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Extended Corresponding States as a Tool for the Prediction of the Thermodynamic Properties of Mixtures[1]

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The principle of corresponding states, with one of its many extensions, is used to predict the thermodynamic properties of the binary mixtures N_2–CH_4 and CH_4–C_2H_6. Comparisons of the predicted properties with experimental data are given to illustrate some of the powers and problems associated with the method. Problems encountered in modeling mixtures, which are not necessarily associated with the mathematical model of the equation of state, are also discussed. Wide-range equations of state for the two binary systems mentioned above are presented.

KEY WORDS: equation of state; ethane; extended corresponding states; methane; mixtures; nitrogen; P–V–T–x.

1. INTRODUCTION

The extended corresponding-states method has been used extensively as a predictive tool for the thermodynamic properties of both pure fluids and mixtures; see, for example, Rowlinson and Watson [1], Leach [2], Mollerup and Rowlinson [3], Mollerup [4], and Haynes et al. [5]. The purpose of this paper is to examine the predictive ability of this method by applying the method to two binary systems for which accurate, wide-range P–V–T–x data are available. Straty and Diller [6] and Haynes and McCarty [7] have measured the P–V–T–x of the nitrogen–methane system from 1 to 27.0 mol $\cdot$ L^{-1} and from low temperatures to 320 K for three different compositions. Haynes et al. [8] have measured the P–V–T–x of the

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methane–ethane systems over a similar range of density, temperature, and composition. The remarks in this paper deal with the performance of the extended corresponding-states method for those two binary systems.

2. EXTENDED CORRESPONDING STATES

The extended corresponding states method is often defined by

$$Z_i(V, T) = Z_o(V/h_{i,o}, T/f_{i,o}) \tag{1}$$

and

$$A_i(V, T) = f_{i,o} A_o(V/h_{i,o}, T/f_{i,o}) \tag{2}$$

where Z is the compressibility factor and A is the residual Helmholtz free energy. V and T are the specific volume and temperature, where the subscripts denote the reference fluid (o) and target fluid (i). The $f_{i,o}$ and $h_{i,o}$ are transformation parameters, defined by

$$f_{i,o} = (T_o^c/T_i^c)\, \theta(T_r, V_r) \tag{3}$$

and

$$h_{i,o} = (V_o^c/V_i^c)\, \phi(T_r, V_r) \tag{4}$$

where T^c and V^c are the critical temperature and volume for the fluids denoted by the subscripts, and T_r and V_r are defined as T_i/T_i^c and V_i/V_i^c, respectively. The $\theta(V_r, T_r)$ and $\phi(V_r, T_r)$ are shape factors. Given a state point defined by V and T and the transformation parameters $f_{i,o}$ and $h_{i,o}$, Eqs. (1) and (2) define an exact transformation from one pure fluid surface to another. The pressure P_i then becomes $(h_{i,o}/f_{i,o})P_o$. In practice, when this method is used to transform the equation of state from fluid o to fluid i, the shape factors θ and ϕ are approximated in a number of different ways. In the present case, the method is being applied to mixtures, and the equation of state for each of the pure fluids is known. Knowledge of the equation of state for each of the pure fluids allows, in principle, the exact calculation of the $f_{i,o}$ and $h_{i,o}$ for each state point, which eliminates the need to approximate the θ and ϕ.

The extension to mixtures is accomplished by the equations

$$f_{ij} = \varepsilon_{i,j}(f_{ii,o} f_{jj,o})^{1/2} \tag{5}$$

$$h_{ij} = \eta_{i,j}(\tfrac{1}{2}h_{ii,o}^{1/3} + \tfrac{1}{2}h_{jj,o}^{1/3})^3 \tag{6}$$

$$h_{x,o} = \sum_i \sum_j x_i x_j h_{ij,o} \tag{7}$$

and

$$f_{x,o} h_{x,o} = \sum_i \sum_j x_i x_j f_{ij,o} h_{ij,o} \tag{8}$$

Table I. Coefficients Used for Eqs. (1) Through (9) in the Extended

Coef.	Nitrogen (1)[a]	Methane (2)[a]	Ethane (3)[a]
N_1	0.1380297495225E−3	0.9898938103506E−5	−0.3204748899754E−3
N_2	0.1084506517509E−1	0.2199608307777E−1	0.6529792338301E−1
N_3	−0.2471324101188E+0	−0.5322788079316E+0	−0.1669704615881E+1
N_4	0.3455258032294E+1	0.2021657992125E+2	0.1147983398106E+3
N_5	−0.4279707754439E+3	−0.2234398959295E+4	−0.1854722025638E+5
N_6	0.1064911582866E−4	0.1067940295914E−4	0.4994149505419E−4
N_7	−0.1140867096735E−2	0.1457922490725E−3	−0.4858871363403E−1
N_8	0.1444902518818E−4	−0.9265816804071E+0	0.1225345794259E+2
N_9	0.1871457595440E+4	0.2915364775442E+3	0.8622616116487E+4
N_{10}	0.8218877009302E−8	0.2313546243475E−6	−0.1081290299112E−5
N_{11}	0.2360990528530E−3	0.1387214294671E−3	0.6279097089566E−2
N_{12}	−0.5144803157865E−1	0.4780467522235E−2	−0.1716912700584E+1
N_{13}	0.4914545086900E−5	0.1176103850525E−4	−0.1640779425450E−4
N_{14}	−0.1151627179560E−3	−0.1982096759536E−3	−0.4356516175917E−2
N_{15}	−0.7168037353462E−1	−0.2512887793445E−1	−0.1966649728305E+1
N_{16}	0.7616667732997E−5	0.9748899971270E−5	0.4026724758003E−3
N_{17}	−0.1130930083065E−6	−0.1202192154914E−6	−0.6498241957831E−5
N_{18}	0.3736831222514E−4	0.4128354000517E−4	0.5111594215169E−2
N_{19}	−0.2039851537977E−6	−0.7215843025524E−6	−0.1113010365585E−3
N_{20}	−0.1719662034615E+4	0.5081738330724E+3	−0.7157747653659E+3
N_{21}	−0.1213055217824E+5	−0.9198903329074E+5	−0.1848571051546E+7
N_{22}	−0.9881399288672E+1	−0.2732264717714E+1	−0.2137365600849E+3
N_{23}	0.5619886977254E+4	0.7499024462744E+5	0.6275080079506E+7
N_{24}	−0.1823043991283E−1	0.1114060924601E−2	−0.9974911204638E+0
N_{25}	−0.2599826537217E+0	0.1083955175152E+1	0.1129115030825E+3
N_{26}	−0.4191893485621E−4	−0.4490960378921E−4	−0.1026469573296E−1
N_{27}	−0.2596406709219E−1	−0.1380337867569E+1	−0.5660525999348E+3
N_{28}	−0.1258683220677E−7	−0.2371902267344E−7	−0.4209846492732E−4
N_{29}	0.1049286615036E−5	0.3761652253053E−4	0.2374523588383E−1
N_{30}	−0.5458369386488E−10	−0.2375166989393E−9	−0.1289637842217E−6
N_{31}	−0.7674511784956E−9	−0.1237640808442E−7	−0.5423801148821E−4
N_{32}	0.5931232959376E−8	0.6766926553835E−6	0.2239717263374E−2
γ	0.56E−2	0.97066175E−2	0.21157025E−1
R	0.00831411	0.00831434	0.00831434
η_{12}	1.019221		
η_{23}	0.998189		
ε_{12}	0.953430		
ε_{23}	0.987883		

[a] The number in parentheses refers to the subscript of the binary interaction parameter.

Table II. Coefficients for Eq. (9) for the Nitrogen–Methane and Methane–Ethane Systems

Nitrogen–methane coefficients			
Coef.	0.28627 nitrogen	0.50116 nitrogen	0.68341 nitrogen
N_1	−0.2416498668004E−1	−0.1422085914937E−2	−0.4564520988116E−2
N_2	0.1136473502146E+1	0.9222685749928E−1	0.2415324916933E+0
N_3	−0.1546041584377E+2	−0.1511390387259E+1	−0.3537657381739E+1
N_4	0.1022090137674E+4	0.1065558820520E+3	0.2418372260679E+3
N_5	−0.4129387356361E+5	−0.5968213848169E+4	−0.1100148941916E+5
N_6	0.6935928635738E−3	0.3437010575717E−4	0.1282648808661E−3
N_7	−0.4892088644275E+0	−0.1778005518894E−1	−0.1245203788035E+0
N_8	0.1248074397051E+3	0.5375634231105E+1	0.4480468025033E+2
N_9	−0.6138370653987E+5	−0.5579527890232E+3	−0.5543876976234E+4
N_{10}	−0.2369503008533E−4	−0.4291240613572E−6	−0.6497443655252E−5
N_{11}	0.5857309833141E−2	−0.4542759160827E−4	0.8814872562146E−2
N_{12}	0.3558887105892E+0	0.3359297740191E−1	−0.3318033192602E+1
N_{13}	0.5447807139229E−3	0.4168487792233E−4	−0.1038167599328E−3
N_{14}	−0.7613188569267E−2	−0.1514269404746E−2	0.5622082739123E−2
N_{15}	0.1629067336291E+2	0.1123802642418E+0	0.1280003971552E+1
N_{16}	−0.6624128290098E−3	0.5208958350064E−4	−0.1972319114230E−3
N_{17}	0.2497396578738E−4	−0.4345234420156E−6	0.2322585233188E−5
N_{18}	−0.4276610123317E−1	−0.1954798548579E−3	−0.2916661024178E−2
N_{19}	0.9151992197225E−3	0.3376033645860E−5	0.5798916219367E−4
N_{20}	0.4872081641422E+5	−0.5392369027595E+2	0.4759273039393E+2
N_{21}	0.4340982134724E+6	0.3096568079487E+5	0.2827657382666E+6
N_{22}	0.7341102778522E+3	−0.2016679270055E+1	0.8383375713013E+2
N_{23}	0.1011942507119E+7	0.8588209915456E+5	0.1022988071313E+6
N_{24}	0.4472309222466E+1	0.7612108747592E−2	0.4055475823974E−2
N_{25}	0.2463853305921E+3	0.1326124741276E+1	0.1035068510740E+2
N_{26}	0.1198786763815E−1	−0.3241342129498E−3	0.6401795624320E−2
N_{27}	−0.4137124384473E+2	0.9519337230474E+1	0.9796086798914E+1
N_{28}	0.6778925187969E−4	0.1721656400241E−5	−0.1234908292540E−4
N_{29}	0.7124784633913E−2	−0.2710802549470E−3	−0.4618256610427E−3
N_{30}	0.1811211162198E−7	−0.2847478137588E−8	0.6948198742341E−7
N_{31}	0.5539024863129E−6	0.1514676323641E−6	0.1348892674000E−5
N_{32}	0.4650189812300E−3	0.6292346148868E−4	0.1491023186987E−4
γ	0.0172	0.0172	0.0172
R	0.00831434	0.00831434	0.00831434

Table continued

Table II *(Continued)*

Methane–ethane coefficients			
Coef.	0.68526 methane	0.50217 methane	0.34528 methane
N_1	-0.2000187787671E-1	0.5087896282223E-1	-0.5240750579034E-1
N_2	0.1114625495912E+1	-0.2430796450032E+1	0.2966186856729E+1
N_3	-0.1793330380240E+2	0.3381056074667E+2	-0.4857682335348E+2
N_4	0.1651209222847E+4	-0.2493089376375E+4	0.4705994994812E+4
N_5	-0.9605273687095E+5	0.9764734968260E+5	-0.2777234994902E+6
N_6	0.3984557389204E-3	-0.8321975451914E-3	0.1228954827582E-2
N_7	-0.4116485099735E+0	0.4759016593625E+0	-0.1502026294679E+1
N_8	0.1514818378189E+3	-0.4397774086278E+2	0.6268789893668E+3
N_9	-0.1546553452747E+5	0.2609971234358E+5	-0.5344508549081E+5
N_{10}	-0.1334547333951E-4	0.3988975585972E-4	-0.4518235412351E-4
N_{11}	0.1002365990121E-1	-0.1398530290155E-1	0.4334313808125E-1
N_{12}	-0.1976668295588E+1	0.3589994893307E+0	-0.1161734853903E+2
N_{13}	0.3267658715114E-3	-0.2395674350273E-3	0.1192104385887E-2
N_{14}	-0.2718696946279E-1	-0.3000681875402E-1	-0.1460018009494E+0
N_{15}	0.3039341978922E+1	-0.4355055227457E+1	0.1431762928525E+2
N_{16}	0.1010616284150E-2	0.2389286555210E-2	0.6663874367808E-2
N_{17}	-0.8763222382732E-5	-0.4354547657923E-4	-0.7685022356103E-4
N_{18}	-0.5651887683956E-2	0.7798065545604E-2	-0.3364477518037E-1
N_{19}	0.1004396881036E-3	-0.1373022765138E-3	0.6803384953990E-3
N_{20}	-0.6151697854355E+4	-0.3797881195969E+5	-0.4779011912240E+5
N_{21}	0.1035374899211E+7	0.1815225260513E+7	0.5492143497338E+7
N_{22}	-0.9812208667605E+2	-0.5493549506492E+3	-0.6449204634047E+3
N_{23}	0.4020041433239E+7	0.6236234112337E+7	0.2151873676141E+8
N_{24}	-0.8622229245845E+0	-0.3029343516190E+1	-0.4434823931693E+1
N_{25}	0.1800310637032E+3	0.9550624049456E+2	0.5972363889474E+3
N_{26}	-0.3697055631502E-2	-0.1426967265227E-1	-0.1551298594892E-1
N_{27}	0.1222168396106E+3	-0.1893220987490E+2	0.4952272623822E+3
N_{28}	-0.4576003901514E-5	-0.2598152364308E-4	-0.1755638739882E-4
N_{29}	0.1546499351594E-2	0.2754327688434E-2	-0.1224569027868E-2
N_{30}	-0.3373738564349E-7	-0.7796773395157E-7	-0.1188247780526E-6
N_{31}	-0.1870264891452E-5	-0.6314692962057E-5	0.2211423619049E-4
N_{32}	0.1249298869931E-2	-0.2013543174658E-2	-0.1154207279944E-2
γ	0.0172	0.0172	0.0172
R	0.00831434	0.00831434	0.00831434

where x_i and x_j are the mole fractions of the pure components. The η_{ij} and ε_{ij} are binary interaction parameters and the previously defined defined $f_{i,\text{o}}$ and $h_{i,\text{o}}$ become $f_{ii,\text{o}}$ and $h_{ii,\text{o}}$. Since the $f_{ii,\text{o}}$ and $h_{ii,\text{o}}$ are determined directly from the equations of state for the pure fluids, the only potentially adjustable parameters are the η_{ij} and ε_{ij}. The equation of state chosen to represent the pure fluids is

$$\begin{aligned} P = {} & \rho RT + \rho^2(N_1 T + N_2 T^{1/2} + N_3 + N_4/T + N_5/T^2) \\ & + \rho^3(N_6 T + N_7 + N_8/T + N_9/T^2) \\ & + \rho^4(N_{10} T + N_{11} + N_{12}/T) + \rho^5(N_{13}) \\ & + \rho^6(N_{14}/T + N_{15}/T^2) + \rho^7(N_{16}/T) \\ & + \rho^8(N_{17}/T + N_{18}/T^2) + \rho^9(N_{19}/T^2) \\ & + \rho^3(N_{20}/T^2 + N_{21}/T^3)\exp(-\gamma\rho^2) \\ & + \rho^5(N_{22}/T^2 + N_{23}/T^4)\exp(-\gamma\rho^2) \\ & + \rho^7(N_{24}/T^2 + N_{25}/T^3)\exp(-\gamma\rho^2) \\ & + \rho^9(N_{26}/T^2 + N_{27}/T^4)\exp(-\gamma\rho^2) \\ & + \rho^{11}(N_{28}/T^2 + N_{29}/T^3)\exp(-\gamma\rho^2) \\ & + \rho^{13}(N_{30}/T^2 + N_{31}/T^3 + N_{32}/T^4)\exp(-\gamma\rho^2) \end{aligned} \tag{9}$$

where P is the pressure in MPa, T is the temperature in K, ρ is the density in $\text{mol} \cdot \text{L}^{-1}$, and R is the gas constant. To facilitate the analysis of the nitrogen–methane mixture data, each of the data sets for a constant composition from Straty and Diller [6] were combined with those of Haynes and McCarty [7] and were fit to Eq. (9) as though the data were for a pure fluid. The same procedure was followed for the methane–ethane data of Haynes et al. [8], and the coefficients for Eq. (9) for the three pure fluids and the six constant-composition surfaces are given in Tables I and II. Since the deviation patterns for all six constant-composition data sets are similar for a given calculational method, the methane–ethane system where $x = 0.68526$ of methane is taken as typical for the remainder of this discussion. Figure 1 illustrates the deviations between the experimental densities and those calculated from the constant-composition surface chosen for illustration. Figure 2 illustrates deviations using the same experimental data but using the extended corresponding-states method to obtain the calculated densities. For the corresponding-states calculation the values of η_{ij} and ε_{ij} are given in Table I. The deviation plots for the extended corresponding-states calculations show the deviations to be much larger than those from Eq. (9). The deviation plots for the calculations using

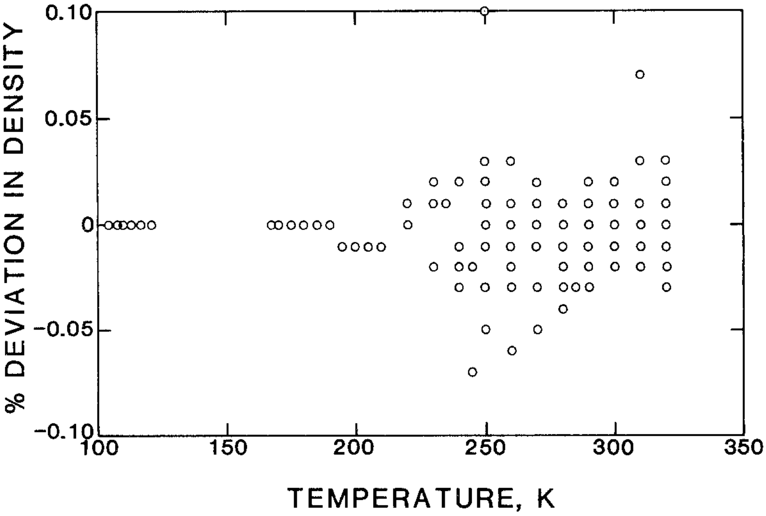

Fig. 1. Deviations between densities calculated from the constant-composition surface chosen for illustration and experimental data.

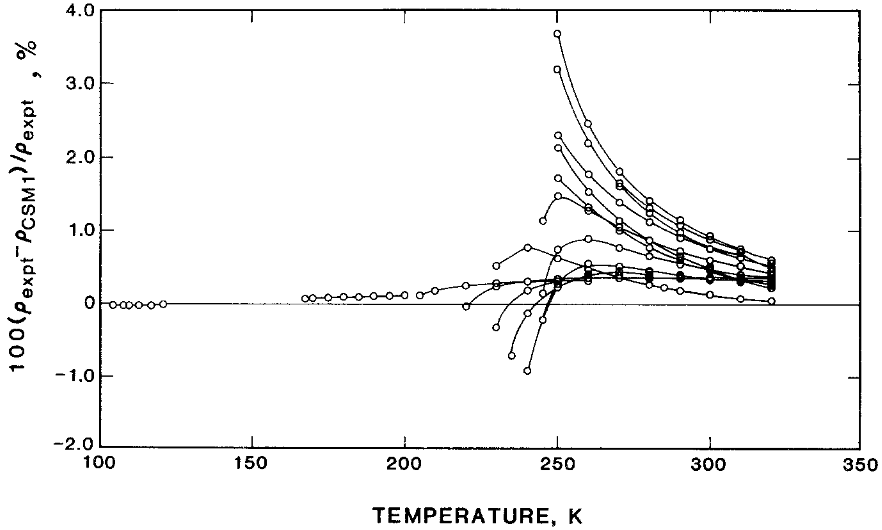

Fig. 2. Deviations between densities calculated by the extended corresponding-states method and experimental data.

Eq. (9) for a constant composition illustrate the internal consistency of the experimental data and demonstrate the feasibility of representing a mixture as a "pseudo-pure fluid." Figure 3 illustrates this data set on a P–T diagram. The points on the isochores in Fig. 3 represent the actual experimental data set. The saturation envelope was constructed from the data of Bloomer et al. [9] and the mixture critical point indicated by the symbol $*$ is from Ellington et al. [10]. There are some interesting features of the representation of these data as a pseudo-pure fluid via Eq. (9). The pseudopure fluid critical point, i.e., the point where $(\partial P/\partial \rho)$ and $(\partial^2 P/\partial \rho^2) = 0$, is at $P = 4.3296$ MPa, $T = 223.664$ K, and $\rho = 11.029\ \mathrm{mol \cdot L^{-1}}$. As one might expect, Fig. 3 shows the pseudo-pure fluid critical points to be well inside the mixture's saturation envelope. The dashed lines in Fig. 3 represents the locus of points where $(\partial^2 P/\partial T^2) = 0$ (maxima in C_v), as calculated from the fit of Eq. (9) to the constant composition data. The upturn in the locus at high densities very likely does not represent the true behavior of the surface and is probably an artifact of the least-squares fit to the data. Making these same calculations using the corresponding-states method outlined above, which is also a pseudo-pure fluid representation of the mixture, the resulting locus of $(\partial^2 P/\partial T^2) = 0$ and

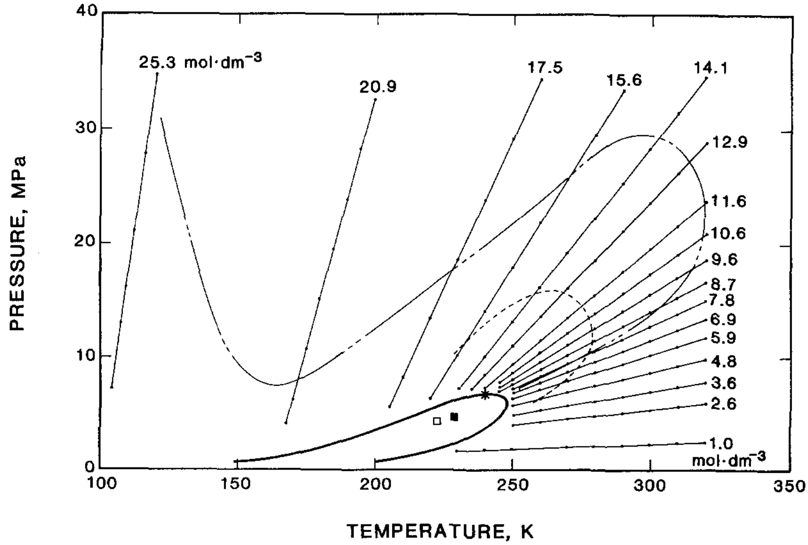

Fig. 3. P–T plot of the experimental data for the methane–ethane system where $x = 0.68526$ of methane. The $*$ denotes the mixture critical point. The ■ denotes the "pseudo-pure fluid" critical point from the extended corresponding states, and the □ denotes the "pseudo-pure fluid" critical point from the constant-composition surface. The – – – is the locus of C_v maxima from the extended corresponding states, and the other dashed line is the same locus from the constant-composition surface.

the pseudo-pure fluid critical point are quite different. The results of the corresponding-states calculation are also shown in Fig. 3 as a dashed line for the locus and a filled square for the critical point.

3. CONCLUSIONS

The application of the extended corresponding-states method to the nitrogen–methane and the methane–ethane binary systems has revealed a number of problems. While in principle, the simultaneous solution of Eqs. (1) and (2) for the pure fluids is a straightforward iterative procedure, in practice the iteration does not converge for many of the points in the mixture data set, especially for densities below 3 $\text{mol} \cdot \text{L}^{-1}$, and some alternate method of approximating θ and ϕ must be used. At these low densities (except near saturation) the standard two parameter transformation may be used, i.e., $\theta = \phi = 1$.

The fit of the constant-composition mixture data to Eq. (9) seems to indicate that the "pseudo-pure fluid" critical point should be well inside the saturation envelope of the mixture surface, while the pseudo-pure fluid critical point from the extended corresponding states calculation is not.

The locus of $(\partial P^2/\partial T^2) = 0$, calculated from the extended corresponding-states surface, does not predict the real locus of the mixture surface. Both these problems may be attributed to the failure of the mixing and/or combining rules.

Although the tone of this paper up to point has been somwhat negative, the extended corresponding-states method is an extremely useful tool for the prediction of the thermodynamic properties of mixtures. On a global equation-of-state basis, the extended corresponding-states method performs much better than any other method known to the author. The lack of experimental data has prevented the comparison of the method with derived thermodynamic properties such as specific heat capacity. However, if the equation of state chosen for the reference fluid performs well for higher-order properties, the predicted higher-order mixture properties should be quite good. It is hoped that the problems revealed in this paper will stimulate new research which will ultimately improve the method. Work is continuing at the National Bureau of Standards to achieve these goals.

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