Continuous Thermodynamics of Phase Equilibria Using a Multivariate Distribution Function and an Equation of State

The dew points of 40 multicomponent fluid mixtures including gas condensates, absorber oils, crude oils, synthetic aromatic heavy oils, and coal liquids were calculated using the method of continuous thermodynamics and the Patel-Teja cubic equation of state. These multicomponent mixtures were characterized by a log normal distribution function in two variables: the boiling point and specific gravity in this work. Comparisons were made with the case when a single variable distribution function is employed and also with the method of Cotterman et al. In general, the new method leads to excellent predictions of both phase equilibria and liquid densities.

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Introduction

Mixtures whose complete compositional analysis is not available are of considerable interest in oil and natural gas processing and in coal liquefaction. These mixtures include gas condensates, absorber oils, crude oils, and coal liquids. The composition of these undefined mixtures can sometimes be characterized by a continuous distribution function in one or two variables. While the approach is not new (Bowman, 1949; Edmister, 1955), it has recently been reformulated for phase equilibrium calculations by Ratzsch and Kehlen (1983) and by Cotterman et al. (1985a,b). In our earlier work, we combined this work on continuous thermodynamics with the effective carbon number concept of Ambrose and Sprake (1970) to calculate dew points of semicontinuous natural gas mixtures (Willman and Teja, 1985a,b). This earlier work included extensions of the regular solution theory and the truncated virial equation to continuous mixtures. A disadvantage of our approach is that the regular solution theory and other activity coefficient models in general cannot be used for phase equilibrium calculations at high pressures. A second disadvantage of our approach, and of other approaches that employ a single distributed variable, is that many continuous mixtures require more than one variable for proper characterization. Thus crude oils, which generally consist of paraffinic, napthenic, and aromatic constituents, require the specification of at least two distributed variables (e.g., boiling point and specific gravity) for their characterization.

In the present work, we have overcome the limitations outlined above, first by use of an equation of state suitable for high-pressure phase equilibrium calculations, and second, by use of a bivariate log normal distribution function to characterize the continuous part of the mixtures. Our calculations of the dew points of semicontinuous natural gas condensates, absorber oils, aromatic light oils, coal liquids, and crude oils are described below. The incorporation of a statistical distribution function into an equation of state has previously been proposed by Whitson (1983) and Cotterman et al. (1985a,b) for gas condensates and crude oils. However, these studies employed a single variable distribution function to characterize the heavy fractions.

Our present work differs from these previous studies in two ways:

1. An equation of state suitable for both phase equilibria and density predictions is employed.
2. A bivariate distribution function is employed so that the method can be used for a wide variety of continuous mixtures, including natural gases, crude oils, and coal liquids.

Development of the Method

Following the work of Ratzsch and Kehlen (1983), Cotterman et al. (1985a,b), and our previous work (Willman and Teja 1985a,b), we can characterize the composition of a mixture with a continuous distribution of components by a distribution func-

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tion $F[I]$, where the distribution variable I can be the molecular weight, boiling point, effective carbon number, or some other suitable characterization variable. The distribution function $F[I]$ is normalized such that:

$$\int_I F[I]dI = 1 \tag{1}$$

Similarly, when a bivariate distribution function $F[I, J]$ is employed, the normalization is:

$$\int_I \int_J F[I, J]dI\,dJ = 1 \tag{2}$$

A semicontinuous mixture is one in which the mole fractions of some components have discrete values while the concentrations of others are described by a distribution function. For a bivariate distribution with k discrete components, the normalization is

$$\sum_i^k x_i + \eta \int_I \int_J F[I, J]dI\,dJ = 1 \tag{3}$$

where $\eta (= 1 - \Sigma_i x_i)$ is the mole fraction of the continuous component.

Phase equilibrium relationships may now be written for the k discrete components as:

$$y_i \phi_i^v = x_i \phi_i^L \tag{4}$$

or

$$f_i^v = f_i^L \tag{4a}$$

and for the continuous fraction as:

$$\eta^v F^v[I, J]\phi^v[I, J] = \eta^L F^L[I, J]\phi^L[I, J] \tag{5}$$

or

$$f^v[I, J] = f^L[I, J] \tag{5a}$$

where $F[I, J]$ is the distribution function, $\phi[I, J]$ the fugacity coefficient for the continuous component, and superscripts L and V refer to the liquid and vapor phases, respectively. Subscript i is the discrete component index, and x and y are the discrete component mole fractions in the liquid and vapor phases, respectively. Note that the use of a multivariate distribution function for the continuous fraction eliminates the need for a separate ensemble (for the paraffinic, napthenic, and aromatic components of crude oil, for example) as described by Cotterman et al. (1985a,b) and the sometimes arbitrary stipulation of *the mole fraction* corresponding to each ensemble.

The distribution function

We have chosen the bivariate log normal distribution function for $F[I, J]$ in Eqs. 3 and 5. This is the simplest two-variable distribution function with qualitatively correct features that may be used to represent the molar composition vs. molecular weight or boiling point behavior of the mixtures studied (Whitson, 1983). A bivariate normal distribution has the following form (Hahn and Shapiro, 1967):

$$F[I, J] = \frac{1}{[4\pi^2\sigma_I^2\sigma_J^2(1-\psi^2)]^{1/2}} \exp\left\{\frac{-1}{2(1-\psi^2)}\left[\left(\frac{I-\mu_I}{\sigma_I}\right)^2 - 2\psi\left(\frac{I-\mu_I}{\sigma_I}\right)\left(\frac{J-\mu_J}{\sigma_J}\right) + \left(\frac{J-\mu_J}{\sigma_J}\right)^2\right]\right\} \tag{6}$$

The nonsymmetry of the log normal distribution is introduced via a logarithmic transformation of the variables I and J. This transformation also introduces an exponential tail in the distribution function and is shown in Figure 1. The bivariate distribution function contains five parameters: means μ_I, μ_J and variances σ_I^2, σ_J^2 for the continuously distributed variables I, J, and a correlation coefficient ψ between variables I and J. Ideally, I and J would be two orthogonal variables and $\psi = 0$. In practice, however, measured properties for heavy fractions and coal liquids only include boiling points, specific gravities, and molecular weights, which are often highly correlated. In the absence of available data for orthogonal variables, therefore, we have chosen I and J as follows:

$$I = \ln(TB - TBO) \tag{7}$$

$$J = \ln(SG - SGO) \tag{8}$$

where TB and SG are the boiling point and specific gravity and TBO, SGO fix the origin where $F[I, J] = 0$. Strictly, the quantity in brackets in Eq. 7 should be divided by unit temperature to make it dimensionless. For convenience, however, the (unit) denominator has been omitted. Note that $-\infty < I < \infty$, $-\infty < J < \infty$, and $SG > SGO$, $TB > TBO$; i.e., continuous variables I and J lead to continuous distributions of boiling points and specific gravities greater than TBO and SGO, respectively.

For the mixtures considered in this work, TBO and SGO were obtained from:

$$TBO = (TB_{LD} + TB_{FC})/2 \tag{9}$$

$$SGO = (SG_{LD} + SG_{FC})/2 \tag{10}$$

where subscripts LD and FC refer to "last discrete" and "first

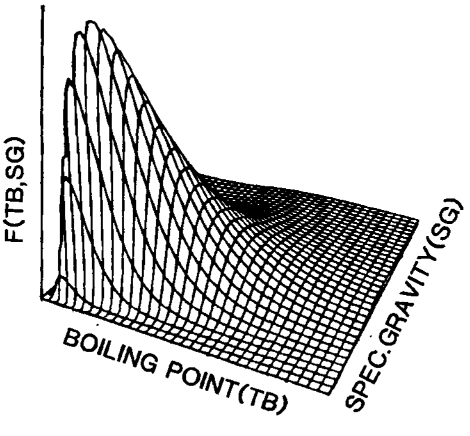

Figure 1. Bivariate log normal distribution function $F[TB, SG]$.

continuous," respectively. Thus, TB_{LD} corresponds to the boiling point of the heaviest component considered to be discrete and TB_{FC} corresponds to the boiling point of the first cut of the fraction considered to be continuous.

Given the molar composition–boiling point–specific gravity analysis of components i of the continuous fraction of any phase, then the distribution function parameters μ_I, μ_J, σ_I, and σ_J may be estimated using the maximum likelihood principle. Thus if we define

$$I_i = \ln(TB_i - TBO) \tag{11}$$

$$J_i = \ln(SG_i - SGO) \tag{12}$$

then the maximum likelihood estimates for the mean and variance are:

$$\mu_I = \sum_i^n z_i I_i \tag{13}$$

$$\mu_J = \sum_i^n z_i J_i \tag{14}$$

$$\sigma_I^2 = \frac{1}{n}\sum_i^n z_i(I_i - \mu_I)^2 \tag{15}$$

$$\sigma_J^2 = \frac{1}{n}\sum_i^n z_i(J_i - \mu_J)^2 \tag{16}$$

Here, n is the number of components considered to be in the continuous fraction and the mole fractions z_i of the components are first normalized using

$$z_i = z_i' \bigg/ \sum_i^n z_i' \tag{17}$$

where z_i' are the experimental mole fractions of the components (determined by boiling point analysis) that were assumed to constitute the continuous fraction of the mixture.

The correlation coefficient ψ is found from the relationship:

$$\psi = \frac{n\sum_i^n I_i J_i - \left(\sum_i^n I_i\right)\left(\sum_i^n J_i\right)}{\sqrt{\left[n\sum_i^n (I_i)^2 - \left(\sum_i^n I_i\right)^2\right]\left[n\sum_i^n (J_i)^2 - \left(\sum J_i\right)^2\right]}} \tag{18}$$

In a dew point calculation, the vapor phase mole fraction–boiling point–specific gravity compositional data are assumed to be available and the vapor phase distribution function parameters μ_I^v, μ_J^v, σ_I^v, σ_J^v, and ψ may be calculated using Eqs. 11–18. The liquid phase distribution function $F^L[I, J]$ is then obtained by solving the phase equilibrium relationships.

Fugacity coefficient relationships and dew point calculations

Given an equation of state and a distribution function, fugacity coefficients for discrete components and continuous fractions may be determined using partial and functional differentiation, respectively. The following relationships for the fugacity coefficient ϕ_i of discrete component i and $\phi[I, J]$ for the continuous fraction are due to Cotterman et al. (1985a).

$$RT\ln\phi_i = \int_V^\infty \left[\left(\frac{\partial P}{\partial n_i}\right)_{T,V,n_j} - \frac{RT}{V}\right] dV - RT\ln\left(\frac{PV}{n_i RT}\right) \tag{19}$$

$$RT\ln\phi[I, J] = \int_v^\infty \left[\left(\frac{\delta P}{\delta\eta F[I, J]}\right)_{T,V,I'=I,J'=J} - \frac{RT}{V}\right] dV - RT\ln\left(\frac{PV}{n_i RT}\right) \tag{20}$$

Phase equilibria may now be calculated using the equality of fugacity constraints, eqs. 4 and 5, and the method of moments as described below. In the calculation of dew points, the vapor phase quantities (y_i, η^v, μ_I^v, μ_J^v, σ_I^v, σ_J^v) and ψ are known or can be calculated. Liquid phase discrete compositions x_i may then be obtained by solving:

$$x_i = y_i\phi_i^v/\phi_i^L \tag{21}$$

and the parameters for the liquid phase distribution function (η^L, μ_I^L, μ_J^L, σ_I^L, σ_J^L) by solving the moment equations and the normalization relationship for the distribution function as follows:

$$\eta^L = \int_I\int_J f^v[I, J]/\phi^L[I, J]\,dI\,dJ \tag{22}$$

$$\mu_I^L = \int_I\int_J \{f^v[I, J]/\eta^L\phi^L[I, J]\}\,I\,dI\,dJ \tag{23}$$

$$\mu_J^L = \int_I\int_J \{f^v[I, J]/\eta^L\phi^L[I, J]\}\,J\,dI\,dJ \tag{24}$$

$$(\sigma_I^L)^2 = \int_I\int_J \{f^v[I, J]/\eta^L\phi^L[I, J]\}(I - \mu_I^L)^2\,dI\,dJ \tag{25}$$

$$(\sigma_J^L)^2 = \int_I\int_J \{f^v[I, J]/\eta^L\phi^L[I, J]\}(J - \mu_J^L)^2\,dI\,dJ \tag{26}$$

subject to:

$$\sum_i^k x_i + \eta^L\int_I\int_J F^L[I, J]\,dI\,dJ = 1 \tag{27}$$

Simplification to the case when the distribution function contains one variable is readily accomplished.

Equations 22–27 constitute a set of coupled nonlinear algebraic equations for the unknown liquid phase quantities in terms of the known vapor phase quantities. Note that solution of the equations requires integration of terms that contain the distribution function. In principle, this integration can be carried out analytically, although in practice this would be rather lengthy and the equations would be complex. An approximate analytical solution is possible if the equation of state constants are assumed *a priori* to be linear functions of the distribution variables, as was done by Cotterman et al. (1985a). However, this assumption did not appear to be valid in our case and the phase equilibrium equations were therefore solved by a 10-point Gauss-Legendre numerical integration procedure. Although this procedure is strictly valid for integration over a finite interval and the distribution function must be integrated over a semiinfinite interval, we have still preferred it over the more conventional Gauss-Laguerre form used by Cotterman et al for the following reasons:

1. The Gauss-Legendre technique avoids the problem of scaling of the quadrature points to the distributed variables, which is required in the Gauss-Laguerre technique.
2. An examination of experimental data reveals that the tail of the distribution function declines very rapidly and the area under the curve can be neglected when the value of the function has declined to less than 10^{-8}. A finite integration interval can therefore readily be chosen.

A number of quadrature schemes were also examined in this work. It was found that as the number of quadrature points increased beyond five, the results remained essentially constant. The very conservative 10-point quadrature technique was therefore used.

Equation of State Considerations

In principle, any equation of state applicable to both the vapor and liquid phases may be used to obtain the fugacity coefficients via Eqs. 19 and 20. In practice, however, it is probably best to use a simple (i.e., cubic) equation because of the complexity of the relationships. In addition, the use of a bivariate distribution function with the boiling point and specific gravity as the distribution variables requires that the equation of state give good fits of both vapor pressures (i.e., boiling points) and liquid densities (i.e., specific gravities) of the pure components. None of the popular cubic equations such as the Redlich-Kwong-Soave and the Peng-Robinson equations are able to do this for heavy components. We therefore chose the cubic equation of Patel and Teja (1982), which overcomes these limitations of the popular cubics.

The Patel-Teja equation is given by:

$$P = \frac{RT}{V - b} - \frac{a[T]}{V(V + b) + c(V - b)} \tag{28}$$

where a, b, c are given by:

$$a[T] = \Omega_a(R^2 T_c^2/P_c)\,\alpha[T_R] \tag{29}$$

$$b = \Omega_b(RT_c/P_c) \tag{30}$$

$$c = \Omega_c(RT_c/P_c) \tag{31}$$

$$\zeta_c = P_c V_c/RT_c \tag{32}$$

$$\Omega_c = 1 - 3\zeta_c \tag{33}$$

$$\Omega_a = 3\zeta_c^2 + 3(1 - 2\zeta_c)\Omega_b + \Omega_b^2 + (1 - 3\zeta_c) \tag{34}$$

and Ω_b is the smallest positive root of the cubic

$$\Omega_b^3 + (2 - 3\zeta_c)\Omega_b^2 + 3\zeta_c^2\Omega_b - \zeta_c^3 = 0 \tag{35}$$

Finally, $\alpha[T_R]$ is obtained from the relationship

$$\alpha[T_R] = [1 + F(1 - T_R)^{1/2}]^2 \tag{36}$$

The equation of state therefore requires a knowledge of four characterization constants, T_c, P_c, ζ_c, and F, for any fluid of interest. In general, ζ_c is not equal to the experimental value of P_cV_c/RT_c but is obtained from one or more liquid density data points, and F is obtained from the vapor pressure of the pure fluids. The equation of state is thus able to reproduce experimental vapor pressures and liquid densities of pure fluids. Specific correlations of ζ_c and F as functions of acentric factor or normal boiling point have been presented by Patel and Teja (1982) for nonpolar fluids and by Georgeton et al. (1985) for several classes of polar fluids. Additional correlations are presented below.

Table 1. Constants of Eqs. 37 and 38

Coefficient Group	PNA Liquids	Aromatic Oil	Coal Liquids
a_0	0.2315	0.3119	0.2582
a_1	46.5926	−5.1327	20.8405
a_2	5.391×10^{-5}	−0.0707	−0.0598
a_3	−14.7867	38.3663	29.512
b_0	−1.0334	−1.9885	0.8478
b_1	5.9887×10^{-3}	0.00535	8.0426×10^{-4}
b_2	1.2123	1.7613	−0.9588
b_3	−0.0047	-3.254×10^{-3}	1.0396×10^{-3}

PNA: Paraffin, napthene, aromatic

Correlation of equation of state constants

Twu (1984) has recently presented correlations for the critical constants as functions of TB and SG for both petroleum and coal fluids. His correlations for T_c and P_c were used without any modification in our work.

The constants F and ζ_c for the gas condensates, absorber oils, and crude oils were obtained from a fit of the vapor pressures and liquid densities of the homologous n-alkane series (representative of the paraffinic content), n-alkyl cyclohexane series (representative of the napthenic content), and the n-alkyl benzene series (representative of the aromatic content of the fluids). This approach is similar to that adopted by Erbar (1977) and Robinson and Peng (1978) in extending the Redlich-Kwong-Soave and Peng-Robinson equations to crude oils. The following correlations with TB and SG were obtained:

$$\zeta_c = a_0 + a_1 TB + a_2/SG + a_3/(TB \cdot SG) \tag{37}$$

$$F = b_0 + b_1 TB + b_2 SG + b_3\, TB \cdot SG \tag{38}$$

The constants a_0–a_3, b_0–b_3 are given in Table 1. In addition, ζ_c and F for the n-alkane series were also correlated with TB so that comparisons could be made between methods using single

Table 2. Constants of Eqs. 37a and 38a

Coefficient Group	PNA Liquids	Aromatic Oil	Coal Liquids
c_0	0.1854	0.2830	0.3128
c_1	73.6952	−8.0891	−34.8137
c_2	−11435.436	10080.063	12619.71
d_0	−0.3678	2.6851	0.4767
d_1	2.494×10^{-3}	-7.532×10^{-4}	9.936×10^{-4}
d_2	106.412	−738.299	−57.574

PNA: Paraffin, napthene, aromatic.

Table 3. Binary Interaction Parameters ξ_{ij} for Discrete Light Components of Natural Gases and Crude Oils

	N_2	CO_2	C_1	C_2	C_3	iC_4	C_4	iC_5	C_5
N_2	1.000 1.000	—	—	—	—	—	—	—	—
CO_2	0.907 0.940	1.000 1.000	—	—	—	—	—	—	—
C_1	0.968 0.970	0.907 0.899	1.000 1.000	—	—	—	—	—	—
C_2	0.940 0.981	0.872 0.870	0.995 0.991	1.000 1.000					
C_3	0.926 0.984	0.872 0.868	0.996 0.987	0.996 0.998	1.000 1.000	—	—	—	—
iC_4	0.946 0.984	0.873 0.874	0.998 0.977	0.997 0.997	0.987 0.944	1.000 1.000	—	—	—
C_4	0.969 0.990	0.885 0.886	0.998 0.990	0.999 0.997	0.990 0.970	1.000 1.000	1.000 1.000	—	—
iC_5	0.989 1.000	0.875 0.849	1.010 0.980	1.001 0.998	0.994 0.980	1.000 1.000	1.000 1.000	1.000 1.000	—
C_5	1.000 1.000	0.865 0.849	1.010 0.999	1.000 0.998	1.000 0.979	1.000 1.000	1.000 1.000	1.000 1.000	1.000 1.000

In each pair, upper number is value calculated by Patel-Teja equation of state; lower number is value calculated by Soave-Redlich-Kwong equation of state.

and bivariate distribution functions. The resulting correlations are given by:

$$\zeta_c = c_0 + c_1/TB + c_2/TB^2 \tag{37a}$$

$$F = d_0 + d_1\, TB + d_2/TB \tag{38a}$$

The constants c_0–c_2 and d_0–d_2 are given in Table 2. Vapor pressure and liquid density data were obtained from American Petroleum Institute Project 44. Average errors obtained using the generalized correlations were of the order of 4% for vapor pressures and 3% for liquid densities. The use of only the *n*-alkane series to obtain c_0–c_2, d_0–d_2 is consistent with the assumption that use of a single variable distribution function implies paraffinic like behavior. It is also consistent with the Twu correlations for T_c and P_c, in which specification of only the boiling point leads to the critical properties of the *n*-alkanes.

Similar correlations were also obtained for F and ζ_c for aromatic oils using vapor pressure and liquid density data of aromatic compounds (when available). The constants are given in

Table 4. Binary Interaction Parameters ξ_{ij} for Discrete Components of Aromatic Oils and Coal Liquids

	H_2	C_1	C_6H_6	C_7H_8	nC_8	*p*-Xylene	*o*-Xylene	Mesi-Xylene	nC_{10}	Coal
H_2	1.000 1.000	—	—	—	—	—	—	—	—	—
C_1	0.74 1.039	1.000 1.000	—	—	—	—	—	—	—	—
C_6H_6	—	0.945 0.938	1.000 1.000	—	—	—	—	—	—	—
C_7H_8	—	0.937 0.935	0.989 0.985	1.000 1.000	—	—	—	—	—	—
nC_8	—	0.940 0.942	1.003 1.007	0.999 0.997	1.000 1.000	—	—	—	—	—
p-Xylene	—	0.938 0.937	0.999 0.999	1.004 1.003	1.000 0.993	1.000 1.000	—	—	—	—
o-Xylene	—	0.938 0.936	0.999 1.000	1.004 1.001	1.000 0.992	1.000 1.000	1.000 1.000	—	—	—
Mesi-tylene	—	0.948 0.951	1.000 1.000	1.000 1.000	1.000 1.000	1.000 1.000	1.000 1.000	1.000 1.000	—	—
nC_{10}	—	0.957 0.966	1.000 1.000	1.000 1.000	1.000 1.000	1.000 1.000	1.000 1.000	1.029 1.022	1.000 1.000	—
Coal	0.192 0.762	0.872 0.881	—	—	—	—	—	—	—	1.000 1.000

Values calculated as noted in Table 3.

Tables 1 and 2. In the case of aromatic oils, the Twu correlation for T_c, P_c cannot be used when only the boiling point is given. Separate correlations of T_c, P_c as functions of TB were therefore developed as follows for single-variable distribution function calculations:

$$T_c = 216.572 + 1.07198\,TB \tag{39}$$

$$P_c = \exp(2.1589 + 732.312/TB) \tag{40}$$

with T_c in K and P_c in bar (kPa = bar × 100).

Correlations for coal liquids were developed using the volatility data of Wilson et al. (1981) for six narrow-boiling coal liquid cuts and the liquid density correlation of Holder and Gray (1983). The constants are given in Tables 1 and 2. Once again, the critical property correlations of Twu can no longer be used when only TB is available for the coal liquids. For single-variable distribution function comparisons, therefore, we have developed the following correlations for coal fluids:

$$T_c = 144.348 + 1.1912\,TB \tag{41}$$

$$P_c = \exp(2.5013 + 523.924/TB) \tag{42}$$

with T_c in K and P_c in bar. The relationships presented above thus provide all the information necessary (T_c, P_c, F, and ζ_c) in the equation of state calculations.

Extension to mixtures

The Patel-Teja equation of state can be extended to mixtures using the following mixing rules for discrete components:

$$a_m = \sum_i \sum_j z_i z_j a_{ij} \tag{43}$$

$$b_m = \sum_i z_i b_i \tag{44}$$

$$C_m = \sum_i z_i c_i \tag{45}$$

and the combining rule:

$$a_{ij} = \xi_{ij}(a_{ii}\,a_{jj})^{1/2} \tag{46}$$

where the binary interaction parameter ξ_{ij} is usually obtained from experimental data.

For a semicontinuous mixture, Eqs. 43–46 must be replaced with:

$$a_m = \sum_i^k \sum_j^k z_i z_j a_{ij} + 2\eta \sum_i^k z_i \int_I \int_J \cdot F[I, J]\, a[i, IJ]\, dI\, dJ + \eta^2 \int_{I^+} \int_{J^+} \int_I \int_J F[I^+, J^+] \cdot F[I, J]\, a[I^+J^+, IJ]\, dI^+\, dJ^+\, dI\, dJ \tag{47}$$

$$b_m = \sum_i^k z_i b_i + \eta \int_I \int_J F[I, J]\, b[IJ]\, dI\, dJ \tag{48}$$

$$c_m = \sum_i^k z_i c_i + \eta \int_I \int_J F[I, J]\, c[IJ]\, dI\, dJ \tag{49}$$

Table 5. Discrete-Continuous Binary Interaction Parameters

	a_i	$b_i \times 10^4$
N_2-PNA*	0.6871 0.8790	10.340 3.286
CO_2-PNA	0.7799 0.8110	2.752 12.850
C_1-PNA	0.9166 0.9510	2.652 4.592
C_2-PNA	0.9315 0.9670	2.250 3.669
C_3-PNA	0.9042 0.9770	2.679 3.124
C_1-aromatic oil	1.3469 1.2990	−10.800 −31.900
C_1-coal liquids	1.3469 0.5329	−10.800 13.870
H_2-coal liquids	0.2423 0.8610	3.256 7.485

Values calculated as noted in Table 3. $\xi_{i,IJ} = a_i + b_i I$ where $I = TB$ for the Patel-Teja equation and $I = M$ for the Soave-Redlich-Kwong equation calculations.

*PNA: continuous fractions of natural gas condensates, absorber oils, and crude oils.

where a_{ij} represents the equation of state constant a for discrete-discrete interactions, $a[i, IJ]$ represents that for discrete-continuous interactions, and $a[I^+J^+, IJ]$ represents that for continuous-continuous interactions. The expressions relating T_c, P_c, F, and ζ_c with the boiling point ($I = TB$) and specific gravity

Table 6. Constants for Eq. 52 and Data References for Mixtures Studied

	a_i	b_j
Bergman et al. (1975)		
Natural Gas (NG) Condensate #67	−120.13	0.587
NG Cond. #25	−98.55	0.5348
NG Cond. #48	−83.09	0.4948
NG Cond. #38	−115.07	0.5722
NG Cond. #1	−97.39	0.5373
NG Cond. #78	−118.39	0.5774
NG Cond. #86	−90.58	0.5143
NG Cond. #65	−139.80	0.6376
NG Cond. #111	−127.04	0.6055
Wilson and Barton (1971)		
122 MW Aromatic Oil	−123.83	0.5868
113 MW Napthenic Oil	−79.65	0.4815
107 MW Paraffinic Oil	−105.44	0.5477
Ramanujam et al. (1985)		
Heavy Aromatic Oil	−78.76	0.4273
Hoffmann et al. (1953)		
Crude Oil	−196.42	0.7708
Pedersen et al. (1984)		
Crude Oil #5	−190.24	0.7447
Crude Oil #8	−188.17	0.7594
Crude Oil #9	−200.57	0.8195
Wilson et al. (1981)		
Coal Liquids	−176.75	0.6538

Table 7. Compositional Data for Bergman et al. (1975) Natural Gas #65 at 2.687 MPa

	Experimental		Calculated				
			DPT	CPT1	CPT2	DSRK	CSRK1
Component	y_i	x_i	x_i	x_i	x_i	x_i	x_i
N_2	0.96599	0.038	0.043	0.062	0.057	0.053	0.061
CO_2	0.40230	0.294	0.469	0.217	0.235	0.5213	0.606
C_1	93.08566	17.274	15.031	17.338	15.246	17.582	20.191
C_2	5.36007	8.056	7.512	7.793	8.856	8.230	9.757
C_3	0.16210	0.579	1.038	0.927	1.289	1.109	1.366
iC_4	0.00160	0.031	0.029	0.0242	0.028	0.0307	0.039
nC_4	0.00160	0.050	0.046	0.0366	0.044	0.0482	0.062
iC_5	0.00100	0.097	0.083	0.0637	0.082	0.0873	0.116
nC_5	0.00060	0.080	0.071	0.0528	0.071	0.0754	0.101
C_6	0.00230	0.727	0.748	—	—	0.9568	—
C_7	0.00785	13.522	12.526	—	—	13.1946	—
C_8	0.00726	39.515	30.763	—	—	29.2986	—
C_9	0.00152	15.276	22.983	—	—	20.988	—
C_{10}	0.00014	3.737	6.840	—	—	6.1713	—
C_{11}	0.00001	0.562	1.813	—	—	1.6985	—
C_{12}	0.0	0.158	—	—	—	—	—
C_{13}	0.0	0.004	—	—	—	—	—
Temp., K	—	246.48	251.46	259.17	248.4	253.15	246.4
η^L	—	0.74	0.76	0.74	0.74	0.73	0.68

($J = SG$) discussed earlier permit the determination of these constants.

Analogous to Eq. 42, a binary interaction parameter may also be introduced for interactions between light discrete components and continuous heavy components. Thus, we may write:

$$a[i, IJ] = \xi_{i,IJ} \sqrt{a_{ij}}\, a[IJ, IJ] \tag{50}$$

where $\xi_{i,IJ}$ is a binary discrete-continuous interaction parameter.

Binary interaction parameters for interactions between discrete light components and between discrete light and continuous heavy components were determined using literature data. The regressed values for both the Soave-Redlich-Kwong and Patel-Teja equations are presented in Tables 3–5. Continuous-continuous binary interaction parameters were assumed to be unity.

Molecular Weight Calculations

To convert molar volumes obtained from the equation of state to specific volumes for comparison with experimental data it proved necessary to calculate the molecular weight of each mixture. For a mixture of k discrete components, the molecular

Table 8. Compositional Data for Wilson and Barton (1971), 113 MW Napthenic Absorber Oil at 8.397 MPa

	Experimental		Calculated				
			DPT	CPT1	CPT2	DSRK	CSRK1
Component	y_i	x_i	x_i	x_i	x_i	x_i	x_i
N_2	0.479	0.061	0.067	0.083	0.080	0.079	0.097
CO_2	0.260	0.273	0.478	0.290	0.276	0.481	0.560
C_1	97.935	39.309	36.789	40.276	39.399	41.493	49.531
C_2	1.188	2.693	2.198	2.801	2.671	2.339	2.738
C_3	0.018	0.115	0.097	0.122	0.115	0.102	0.119
iC_4	0.010	0.108	0.110	0.123	0.119	0.114	0.134
nC_4	0.007	0.126	0.111	0.129	0.123	0.113	0.131
iC_5	0.006	0.177	0.191	0.217	0.209	0.200	0.234
nC_5	0.003	0.132	0.124	0.147	0.139	0.131	0.152
C_6	0.006	0.692	0.469	—	—	0.560	—
C_7	0.018	4.301	3.864	—	—	3.756	—
C_8	0.049	27.901	30.203	—	—	28.319	—
C_9	0.020	22.498	22.325	—	—	19.989	—
C_{10}	0.001	1.119	2.972	—	—	2.6337	—
C_{11}	0.0	0.496	—	—	—	—	—
Temp., K	—	255.37	263.61	247.8	253.5	264.24	252.09
η^L	—	0.57	0.60	0.56	0.57	0.55	0.46

Table 9. Compositional Data for Ramanujam et al. (1985), Aromatic Oil at 5.617 MPa

	Experimental		Calculated			
			DPT	CPT1	CPT2	DSRK
Component	y_i	x_i	x_i	x_i	x_i	x_i
C_1	70.6	8.2	8.98	10.01	8.54	14.255
C_6H_6	19.5	40.3	41.99	41.14	44.15	40.238
$C_6H_6CH_2$	5.4	18.3	17.52	16.95	18.53	16.184
nC_8	0.08	0.30	0.271	0.278	0.277	0.2935
p-Xylene	1.9	9.2	9.24	8.89	9.75	8.258
o-Xylene	0.44	2.2	2.36	2.24	2.49	2.036
Mesitylene	0.19	1.3	1.40	1.33	1.47	1.1792
nC_{10}	1.5	10.9	9.68	9.84	9.90	10.947
Napthalene	0.39	6.2	6.59	—	—	4.748
1-Methylnapthalene	0.05	1.3	1.18	—	—	0.892
Biphenyl	0.01	0.51	0.30	—	—	0.202
Acenapthene	0.01	0.34	0.47	—	—	0.328
Fluorene	0.0	0.38	—	—	—	—
1-Phenyl napthalene	0.0	0.25	—	—	—	—
Phenanthrene	0.0	0.15	—	—	—	—
Fluoranthene	0.0	0.1	—	—	—	—
Chrysene	0.0	0.06	—	—	—	—
Temp. K	—	494.4	491.27	492.29	494.32	509.21
η^L	—	0.09	0.091	0.093	0.048	0.067

Table 10. Compositional Data for Hoffmann et al. (1953) Crude Oil at 3.359 MPa

	Experimental		Calculated				
			DPT	CPT1	CPT2	DSRK	CSRK1
Component	y_i	x_i	x_i	x_i	x_i	x_i	x_i
C_1	92.09	10.43	10.58	14.80	11.16	11.912	13.385
C_2	4.02	2.09	1.48	2.044	1.68	1.584	2.016
C_3	1.56	1.97	1.32	1.81	1.51	1.384	1.931
iC_4	0.35	0.75	0.55	0.67	0.58	0.557	0.830
nC_4	0.44	1.30	0.88	1.04	0.94	0.878	1.343
iC_5	0.14	0.65	0.51	0.61	0.55	0.5097	0.833
nC_5	0.20	1.15	0.88	1.03	0.96	0.8634	1.446
C_6	0.36	4.24	3.44	—	—	3.257	—
C_7	0.312	7.88	6.23	—	—	5.939	—
C_8	0.235	9.29	9.65	—	—	9.102	—
C_9	0.156	8.83	12.87	—	—	12.462	—
C_{10}	0.073	8.553	11.94	—	—	11.803	—
C_{11}	0.035	8.178	11.13	—	—	11.414	—
C_{12}	0.018	7.839	11.19	—	—	10.979	—
C_{13}	0.009	7.603	12.01	—	—	11.828	—
C_{14}	0.002	6.719	5.32	—	—	5.564	—
C_{15}	—	4.519	—	—	—	—	—
C_{16}	—	2.776	—	—	—	—	—
C_{17}	—	1.813	—	—	—	—	—
C_{18}	—	1.246	—	—	—	—	—
C_{19}	—	0.857	—	—	—	—	—
C_{20}	—	0.593	—	—	—	—	—
C_{21}	—	0.372	—	—	—	—	—
C_{22}	—	0.234	—	—	—	—	—
C_{23}	—	0.113	—	—	—	—	—
Temp., K	—	367.04	367.73	363.3	362.03	371.2	344.69
η^L	—	0.82	0.84	0.78	0.83	0.82	0.78

Table 11. Compositional Data for Wilson et al. (1981), Coal Liquid III at 13.1 MPa

	Experimental		Calculated		
			DPT	CPT1	DSRK
Component	y_i	x_i	x_i	x_i	x_i
H_2	81.19	12.24	9.52	7.17	13.267
CH_4	11.73	3.01	2.24	1.09	2.716
Coal	7.08	84.75	88.23	91.74	84.220
Temp., K	—	685.93	643.35	662.37	635.26
η^L	—	0.85	0.88	0.92	0.84

weight may be obtained from:

$$M_m = \sum_i^k z_i M_i \tag{51}$$

Molecular weights for heavy fractions were found to correlate well with the boiling point as follows

$$M[I] = a_j + b_j TB \tag{52}$$

where the constants a_j, b_j for the mixtures studied are given in Table 6. Thus, for a semicontinuous mixture, the molecular weight is given by:

$$M_m = \sum_i^k z_i M_i + \eta \int_I M[I] F[I] dI \tag{53}$$

Cotterman et al. (1985a, b) used the molecular weight as the distribution variable and therefore, whenever comparisons are made with their method, the mixture molecular weight is calculated using

$$M_m = \sum_i^k z_i M_i + \eta^L \overline{M} \tag{54}$$

where $\overline{M}$ is the mean molecular weight obtained from the liquid phase distribution function.

Results

The dew points of 40 multicomponent mixtures divided equally among natural gas condensates, absorber oils, crude oils, synthetic aromatic heavy oils, and coal liquids were calculated in this study. The mixtures are identified and the data references are given in Table 6. Five different methods of calculation were used and the results compared. The five methods and their identifying abbreviations are:

1. Semicontinuous thermodynamics method using the Patel-Teja equation and a bivariate distribution function with *TB* and *SG* as the distributed variables (CPT2).
2. Semicontinuous thermodynamic method using the Patel-Teja equation and a single variable distribution function with *TB* as the distributed variable (CPT1).
3. Semicontinuous thermodynamic method using the Redlich-Kwong-Soave equation of state and a single-variable distribution function with the molecular weight as the distributed variable (CRKS1). This method was proposed by Cotterman et al., and their correlations for the equation of state constants as functions of the molecular weight were used in our comparisons. In most cases, paraffin ensemble values reported by Cotterman et al. (1985b) were used by us as it was not possible to determine the relative amounts of paraffins, napthenes, and aromatics in the heavy fractions considered in this study.
4. Discrete thermodynamic method using the Patel-Teja equation of state (DPT).
5. Discrete thermodynamic method using the Soave-Redlich-Kwong equation of state (DSRK).

Detailed results for five typical mixtures are given in Tables 7–11 where experimental data are tabulated along with calculated liquid phase compositions, temperatures, and heavy fraction amounts. As can be seen in the tables, the CSRK1 method did not converge for the heavy aromatic oils and coal liquids. This is not surprising since highly aromatic fluids are appreciably different from the type of fluids correlated by Cotterman et al. The experimental phase equilibrium data on coal liquids (Wilson et al., 1981) were reported on a *weight fraction* vaporized basis and were converted to a molar basis using the reported molecular weights. In addition, a boiling point vs. cumulative wt. % distilled curve was also reported for the coal liquids. The curve was numerically differentiated and converted to a molar basis so that a distribution function could then be fitted to the data. As no specific gravity data were reported for these coal liquids, calculations were only performed using the CPT1, CSRK1, DPT, and DSRK methods. A summary of the results for the 40 mixtures studied is given in Table 12 and an overall summary for the five classes of fluids is presented in Table 13. Experimental liquid densities were available for 13 of the mixtures; error summaries for these are presented in Table 14.

Tables 10–13 show that the CPT1 and CPT2 methods are comparable in their ability to predict dew point temperatures, with the CPT1 method giving overall average absolute deviations (OAAD) of 3.1% and the CPT2 method giving 3.6% for the 40 mixtures studied. The CSRK1 method leads to an OAAD of 5.1%. However, no convergence was obtained using this method for 18 highly aromatic mixtures even when the aromatic ensemble values of the constants were used from Cotterman et al. All three methods generally underpredict the dew point temperature and the amount of the heavy fraction.

The CPT1 and CPT2 methods also yield good predictions of liquid densities, with OAAD's of 5.1 and 2.5%, respectively, as shown in Table 14. In contrast the CSRK1 method gives an OAAD of 28.1%. This is not surprising, since the limitations of the Soave-Redlich-Kwong equation for density predictions are well known.

Although not shown in these tables, the DPT and DSRK methods led to dew point temperatures that were too low by 5–10% and liquid densities that were too low by 15–20%, with the DPT method deviations being the lower of the two values in each case.

Discussion

The two semicontinuous methods (CPT1 and CPT2) employing the Patel-Teja equation of state were, in general, found to be superior to the discrete methods (DPT, DSRK) and to the semicontinuous method of Cotterman et al. (CSRK1) for the prediction of dew point temperatures and liquid phase densities of a

Table 12. Calculated and Experimental Dew Point Temperature and Heavy Fraction Compositions

				Calculated					
	Experimental			CPT1		CPT2		CSRK1	
System	Pres. MPa	Temp. K	η^L	Temp. K	η^L	Temp. K	η^L	Temp. K	η^L
Gas Condensates									
Bergman et al. (1975)									
National Gas (NG) Condensate #67	2.015	259.8	0.83	272.1	0.83	253.8	0.81	254.4	0.75
NG Cond. #25	4.131	277.6	0.69	284.9	0.77	259.2	0.73	251.2	0.45
NG Cond. #48	1.008	265.9	0.51	266.0	0.51	262.6	0.47	262.4	0.41
NG Cond. #38	3.359	260.9	0.75	272.9	0.75	250.2	0.68	245.9	0.61
NG Cond. #1	2.015	265.9	0.81	271.7	0.81	249.3	0.73	251.4	0.71
NG Cond. #78	5.374	249.8	0.65	255.4	0.65	236.4	0.49	241.6	0.52
NG Cond. #86	4.702	259.8	0.72	264.1	0.71	249.9	0.58	253.5	0.59
NG Cond. #65	2.687	246.5	0.74	259.4	0.74	248.4	0.74	246.4	0.68
NG Cond. #111	3.359	264.8	0.14	265.9	0.14	265.9	0.14	269.2	0.15
Absorber Oils									
Wilson and Barton (1971)									
122 MW Arom. Oil	8.397	233.5	0.38	222.19	0.38	214.8	0.14	†	—
122 MW Arom. Oil	10.07	233.5	0.14	207.4	0.17	207.4	0.17	†	—
122 MW Arom. Oil	6.717	222.0	0.08	233.3	0.08	217.8	0.06	†	—
113 MW Napth. Oil	3.359	277.6	0.80	289.6	0.80	277.2	0.08	276.3	0.77
113 MW Napth. Oil	8.397	255.4	0.57	247.8	0.55	253.5	0.55	252.5	0.46
113 MW Napth. Oil	10.076	233.2	0.40	235.2	0.40	225.4	0.37	214.4	0.34
Wilson et al. (1968)									
103 MW Parafinnic Oil	10.076	277.6	0.51	255.4	0.50	276.4	0.62	270.1	0.42
103 MW Paraf. Oil	3.359	233.2	0.39	239.0	0.39	244.4	0.45	230.9	0.30
103 MW Paraf. Oil	6.717	255.4	0.36	257.1	0.36	251.6	0.33	252.8	0.30
Heavy Aromatic Oil									
Ramanujam et al. (1985)									
Heavy Arom. Oil	3.267	550	0.22	547.5	0.20	541.6	0.15	†	—
Heavy Arom. Oil	5.074	550	0.16	548.1	0.16	544.1	0.13	†	—
Heavy Arom. Oil	7.285	550	0.16	545.8	0.15	539.8	0.12	†	—
Heavy Arom. Oil	8.865	550	0.13	546.7	0.13	540.5	0.10	†	—
Heavy Arom. Oil	5.617	494.4	0.09	492.3	0.09	488.9	0.06	†	—
Heavy Arom. Oil	9.882	494.4	0.08	490.03	0.018	491.6	0.04	†	—
Heavy Arom. Oil	3.544	494.4	0.11	495.6	0.11	493.0	0.08	†	—
Crude Oils									
Hoffman et al. (1953)									
Crude Oil	3.359	367.04	0.82	367.84	0.82	362.03	0.83	344.69	0.70
Crude Oil	6.717	367.04	0.70	370.04	0.73	361.2	0.68	342.40	0.62
Crude Oil	10.076	367.04	0.61	357.7	0.65	354.3	0.63	339.57	0.51
Crude Oil	13.43	367.04	0.55	350.5	0.57	348.9	0.47	332.49	0.42
Pedersen et al. (1984)									
Crude Oil #5	18.20	387.6	—	361.5	0.52	352.3	0.36	328.4	0.35
Crude Oil #8	18.51	346.2	—	314.2	0.51	309.7	0.54	316.3	0.44
Crude Oil #9	20.42	346.2	—	304.7	0.54	299.2	0.57	301.5	0.43
Coal Liquids									
Wilson et al. (1981)									
Coal #I	10.076	644.26	0.88	628.94	0.88	Δ	—	†	—
Coal #I	16.12	644.26	0.82	638.6	0.82	Δ	—	†	—
Coal #I	13.10	727.6	0.80	714.6	0.80	Δ	—	†	—
Coal #II	13.10	685.9	0.84	672.8	0.91	Δ	—	†	—
Coal #II	13.10	727.6	0.84	724.7	0.90	Δ	—	†	—
Coal #III	13.10	644.26	0.86	638.3	0.93	Δ	—	†	—
Coal #III	13.10	727.59	0.90	755.46	0.90	Δ	—	†	—
Coal #III	13.10	685.93	0.85	662.37	0.92	Δ	—	†	—

†Indicates no convergence with CSRK1 method.

ΔCPT2 method could not be used on these mixtures as no specific gravity data were available.

‡Data not available.

Table 13. Overall Average Errors for Five Classes of Fluids

Class	No. of Mixtures	OAAD*, %		
		CPT1	CPT2	CSRK1
Gas condensates	9	2.64	3.43	3.50
Absorber oils	9	4.49	3.56	2.41**
Synthetic aromatic oil	7	0.56	1.08	†
Crude oil	7	5.15	6.36	9.52
Coal liquid	8	1.95	Δ	†
Total	40	3.11	3.59	5.11

*Overall average absolute derivation.

**No convergence obtained for 122 MW aromatic absorber oil of Wilson et al. (1971).

†Indicates no convergence with CSRK1 method.

ΔCPT2 method could not be used on these mixtures as no specific gravity data were available.

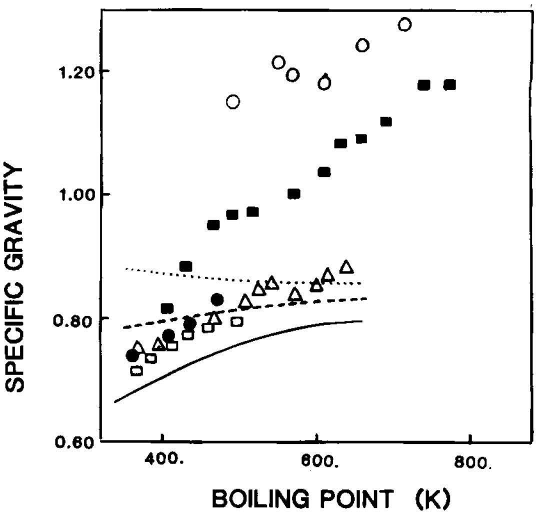

Figure 2. Specific gravity—boiling point relationships.

Table 14. Comparison of Liquid Densities, g/cm^3

System	Experimental			Calculated ρ^L		
	Pres. MPa	Temp. K	ρ^L	CPT1	CPT2	CSRK1
Bergman et al. (1975)						
Natural gas (NG) Condensate #67	2.015	259.8	0.7600	0.7438	0.7715	0.5442
NG Cond. #25	4.131	277.59	0.7048	0.7699	0.7255	0.4519
NG Cond. #48	1.007	265.93	0.6744	0.6705	0.6896	0.5481
NG Cond. #38	3.359	260.93	0.7434	0.6902	0.7307	0.5339
NG Cond. #1	2.015	265.93	0.7558	0.7987	0.8018	0.5549
NG Cond. #78	5.374	249.82	0.7493	0.6747	0.7186	0.5156
NG Cond. #86	4.702	259.82	0.6586	0.6654	0.6530	0.5322
NG Cond. #65	2.687	246.48	0.7337	0.6440	0.6715	0.5190
NG Cond. #111	3.359	264.81	0.5846	0.5781	0.5874	0.5036
Hoffman et al. (1953)						
Crude Oil	3.359	367.04	0.7209	0.7741	0.7313	0.4621
Crude Oil	6.717	367.04	0.7160	0.7319	0.7204	0.4543
Crude Oil	10.076	367.04	0.6753	0.6543	0.6319	0.4648
Crude Oil	13.434	367.04	0.6538	0.6257	0.6450	0.4560
*OAAD %	—	—	—	5.08	2.48	28.09

*Overall average absolute derivation.

wide variety of complex mixtures, including natural gas condensates, absorber oils, crude oils, heavy aromatic oils, and coal liquids. The method based on the bivariate distribution function (CPT2) is particularly good for the prediction of liquid densities. On the other hand, there is little difference between the CPT1 and CPT2 methods for the prediction of phase equilibria. This is probably due to the high degree of correlation between the two distributed variables *TB* and *SG*, chosen in our work, as shown in Figure 2. This choice was dictated by the available experimental information and it is likely that better results would have been obtained with the bivariate distribution method if orthogonal variables could have been chosen.

The use of the Cotterman et al. method (CSRK1) requires a knowledge of the relative amounts of paraffins, napthenes, and aromatics (PNA) in the heavy fraction in order to choose the correct constants for the equation of state. Although this may be possible in some cases, use of PNA correlations may sometimes lead to negative compositions (as discussed by Whitson, 1984, for the Peng-Robinson PNA correlation). Calculations using the method developed above show that the CPT2 method on the other hand can readily accommodate mixtures with varying PNA amounts.

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