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Prediction of Enthalpy and Entropy Departures Using a Two-Fluid Corresponding-States Principle

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The generalized corresponding-states principle (GCSP), based on the properties of two nonspherical reference fluids, has been shown to be a powerful technique for the correlation and prediction of thermodynamic properties. In this work we show GCSP calculations of enthalpy and enropy departures for pure fluids and fluid mixtures. The mixtures studied include those conforming well to traditional corresponding states theory (e.g., *n*-pentane + *n*-octane), as well as those that have not hitherto been amenable to such treatments (e.g., *n*-pentane + ethanol). It is shown that the GCSP method works well for all classes of mixtures and compares favorably with other methods of prediction. The use of cubic equations of state to represent the reference fluids gives the GCSP method flexibility while maintaining accuracy in the prediction. No adjustable parameters are required in the GCSP calculations of enthalpy and entropy departures.

KEY WORDS: corresponding states; enthalpy; entropy; mixtures.

1. INTRODUCTION

The corresponding-states principle (CSP) is a useful tool for the prediction of thermodynamic properties of fluids and fluid mixtures from the known properties of pure substances. The principle originated with van der Waals, who postulated that all fluids behave similarly at the same reduced temperature and volume. This two-parameter CSP (since a knowledge of two parameters, T_c and V_c, is required to predict the properties of any one fluid) is applicable only to spherical molecules. Pitzer [1] proposed a

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three-parameter corresponding-states principle and showed that fluids not exhibiting strong polarity or association could be well correlated using the three parameters T_c, P_c, and ω. The Pitzer formulation was recently put into a form suitable for digital computation by Lee and Kesler [2]. The three-parameter CSP is, in theory, applicable only to nonpolar fluids. However, a more general form [3] using two reference fluids can be applied to a wider range of fluids, including those exhibiting polarity. The superiority of this general form, termed the generalized corresponding-states principle (GCSP), has been demonstrated for the calculation of thermodynamic and transport properties [4–6] and phase equilibria [7, 8] in the recent literature. In this work, we describe the extension of the method to enthalpy and entropy calculations. Tarakad and Danner [9] have compared a number of equation of state methods, as well as the Lee–Kesler corresponding-states method, for their ability to predict enthalpies of a variety of fluids and concluded that the Lee–Kesler method gave the best overall predictions of this thermodynamic property. The GCSP method has therefore been compared with the Lee–Kesler method in the calculations described below.

2. GENERALIZED CORRESPONDING-STATES PRINCIPLE

The basic mathemtical statement of the three-parameter corresponding-states principle proposed by Pitzer is given by

$$Z[T_r, P_r, \omega] = Z^{(0)}[T_r, P_r] + \omega Z^{(1)}[T_r, P_r] \quad (1)$$

In this equation, $Z^{(0)}$ is the compressibility of a simple spherical fluid (argon) at the same reduced temperature T_r ($= T/T_c$) and reduced pressure P_r ($= P/P_c$) as the fluid of interest, and $Z^{(1)}$ is a complicated deviation function. In the Pitzer formulation, $Z^{(0)}$ and $Z^{(1)}$ are given in tabular form, as are other thermodynamic functions which can be derived from the compressibility.

In order to obtain an analytical representation of the Pitzer method suitable for digital computation, Lee and Kesler [2] reformulated the three-parameter corresponding-states principle as follows:

$$Z = Z^{(0)} + [\omega/\omega^{(r)}]\{Z^{(r)} - Z^{(0)}\} \quad (2)$$

where $Z^{(1)}$ in Eq. (1) has been replaced by an interpolation based on the properties of a (heavy) nonspherical reference fluid (r) and a spherical reference fluid (0).

Both Eq. (1) and Eq. (2) consider the compressibility of a real fluid as a Taylor-series expansion about the compressibility of a spherical reference fluid, with the acentric factor ω being the expansion variable and the Taylor series being truncated after the first-order term. It should be noted that the derivative $(\partial Z/\partial\omega) = Z^{(1)}$ in Eq. (1) has been replaced by its finite difference $[Z^{(r)} - Z^{(0)}]/[\omega^{(r)} - 0]$ in Eq. (2).

Interpreting Eq. (1) as a Taylor-series expansion around a spherical reference fluid suggests an alternative formulation of the corresponding-states principle which will greatly extend its accuracy as a well as its applicability. This reformulation, termed the generalized corresponding-states principle (GCSP), consists of a Taylor-series expansion about some suitably chosen nonspherical reference fluid and is given by

$$Z = Z^{(\mathrm{r1})} + \{\omega - \omega^{(\mathrm{r1})}/\omega^{(\mathrm{r2})} - \omega^{(\mathrm{r1})}\} \cdot (Z^{(\mathrm{r2})} - Z^{(\mathrm{r1})}) \tag{3}$$

Here, superscripts r1 and r2 refer to two reference fluids which are chosen so that they are similar to the pure fluid(s) of interest or, in the case of mixtures, to the key components in the mixture. If one of the reference fluids is taken to be a spherical fluid with zero acentric factor, then Eq. (3) reduces to Eq. (2). However, with a suitable choice of reference fluids, Eq. (3) might be expected to yield more accurate predictions of thermodynamic properties for a wider variety of fluids than Eq. (2), and we have confirmed this in our previous studies.

The linear dependence of Z with ω makes it possible to develop expressions of a similar form for derived properties. Differentiation of Eq. (3) with respect to T_{r} at constant P_{r} leads to

$$X = X^{(\mathrm{r1})} + \left\{\frac{\omega - \omega^{(\mathrm{r1})}}{\omega^{(\mathrm{r2})} - \omega^{(\mathrm{r1})}}\right\} \{X^{(\mathrm{r2})} - X^{(\mathrm{r1})}\} \tag{4}$$

where

$$x = \frac{H^0 - H}{RT_{\mathrm{c}}} \quad \text{or} \quad \frac{S^0 - S}{R} \tag{5}$$

and the individual terms are evaluated using particular reference fluid properties. Equations (4) and (5) form the basis of our enthalpy and entropy calculations described below.

2.1. Extension to Mixtures

The GCSP can be readily extended to mixtures using a one-fluid model to calculate the pseudocritical properties T_{cm}, P_{cm}, and ω_{m}. The choice of mixing ruls is of special importance in corresponding-states theory, and we have developed [7, 8] an appropriate set of mixing rules for the GCSP. These are given by

$$\omega_{\mathrm{m}}(T_{\mathrm{cm}}/P_{\mathrm{cm}})^{2/3} = \sum_i \sum_j x_i x_j \omega_{ij}(T_{\mathrm{c}ij}/P_{\mathrm{c}ij})^{2/3} \tag{6}$$

$$(T_{\mathrm{cm}}^2/P_{\mathrm{cm}}) = \sum_i \sum_j x_i x_j (T_{\mathrm{c}ij}^2/P_{\mathrm{c}ij}) \tag{7}$$

$$(T_{\mathrm{cm}}/P_{\mathrm{cm}}) = \sum_i \sum_j x_i x_j (T_{\mathrm{c}ij}/P_{\mathrm{c}ij}) \tag{8}$$

with the cross interaction terms ($i \neq j$) given by

$$T_{\mathrm{c}ij} = \xi_{ij} \cdot (T_{\mathrm{c}ii} T_{\mathrm{c}jj})^{1/2} \tag{9}$$

$$(T_{\mathrm{c}ij}/P_{\mathrm{c}ij})^{1/3} = \eta_{ij} \cdot \{(T_{\mathrm{c}ii}/P_{\mathrm{c}ii})^{1/3} + (T_{\mathrm{c}jj}/P_{\mathrm{c}jj})^{1/3}\}/2 \tag{10}$$

$$\omega_{ij} = (\omega_{ii} + \omega_{jj})/2 \tag{11}$$

Here ξ_{ij} and η_{ij} are binary interaction coefficients which are usually obtained from experimental data. In all the calculations that follow, however, ξ_{ij} and η_{ij} have been set equal to unity, so that the properties of mixtures are predicted from the properties of the pure reference fluids.

The mixing rules have been tested and found to yield good predictions for hydrocarbon–hydrocarbon, hydrocarbon–alcohol, and hydrocarbon–water systems. They appear to work well for both thermodynamic and transport properties.

It should be noted that the reducing parameters T_{cm} and P_{cm} are determined solely by Eqs. (7) and (8). The mixture acentric factor given by Eq. (6) is then a surface fraction weighted average of the pure component acentric factors, since $T_{\mathrm{cm}}/P_{\mathrm{cm}}$ is proportional to the reduced volume. It should also be noted that Eqs. (6)–(8) can be solved without any iterations.

2.2. Reference-Fluid Properties

An important characteristic of the generalized corresponding-states principle is the freedom to choose reference substances which are similar to the particular fluids of interest. We have established [4] that this ability to choose the reference substances leads to very accurate, easy-to-apply corresponding-states theory. We have further shown [7, 8] that the ability to vary the reference substances is more important than providing a highly accurate representation of fixed substances. Thus, for example, using the GCSP with a simple cubic equation-of-state representation for one hydrocarbon and one alcohol (the reference fluids) yields accurate predictions of phase equilibria for hydrocarbon–alcohol systems. Moreover, these predictions have been shown to be more accurate than those of the Lee–Kesler corresponding states method, which uses the 11-constant BWRS equation for the two (fixed) reference fluids. In view of these findings, we have chosen to represent our reference-fluid properties by the cubic equation of state of Patel and Teja [10] in this work. This equation reproduces many of the good features of the Soave and Peng–Robinson equations of state for nonpolar fluids but overcomes some of the limitations of these equations for polar fluids. The Patel–Teja (PT) equation is of the form

$$P = RT/(v-b) - a[T]/\{v(v+b) + c(v-b)\} \tag{12}$$

where R is the gas constant, $a[T]$ is a Soave-type temperature-dependent function (which contains a single substance-dependent parameter F), and b and c are constants related to T_c, P_c, and ζ_c (which is equal to the calculated value of $P_c V_c/RT_c$). The equation of state therefore contains four substance-specific parameters, T_c, P_c, ζ_c, and F. For nonpolar fluids, ζ_c and F can be correlated with the acentric factor ω, so there are only three substance-specific parameters for such fluids, as with other cubic equations of state. An important difference between the PT equation and other cubic equations is that the PT equation does not require *all* fluids to have the same critical compressibility ζ_c. This leads to improved predictions of liquid densities while, at the same time, maintaining an accurate description of the vapor pressure curve via $a[T]$.

3. RESULTS AND DISCUSSION

An extensive evaluation of six different methods for the calculation of enthalpy was made by Tarakad and Danner [9] using 5632 experimental data points. Overall the methods of Starling [11] and Lee and Kesler [2] were selected as being superior to other equation-of-state and corresponding-states methods and the Lee–Kesler method was found to be the most reliable. We have used a subset of the Tarakad and Danner data and have compared enthalpy departures using the GCSP and the Lee–Kesler methods. Table I gives a summary of the systems studied, the range of temperature and pressure of the data, and the data references. Only single-phase data were used in the study, as two-phase enthalpies would require additional calculations that are not relevant to the comparison. Data were then divided into groups of high-density and low-density data based on the two-phase enthalpies.

Table I. Summary of Systems Studied

No.	System	Temperature range (K)	Pressure range (MPa)	No. of points	Ref. No.
1	Benzene	466–644	1.38–9.65	218	15
2	*n*-Octane	297–589	1.38–9.65	131	16
3	*n*-Hexadecane	297–622	0.17–9.65	72	17
4	*cis*-Decalin	297–589	0.17–9.65	27	18
5	Tetralin	297–622	0.17–9.65	66	19
6	Benzene + *n*-pentane	297–644	1.38–9.65	712	20
7	Benzene + *n*-octane	466–589	1.38–9.65	417	15
8	*n*-Pentane + *n*-octane	297–589	1.38–9.65	424	16
9	*n*-Pentane + tetralin	297–611	0.17–9.65	398	19
10	Benzene + ethanol	394–533	0.69–10.34	116	21
11	Pentane + ethanol	394–533	0.69–10.34	158	21
12	Benzene + cyclohexane	511–583	2.76–9.75	393	22
13	Methane + CO_2	273–363	3.0–13.7	42	23
14	Methane + ethane + CO_2	263–363	3.0–13.7	56	12
15	Benzene + *n*-octane + tetralin	297–589	0.28–9.65	110	24
16	Methane + nitrogen	111–366	0.07–10.34	615	13

Table II gives the absolute average deviation and percentage deviation between experimental and calculated properties for the Lee–Kesler and GCSP methods. It should be noted that, although low-density systems are close to the ideal-gas state, the percentage deviations between experimental and predicted enthalpy departures are large for these systems because of the absolute magnitude of the enthalpies involved. Therefore, absolute average deviations in enthalpy departures are also shown in Table II in order to put errors into perspective. The GCSP predictions are comparable with the LKCSP predictions, with the LKCSP method being slightly better for hydrocarbon systems and the GCSP method being slightly better for nonhydrocarbons.

The LKCSP method uses an 11-constant modified BWR equation of state to represent the (fixed) reference fluids. Their spherical reference-fluid equation of state is based primarily on the properties of methane, while the nonspherical reference equation is based on the properties of *n*-octane. However, Lee and Kesler adjusted the constants somewhat to yield quantitatively correct behavior for many hydrocarbon systems. In contrast, the GCSP method uses a less accurate (and simpler) equation of state to represent the reference fluids but has the flexibility of reference-fluid choice.

For the binary systems studied, the reference fluids chosen for the GCSP calculations were generally the system components. For

Table II. Comparison of Experimental and Predicted Enthalpy and Entropy Departures

System No.[a]	Liquid				Vapor			
	GCSP		LKCSP		GCSP		LKCSP	
	AAPD[b]	AAD[c]	AAPD[b]	AAD[c]	AAPD[b]	AAD[c]	AAPD[b]	AAD[c]
				Enthalpy departures				
1	2.81	0.374	4.30	0.471	4.93	0.129	3.16	0.093
2	2.27	0.468	1.59	0.324	16.71	0.877	10.19	0.529
3	2.21	1.280	1.76	0.997	51.90	2.190	39.10	1.680
4	1.18	0.424	1.53	0.547	36.00	0.868	19.40	0.574
5	0.79	0.293	1.06	0.388	23.70	0.386	10.72	0.161
6	5.39	0.471	8.67	0.860	17.44	0.377	15.73	0.349
7	4.90	0.708	7.64	1.100	11.45	0.301	12.19	0.317
8	5.06	0.711	3.37	0.418	19.57	0.743	18.17	0.679
9	5.58	0.867	5.46	0.873	21.67	0.372	19.24	0.326
10	10.81	1.796	16.91	2.491	29.90	0.400	47.26	0.667
11	11.38	1.079	19.15	1.882	26.50	0.363	34.73	0.492
12	5.51	0.558	10.84	1.237	13.03	0.490	17.54	0.669
13					5.01	0.116	3.32	0.127
14					8.99	0.303	8.20	0.344
15	4.07	0.844	5.45	1.039	14.34	0.267	10.24	0.190
				Entropy departures				
16					2.01		1.56	

[a] Numbers correspond to systems given in Table I.

[b] $\mathrm{AAPD} = (1/n) \sum [|H_{i,\mathrm{calc}} - H_{i,\mathrm{exp}}|/H_{i,\mathrm{exp}}] \times 100$, in %.

[c] $\mathrm{AAD} = (1/n) \sum |H_{i,\mathrm{calc}} - H_{i,\mathrm{exp}}|$, in $\mathrm{kJ \cdot mol^{-1}}$.

hydrocarbon–hydrocarbon mixtures such as *n*-pentane + *n*-octane, the LKCSP method is better, as expected, because of the more accurate reference-fluid representation. When one of the components is an aromatic substance, however, as in the case of the benzene + *n*-pentane and benzene + *n*-octane systems, the GCSP method gives better predictions.

Figures 1 and 2 show deviation plots of the benzene + *n*-pentane system for the GCSP and LKCSP methods. High percentage errors can be expected for both methods in the region of low reduced pressures and high reduced temperatures, since the ideal gas is used as the reference state and the magnitude of the enthalpy deviations is small. In the compressed liquid region and fluid region where enthalpy values are large, the GCSP method gives better predictions by about 3%.

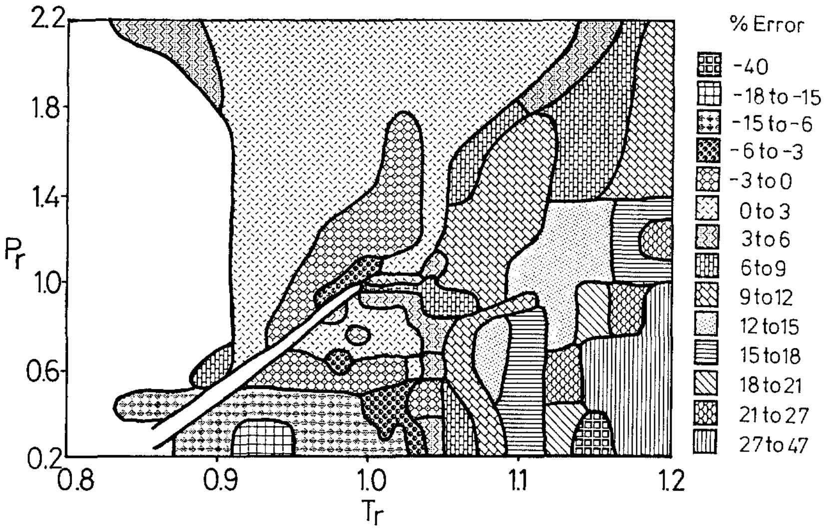

Fig. 1. GCSP error map of the 0.814 mol% benzene + 0.186 mol% *n*-pentane system.

When the reference fluids are different from the system components, as is the case with the *n*-pentane + tetralin system, predictions using the GCSP method are similar to those using the LKCSP method. We found that in choosing reference fluids, it is important that the reference-fluid acentric factors bracket the acentric factors of the system components. That

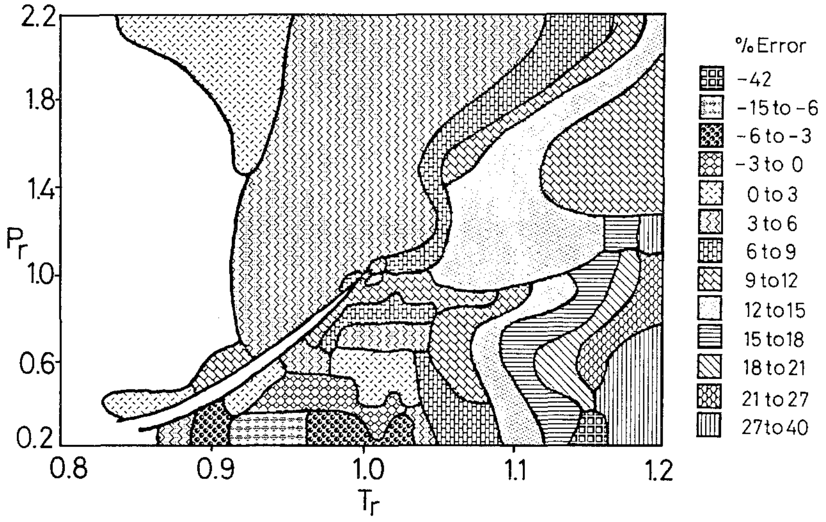

Fig. 2. LKCSP error map of the 0.814 mol% benzene + 0.186 mol% *n*-pentane system.

is, it is generally less accurate to perform extrapolations of a property with the acentric factor, unless the properties of the reference fluids are known accurately.

The benzene + cyclohexane system is peculiar in that the chemical nature of the components is similar and the acentric factors are identical. For such a case, the reference fluids must be chosen to be different from the pure components (in this case, benzene + *n*-hexane). A suitable choice can usually be found using components of similar chemical nature whose acentric factors bracket the acentric factors of the system components.

Systems containing alcohols are much more difficult to predict and can be expected to yield higher errors due to hydrogen bonding that is not accounted for by the GCSP method. Nevertheless, the predictions using the GCSP method are better than those using the LKCSP method. However, the overall predictions for both methods are somewhat higher than for the other systems.

A binary system and a ternary system containing carbon dioxide were also examined. Ng and Mather [12] determined residual enthalpies of these mixtures from isothermal throttling experiments and compared their results with predictions using six different methods, including the LKCSP method. High errors were found for the LKCSP method. We also found that the GCSP method gave high errors for these mixtures and attribute this to the inability of ω to account adequately for quadrupolar forces.

Entropy departures were compared using the data of Bloomer [13]. Both methods gave low errors as expected for this simple system.

One of the advantages of using a cubic equation of state for the reference fluids is that very little information is required for the particular reference fluids chosen. In the case of the Patel–Teja equation, a knowledge of T_c, P_c, a vapor pressure datum, and a liquid density datum is sufficient to obtain the equation-of-state constants. If the vapor pressure and liquid density are not available, we have shown recently [14] that the boiling point can be used to obtain the constants F and ζ_c via the effective carbon number concept. Thus, the reference-fluid equation-of-state constants can be generated from a minimum of data.

4. CONCLUSIONS

The GCSP is a valuable technique for thermodynamic property prediction. It is a simple technique, and no iterations are required for entropy and enthalpy calculations. Using a cubic equation to represent the reference fluids gives the method flexibility, while maintaining accuracy. In general, the GCSP method leads to better predictions of enthalpy and entropy deviations than other methods which employ complex equations for (fixed) reference fluids.

When using the acentric factor as the third correlating parameter, it is important that the reference fluids should be chosen such that they are similar to the system components and their acentric factors should lie on either side of the acentric factors of the system components.

Good predictions for systems containing polar molecules can also be obtained using this method, although the errors can be expected to be greater than those obtained for nonpolar mixtures, unless adjustable parameters are included in the treatment.

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