) \quad (1)$$

where J_0 is the simple fluid value of the property J at the given reduced conditions, α is a size-shape constant, and β is a polarity constant. The third and fourth CSP parameters, α and β , are specific to each fluid and are defined below.

To apply Eq. (1) to a fluid, both the partial derivatives and the third and fourth CSP parameters must be defined. Additionally, we assume that terms in the expansion beyond linear are negligible. The partial derivative $(\partial J / \partial \alpha)_{T_r, P_r, \beta}$, which represents the manner in which the property J changes due only to size effects, is approximated using a linear relation derived from the known properties of a nonspherical, nonpolar reference fluid (subscript 1),

$$(\partial J / \partial \alpha)_{T_r, P_r, \beta} = [(J_1 - J_0) / (\alpha_1 - \alpha_0)] \quad (2)$$

where the properties are evaluated at the same T_r and P_r as for the test fluid. Similarly, the partial derivative $(\partial J / \partial \beta)_{T_r, P_r, \alpha}$, which represents how the fluid property changes due solely to polar interactions, can be estimated from a third reference fluid (subscript 2) by

$$(\partial J / \partial \beta)_{T_r, P_r, \alpha} = [(J_2 - J'_2) / (\beta_2 - \beta'_2)] \quad (3)$$

where J_2 represents a hypothetical fluid of identical geometry to reference fluid 2 but with no polar effects; i.e., $\beta'_2 = 0$ and $\alpha'_2 = \alpha_2$. The value J_2 can be readily obtained from the application of Eq. (1) to this homomorphic fluid. In this case,

$$J_2 = J_0 + \alpha_2(J_1 - J_0)/\alpha_1 \quad (4)$$

since the polar term disappears. Substitution of Eqs. (2)–(4) into Eq. (1) provides a general four-parameter CSP equation applicable to all types of fluids:

$$J = J_0 - \alpha(J_1 - J_0)/\alpha_1 + \beta\{J_2 - [J_0 + \alpha_2(J_1 - J_0)/\alpha_1]\}/\beta_2 \quad (5)$$

Equation (5) contains two perturbation (size/shape and polar correction) terms to the simple fluid, which itself obeys the CSP. The perturbational nature of this equation is visibly preserved by writing Eq. (5) as

$$J = J_0 + \alpha J^{(1)} + \beta J^{(2)} \quad (6)$$

where the definitions of the deviation terms are easily seen by direct comparison of Eqs. (5) and (6). To use either Eq. (5) or Eq. (6), the reduced temperature and pressure are calculated from the critical constants of the test fluid. Using reference fluid equations of state, values of J are computed for all three reference fluids at the same reduced conditions. Finally, the values of α and β for the test fluid are used in conjunction with Eq. (5) and the J_i to compute the value of J for the test fluid.

The geometrical parameter α must be independent of polarity for Eq. (1) to be a true Taylor's series expansion. Although the most commonly used and accepted third parameter for the extended CSP has been the acentric factor, ω , its empirical definition in terms of vapor pressure includes in some complex fashion at least partial effects due to geometry and polarity and therefore precludes its use in this work. We have chosen instead to base α on the radius of gyration, r , a fundamental and purely geometric quantity reasonably available for data-base inclusion [2–4]. However, in view of the success of the acentric factor in correlating non-polar fluid properties, it seems appropriate to require α and ω to be nearly identical when $\beta = 0$. This was implemented by correlating ω for 80 non-polar fluids as a function of the radius of gyration. A plot of this correlation is shown in Fig. 1 including the least-squares-fitted polynomial relationship:

$$\alpha = -7.706 \times 10^{-4} + 0.0330r + 0.01506r^2 - 9.997 \times 10^{-4}r^3 \quad (7)$$

It is important to realize that this correlation is applicable to all fluids regardless of polarity and represents only geometrical effects. Obviously,

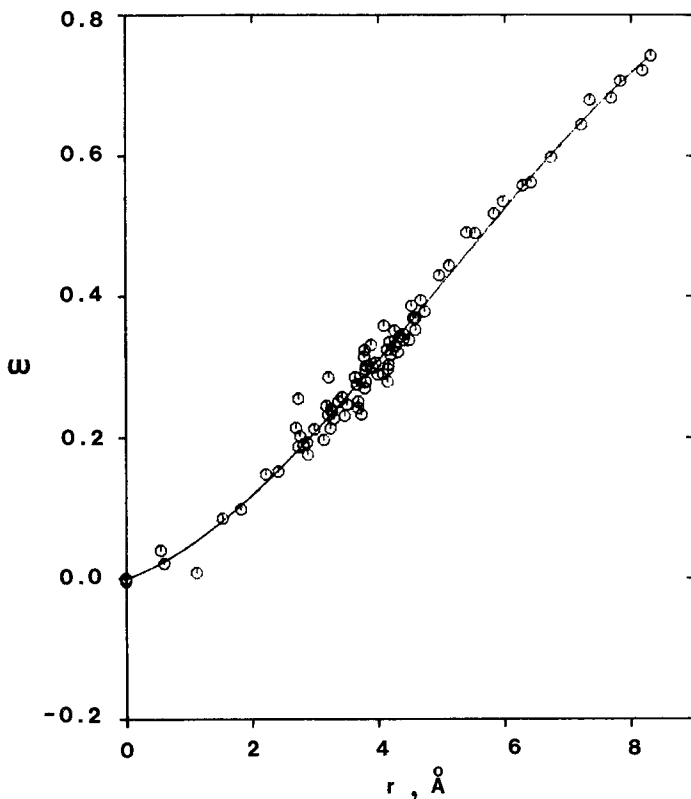


Fig. 1. Correlation for acentric factor for 80 nonpolar fluids as a function of radius of gyration.

this definition of α , when used in Eq. (5) or (6) for nonpolar fluids ($\beta = 0$), reduces to the successful LK method, but for polar fluids $\alpha \neq \omega$ and the polar effects are properly accounted for in the second perturbation term.

The polarity parameter, β , is obtained by applying Eq. (5) to any known value of J . As liquid densities at some T_r and P_r are commonly available and are very sensitive to polar interactions, we set $J = Z$, the compressibility factor, and solve for β directly from Eq. (5).

$$\beta = [Z - Z_0 - \alpha(Z_1 - Z_0)/\alpha_1]/(Z_2 - Z'_2) \quad (8)$$

where Z'_2 is calculated from Eq. (4). Without loss of generality, β_2 was set to unity since only the ratio β/β_2 appears in all predictive equations. β can now be calculated from Eq. (8) using the known density value converted to a compressibility factor. Once β has been determined for a particular test

Table I. Reference Fluid Equations of State and Their Constants^a

| (A) Equations | | | | | | | |
|---------------------------------|--|---|---------------------------------------|-------------|------------|------------|-------------|
| Ref. fluid | Equation | Definitions | | | | | |
| 1, 2 | $Z = 1 + B/V_r + C/V_r^2 + D/V_r^5 + c_4(\delta + \lambda) \exp(-\lambda) T_r^{-3} V_r^{-2}$ | $B = b_1 - b_2/T_r - b_3/T_r^2 - b_4/T_r^3$ $C = c_1 - c_2/T_r + c_3/T_r^3$ $D = d_1 + d_2/T_r$ $\lambda = \gamma/V_r^2$ | | | | | |
| 3 | $Z = [1 + \rho Q + \rho^2(\partial Q/\partial \rho)_\tau]$ | $Q = (\tau - B_0) \sum_{j=1}^7 (\tau - B_j)^{j-2}$ $\times \left[\sum_{j=1}^8 A_{ij}(\rho - C_j)^{j-1} + \exp(-4.8\rho)(A_{0j} + A_{10j}\rho) \right]$ $\tau = 1000/T \text{ (K)}$ | | | | | |
| (B) Reference fluid 1 constants | | | | | | | |
| <i>i</i> | <i>b_i</i> | <i>c_i</i> | <i>d_i × 10⁵</i> | δ | γ | | |
| 1 | 0.1181193 | 0.0236744 | 1.55488 | 0.65392 | 0.060167 | | |
| 2 | 0.265728 | 0.0186984 | 6.23689 | | | | |
| 3 | 0.154790 | 0.0 | | | | | |
| 4 | 0.030323 | 0.042724 | | | | | |
| (C) Reference fluid 2 constants | | | | | | | |
| <i>i</i> | <i>b_i</i> | <i>c_i</i> | <i>d_i × 10⁵</i> | δ | γ | | |
| 1 | 0.2026579 | 0.0313385 | 4.8736 | 1.226 | 0.03754 | | |
| 2 | 0.331511 | 0.0503618 | 0.0740336 | | | | |
| 3 | 0.027655 | 0.016901 | | | | | |
| 4 | 0.203488 | 0.041577 | | | | | |
| (D) Reference fluid 3 constants | | | | | | | |
| <i>A_{ij}</i> | | | | | | | |
| <i>j</i> | | | | | | | |
| <i>i</i> | 1 | 2 | 3 | 4 | 5 | 6 | 7 |
| 1 | 29.492937 | -5.1985860 | 6.8335354 | -0.1564104 | -6.3972405 | -3.9661401 | -0.69048554 |
| 2 | -132.13917 | 7.7779182 | -26.149751 | -0.72546108 | 26.409282 | 15.453061 | 2.7407416 |
| 3 | 274.64632 | -33.301902 | 65.326396 | -9.2734289 | -47.740374 | -29.142470 | -5.1028070 |
| 4 | -360.93828 | -16.254622 | -26.181978 | 4.3125840 | 56.323130 | 29.568796 | 3.9636085 |
| 5 | 342.18431 | -177.31074 | 0 | 0 | 0 | 0 | 0 |
| 6 | -244.50042 | 127.48742 | 0 | 0 | 0 | 0 | 0 |
| 7 | 155.18535 | 137.46153 | 0 | 0 | 0 | 0 | 0 |
| 8 | 5.9728487 | 155.97836 | 0 | 0 | 0 | 0 | 0 |
| 9 | -410.30848 | 337.31180 | -137.46618 | 6.8784983 | 136.87317 | 79.847970 | 13.041253 |
| 10 | -416.05860 | -209.88866 | -733.96848 | 10.401717 | 645.81880 | 399.17570 | 71.531353 |

^a $B_0 = B_1 = 1.544912$; $B_{j>1} = 2.5$. $C_1 = 0.634$; $C_{j>1} = 1.0$.

fluid, it is treated as a fundamental constant and can be tabulated and used as any other fundamental pure component constant. This provides the flexibility of maintaining either β values or liquid density points in a data base; the latter have been used in some [2] previous data bases.

Reference fluids were chosen based on available data over a wide range of reduced temperatures and pressures. The simple and nonpolar reference fluids used in the LK method were retained here and water was chosen as the third or polar reference fluid. Whereas a modified BWR equation of state is used for the first two reference fluids, it was found unsatisfactory for correlation of water properties over the required T - P range. Consequently, the equation of Keenan et al. [5] was used for water. The equations of state used and the values of the constants applicable for each reference fluid are tabulated in Table I.

Writing Eqs. (5) and (6) for the compressibility factor ($J = Z$) allows computation of other thermodynamic properties using thermodynamic identities. Relationships for the enthalpy and entropy departure functions and the fugacity coefficient are shown in Table II. It has been found that these derivative properties for some fluids, particularly alcohols and other hydrogen bonding substances, are not as accurately predicted as the

Table II. Reference Fluid Departure Functions

| Ref. fluid | Equations |
|------------|--|
| 1, 2 | $\frac{H^0 - H}{RT_c} = -T_r [Z - 1 - (b_2 + 2b_3/T_r + 3b_4/T_r^2)/T_r V_r - (c_2 - 3c_3 T_r^2)/2T_r V_r^2 + d_2/5T_r V_r^5 + 3E]$ $\frac{S^0 - S}{R} = -\ln \frac{P^0}{P} - \ln Z + (b_1 + b_3/T_r^2 + 2b_4 T_r^3)/V_r + (c_1 - 2c_3/T_r^3)/V_r^2 + d_1/5V_r^5 - 2E$ $\ln \frac{f}{P} = Z - 1 - \ln Z + B/V_r + C/2V_r^2 + D/5V_r + E$ <p>where $E = c_4[\delta + 1 - (\delta + 1 + \lambda) \exp(-\lambda)]/2T_r^3 \gamma$</p> |
| 3 | $\frac{H^0 - H}{RT_c} = -T_r \rho \tau (\partial Q / \partial \tau)_\rho + \rho Q + \rho^2 (\partial Q / \partial \rho)_\tau$ $\frac{S^0 - S}{R} = -\ln Z + \rho Q - \rho \tau (\partial Q / \partial \tau)_\rho - \ln(P^0/P)$ $\ln \frac{f}{P} = -T_r \left[\frac{H^0 - H}{RT_c} \right] + \left[\frac{S^0 - S}{R} \right]$ |

volumetric properties. We believe this is because of a fundamental difference in the way that polarity affects volumetric, as opposed to enthalpic, properties and should be reflected in a different value of β . For ease of discussion, we call the value of β used in enthalpic calculations β_h , reserving the symbol β for the compressibility factor calculation. A hierarchy of three methods by which β_h can be determined is now described in order of increasing accuracy but also increasing input requirements. Method 1: Defining $\beta_h = \beta$ requires no additional information but, as already stated, may lead to significant errors in those fluids that hydrogen bond. Method 2: Calculating β_h from only the normal boiling point, T_b , significantly improves the accuracy for most fluids. Method 3: Calculating β_h from the heat of vaporization, ΔH_v , at the normal boiling point produces excellent results and was used to produce the results reported herein.

Methods 2 and 3 use the reference equations of state to calculate the enthalpy departure functions of the saturated vapor and liquid at the reduced conditions corresponding to the normal boiling point of the test fluid. Application of Eq. (5) to the enthalpy departure function for both the saturated liquid and the vapor allows the formulation of an equation for the heat of vaporization of the test fluid which can then be solved for β_h :

$$\beta_h = [\Delta H_v - \Delta H_{v0} - \alpha(\Delta H_{v1} - \Delta H_{v0})/\alpha_1]/(\Delta H_{v2} - \Delta H'_{v2}) \quad (9)$$

where in analogy with Eq. (4),

$$\Delta H'_{v2} = \Delta H_{v0} + \alpha_2(\Delta H_{v1} - \Delta H_{v0})/\alpha_1 \quad (10)$$

Although method 3 is preferred to method 2, it requires the heat of vaporization at the normal boiling point, which may not be known. Method 2 is computationally the same as method 3 but estimates ΔH_v for the test fluid from a CSP correlation. We recommend the equation by Procopio and Su [6]:

$$\Delta H_v = 1.024RT_c T_{br}(\ln P_c)(1 - P_c^{-1})/(1 - T_{br}) \quad (11)$$

3. RESULTS

Calculations have been performed on 10 polar fluids. Critical properties and calculated α , β , and β_h values are shown in Table III. Results for compressibility factors are shown in Table IV as average absolute deviations (AAD) from experimental values. Also shown are predictions

Table III. Corresponding-States Parameters for Several Polar Fluids

| Fluid | T_c (K) | P_c (atm) | r (Å) | α | β | β_h |
|---------------------|-----------|-------------|---------|----------|---------|-----------|
| Ammonia | 405.6 | 111.3 | 0.8533 | 0.3775 | 0.7704 | 0.7047 |
| Ethanol | 516.2 | 63.0 | 2.2495 | 0.1383 | 0.4958 | 1.7415 |
| Acetone | 508.1 | 46.4 | 2.7404 | 0.1822 | 0.6053 | 0.4744 |
| Methanol | 512.6 | 79.9 | 1.5360 | 0.0819 | 0.9119 | 1.3910 |
| Hydrogen chloride | 324.6 | 82.0 | 0.2989 | 0.0104 | 0.4844 | 0.3423 |
| Methyl chloride | 416.3 | 65.9 | 1.4500 | 0.0757 | 0.3136 | 0.2406 |
| Methyl acetate | 506.8 | 46.3 | 2.8616 | 0.1936 | 0.3814 | 0.4437 |
| Methyl ethyl ketone | 535.6 | 41.0 | 3.1395 | 0.2204 | 0.4391 | 0.3070 |
| 1-Propanol | 536.7 | 51.0 | 2.7359 | 0.1818 | 0.3974 | 1.7411 |
| 2-Propanol | 508.3 | 47.0 | 2.7264 | 0.1809 | 0.4671 | 1.8207 |

using the LK method and a new four-parameter CSP method by Wu and Stiel [7] developed simultaneously to, but independently of, the present method. The method of Wu and Stiel employs the same reference fluids used in this work; however, it retains the acentric factor as the third parameter and determines the fourth parameter by a best-fit procedure

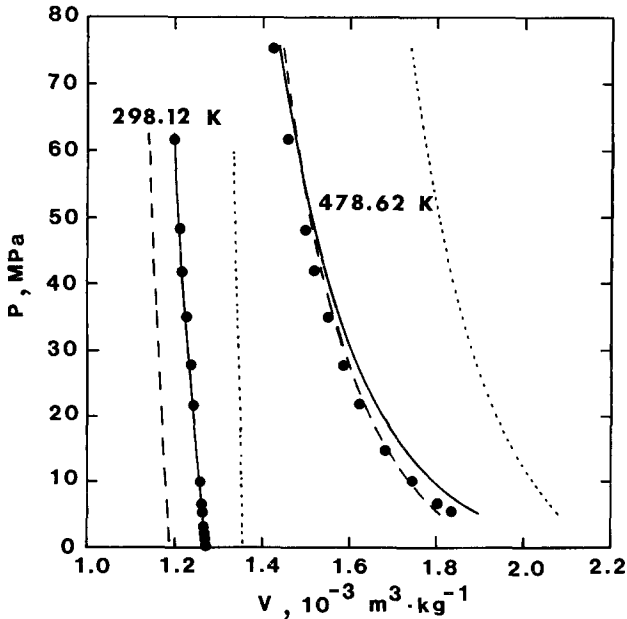


Fig. 2. P - V plot for liquid methanol on the 298.12 and 478.62 K isotherms comparing literature (\bullet) values to those calculated using this method (—), LK, (\cdots), and Wu-Stiel (---).

Table IV. Average Absolute Percentage Deviations (AAD) for Calculated Compressibility Factors

| Compound | Phase | T_r | P_r | No. of pts. | AAD (%) | | | Ref. No. |
|-------------------|-------|-----------|-------------|-------------|-----------|------|----------|----------|
| | | | | | This work | LK | Wu-Stiel | |
| Ammonia | L | 0.48-1.48 | 0.001-8.87 | 51 | 2.15 | 17.1 | 2.36 | 8 |
| | V | 0.48-1.48 | 0.001-4.43 | 50 | 0.72 | 1.76 | 0.76 | 8 |
| Ethanol | L | 0.92-1.21 | 1.30-9.18 | 42 | 1.74 | 4.17 | 5.29 | 9 |
| | V | 0.53-0.93 | 0.0001-4.97 | 23 | 1.12 | 1.28 | 1.27 | 10 |
| Acetone | L | 0.59-1.06 | 0.021-8.34 | 32 | 1.31 | 15.5 | 0.97 | 11, 12 |
| Hydrogen chloride | L | 0.84-1.04 | 0.42-2.24 | 37 | 2.21 | 8.87 | 2.12 | 13 |
| Methyl acetate | L | 0.50-0.62 | 4.19-12.16 | 12 | 1.34 | 5.94 | — | 14 |
| Methanol | L | 0.58-0.93 | 0.06-12.8 | 45 | 0.85 | 13.9 | 3.48 | 15 |
| | V | 0.81-1.12 | 0.05-2.55 | 24 | 4.55 | 7.08 | 2.65 | 16 |
| Methyl chloride | L | 0.75-0.90 | 0.13-4.73 | 25 | 0.68 | 6.55 | 0.51 | 17 |
| 2-Propanol | L | 0.93-1.13 | 1.45-9.84 | 48 | 1.95 | 0.90 | 0.89 | 18 |
| | V | 0.73-0.93 | 0.004-0.54 | 62 | 2.21 | 1.82 | 1.88 | 19 |

based on data available for each fluid. The composite AAD for the compressibility factor was found to be 6.68, 2.08, and 1.73% for the LK, Wu–Stiel, and present methods, respectively. Particularly informative examples of these comparisons are shown in Figs. 2–5. Figure 2 illustrates the compressibility factor errors that can result in using the LK method for polar fluids, for which it is not designed. The new four-parameter CSP methods do substantially better, with this method doing slightly better than the similar Wu–Stiel method, particularly at lower temperatures. In terms of volumetric properties, the significance of these errors can be seen in the $\log(V)$ plot (Fig. 3) for ammonia, where the results are very poor for the three-parameter method. Both four-parameter methods do quite well, although this method does considerably better for the liquid region and the Wu–Stiel method actually does better in the vapor phase. Figure 4 shows a supercritical isotherm for HCl; again there is a substantial improvement in utilizing four-parameter CSP techniques.

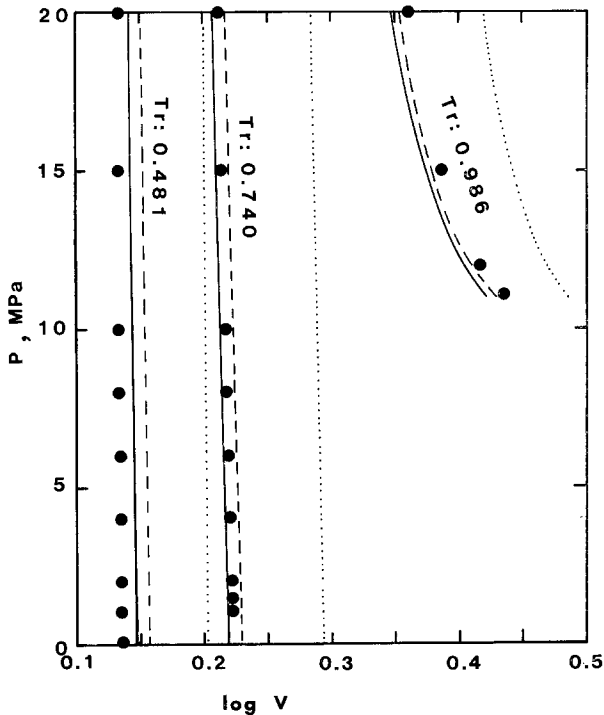


Fig. 3. P - $\log(V)$ plot for liquid ammonia isotherms comparing literature values (\bullet) to those calculated using this work (—), LK (·····), and Wu–Stiel (---). The quantity V is in $10^{-3} \text{ m}^3 \cdot \text{kg}^{-1}$.

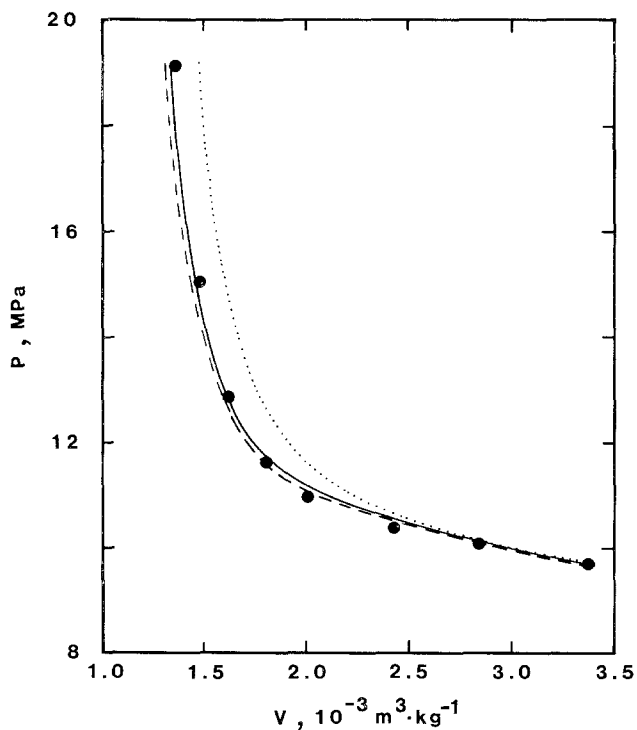


Fig. 4. P - V plot for the 338.15 K HCl isotherm comparing literature values (\bullet) to those calculated using this work (—), LK (\cdots), and Wu-Stiel (—).

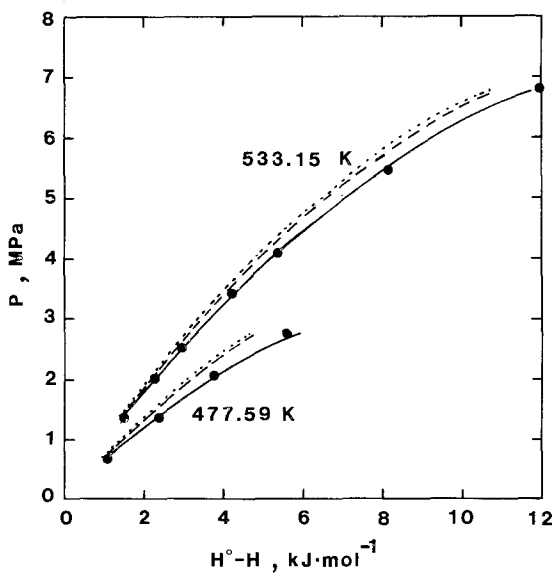


Fig. 5. Enthalpy departure function isotherms for ethanol comparing literature values (\bullet) to those calculated using this work (—), LK (\cdots), and Wu-Stiel (—).

Table V. Average Absolute Deviations (AAD) for Calculated Enthalpy Departure Functions

| Compound | Phase | T_r | P_r | No. of pts. | AAD (J/mol) | | | Ref. No. |
|------------------------|-------|------------|---------------|-------------|-------------|------|----------|----------|
| | | | | | This work | LK | Wu-Stiel | |
| Ammonia | L | 0.48-1.48 | 0.001-8.87 | 33 | 119 | 385 | 209 | 8 |
| | V | 0.48-1.48 | 0.001-4.43 | 34 | 68.4 | 149 | 66.1 | 8 |
| Ethanol | L | 0.53-0.60 | 0.0001-0.0025 | 3 | 764 | 1968 | 1812 | 10 |
| | V | 0.53-1.03 | 0.0001-1.08 | 31 | 184 | 429 | 399 | 10, 20 |
| Acetone | L | 0.78-0.995 | 0.294-1.17 | 3 | 90.3 | 737 | 334 | 21 |
| | V | 0.78-1.05 | 0.103-1.17 | 7 | 16.4 | 199 | 36 | 21 |
| Methanol | V | 0.88-0.99 | 0.085-0.85 | 15 | 433 | 676 | 518 | 22 |
| 1-Propanol | L | 0.57-0.90 | 0.0001-0.417 | 7 | 1682 | 3816 | 1494 | 23 |
| | V | 0.84-1.02 | 0.17-0.77 | 20 | 260 | 195 | 200 | 23 |
| Methyl ethyl ketone | L | 0.84-0.94 | 0.33-0.996 | 3 | 894 | 1479 | — | 21 |
| | V | 0.84-1.02 | 0.13-0.996 | 6 | 977 | 1074 | — | 21 |

Enthalpy departure function predictions were made for those fluids for which experimental data were available and the comparison results are contained in Table V. An overall comparison of the three methods as applied to these fluids produced AADs of 531, 330, and 249 J·mol⁻¹ for the LK, Wu–Stiel, and present methods, respectively. Figure 5 shows the substantial errors inherent in using the three-parameter CSP for polar fluids. In the case of ethanol, the Wu–Stiel method gives results similar to those of the LK method, although this is not generally true for other fluids.

4. GENERAL USE OF THE METHOD

The four-parameter CSP method described herein is primarily a computer method. The computer code used to generate the predicted values of the previous section utilizes some procedures that are not obvious but that are made necessary due to the use of fixed reference fluids of different types. The code used in this work uses a modified Newton–Raphson technique to solve for the compressibility factor roots of the reference fluid equations of state. However, due to the fact that the two-parameter CSP is not obeyed by the second and third reference fluids and usually not by the test fluid, some reduced conditions correspond to one phase for some of the reference fluids and the opposite phase for the others. However, if a liquid root is desired for the test fluid, then obviously a liquid root must be determined for each reference fluid. There are at least three different ad hoc methods to obtain a value for this hypothetical condition including isothermal continuation into the two-phase dome, replacement with the saturated root at the given pressure, and linear isothermal extrapolation into the two-phase dome based on points near saturation. The latter method was used in this work and is generally comparable to the first method except for cases where substantial extrapolation is required, in which case the first method may not converge to any root of the correct phase. The code itself is available from the authors in either BASIC or FORTRAN. Further details of the numerical techniques employed are available [24]. For quick approximate calculations, this method can be easily used in the form of Eq. (6) by interpolating the deviation functions from computer-generated tables available from one of the authors (RLR). To do so, α is calculated from Eq. (7), and β is determined from a liquid density and Eq. (8) using the tabulated deviation functions evaluated at the reduced conditions for the liquid density point. For simplicity β_h could be set equal to β , but for increased accuracy, β_h can be determined as previously described and the final test fluid property computed from Eq. (6), again interpolating from the tabulated deviation functions at the desired reduced conditions. Around the liquid–vapor phase boundary the above-mentioned problem of some

reference fluids being in the wrong phase at the test conditions and interpolation problems at the discontinuity have been solved by the generation of auxiliary tables also available from RLR. These values correspond to the opposite phase and are calculated by the procedure mentioned above.

It is quite often desirable to calculate the properties of a fluid at specified conditions without prior knowledge of its phase. Phase determination was included in the code used in this work in a consistent form by extension of the LK vapor pressure correlation using, again, the Taylor's series perturbation technique. Correlating the vapor pressure for water and using the LK equations for the first two reference fluids [1] yields

$$\ln(P_{vp,r})_0 = 5.9271114 - 6.09648/T_r - 1.28862 \ln T_r + 0.169347T_r^6 \quad (12)$$

$$\ln(P_{vp,r})_1 = 11.99431 - 12.33697/T_r - 6.647821 \ln T_r + 0.342696T_r^6 \quad (13)$$

$$\ln(P_{vp,r})_2 = 9.76059 - 10.05808/T_r - 4.15481 \ln T_r + 0.298975T_r^6 \quad (14)$$

With the assignment of $J = \ln(P_{vp,r})$ Eq. (5) can be used in conjunction with Eqs. (12)–(14) to compute the vapor pressure at any reduced temperature. This value can then be compared to the actual system pressure to determine the phase behavior.

5. CONCLUSIONS

A four-parameter CSP method utilizing three fixed reference fluids has been developed for accurate prediction of thermodynamic properties of polar and nonpolar fluids alike. The method requires only the critical temperature, the critical pressure, the radius of gyration, and one liquid-phase density point as input data. However, for more accurate calculations of enthalpy-related departure functions, it is recommended that at least the normal boiling point also be included and, preferably, the heat of vaporization at the normal boiling point. While the method is essentially a computer method, generalized tables of deviation functions have been prepared for hand calculations.

The method has been used to predict properties of several polar fluids. These results have been compared to the LK method and that of Wu and Stiel. The method described herein proved to be equivalent to the LK method for nonpolar fluids and far superior for polar fluids. While the Wu–Stiel method is similar in many respects to this method, the main difference is in the choice of the third and fourth parameters. In this work, properly decoupling the size/shape and polar effects in a true Taylor's series

expansion implies that β should be a true fundamental constant. Wu and Stiel's choice of the acentric factor as the third parameter does not achieve this and the results tend to show larger errors where data were not used to fit the fourth parameter.

The average error for the compressibility factor for all fluids tested was 1.9% for the vapor phase and 1.6% for the liquid. Vapor and liquid enthalpy departure functions showed average errors of 250 and 422 J · mol⁻¹, respectively. We are currently formulating and testing mixing rules for application of this technique to mixtures.

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