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DEVELOPMENT OF A SELF-CONSISTENT THERMODYNAMIC-AND TRANSPORT-PROPERTY CORRELATION FRAMEWORK FOR THE COAL CONVERSION INDUSTRY-PHASE I

Semiannual Report for Period September 1, 1980—February 28, 1981

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U. S. DEPARTMENT OF ENERGY

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- A. Calculation of distillable coal fluid thermodynamic properties
using a multiparameter corresponding states correlation.
- B. The most general density-cubic equation of state: application
to pure non-polar fluids.

ABSTRACT

During the first half year of this research program the following elements of research have been performed: (1) the development of an improved pure component data bank, including collection and processing of data which is 70% complete as to substance, (2) calculation of distillable coal fluid thermodynamic properties using a multiparameter corresponding states correlation, (3) application of the most general density-cubic equation to pure fluids and (4) initiation of research to extend the corresponding states correlation framework to polar fluids. Primary conclusions of the first phase of this research program are that the three parameter corresponding states correlation predicts lighter coal fluid properties to a reasonable level of accuracy, and that a cubic equation can predict pure fluid thermodynamic properties on par with non-cubic equations of state.

1. Summary and overview.

During the first six months of this research program the major thrust has been to provide the industry with the state of the art non-polar and lightly polar distillable coal fluid thermodynamic properties correlation. This task has been completed. In order to build the basis for future research, an improved coal fluid based data bank is under development. Here, thermodynamic property data from several laboratories (Purdue University, Texas A&M, Colorado School of Mines, Rice University, etc.) and literature sources are being collected and entered in the original units of the author(s) publishing the data. In the search for a better vehicle in the corresponding states correlation framework, a simple but most general density-cubic equation of state was developed. The cubic equation predicts pure fluid thermodynamic properties including liquid densities and low temperature vapor pressures quite accurately and hence is superior to other cubic equations which are in use today.

2. Calculation of distillable coal fluid thermodynamic properties using a three parameter corresponding states correlation.

The use of petroleum correlations to estimate coal fluid properties without modification of the correlation characterization parameters may lead to potentially large errors in design due to the higher aromatic content of coal fluids. To provide the design engineer with a reliable design correlation, available thermodynamic property information on pure coal fluids and binary and multicomponent mixtures of light gases with coal fluids were used to estimate some of the characterization parameters

and unlike binary interaction parameters in a three parameter corresponding states correlation framework. The resultant correlation was applied to undefined coal fluid mixtures with reasonable success in properties prediction. The design correlation and the predictive capabilities for coal fluids are presented in detail in Appendix A.

3. Development of the most general density-cubic equation of state.

In the search for a better vehicle in the corresponding states correlation framework, a simple but most general density-cubic equation of state was developed. For pure non-polar and slightly polar fluids the equation of state is superior to the Peng-Robinson equation and is on par with BWR-type equations such as the three parameter corresponding states modified BWR equation presented in Appendix A. The equation of state can be easily extended to polar and associative fluids with adequate characterization. The development of the most general density-cubic equation and the predictions of pure fluid properties is discussed in Appendix B.

4. Conclusions and plans.

A three parameter corresponding states correlation has been applied successfully to predict thermodynamic properties of light coal systems. A simple but most general density-cubic equation of state has been developed as an alternate vehicle in the multiparameter corresponding states correlation framework. Ongoing research efforts are directed towards the extension of the corresponding states framework to polar fluids. Other ancillary research activities presently underway include the determination of corresponding states correlation parameters from both thermodynamic and transport properties data. It is envisioned at present that the use of molecular weight, specific gravity, boiling

temperature at a low pressure and a viscosity datum will provide a reasonable characterization of coal fluid fractions. The simultaneous use of pure fluid and mixture thermodynamic properties to develop multiparameter corresponding states parameter relations and mixing rules is also being studied.

APPENDIX A

CALCULATION OF DISTILLABLE-COAL-
FLUID THERMODYNAMIC PROPERTIES
USING A MULTIPARAMETER
CORRESPONDING-STATES CORRELATION

by

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January 30, 1981

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CALCULATION OF DISTILLABLE-COAL-FLUID THERMODYNAMIC PROPERTIES USING A MULTIPARAMETER CORRESPONDING-STATES CORRELATION¹

by

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ABSTRACT

A multiparameter corresponding-states correlation has been developed to describe fossil-fluid thermodynamic properties needed to design separation, heat-exchange, and other unit operations in coal-liquefaction plants. Three equation-of-state parameters, a molecular-size/separation parameter, a molecular-energy parameter, and a molecular-orientation parameter are used to characterize nonpolar and slightly polar aromatic hydrocarbons. A conformal-solution model is applied to predict thermodynamic properties and vapor/liquid equilibrium (VLE) of coal-related mixtures.

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SCOPE

The objective of this work was to develop first-generation methodologies for predicting thermodynamic properties of coal-derived fluids using current equation-of-state technology. Previously, most equations of state could not be applied directly to coal fluids. A corresponding-states framework has been modified to rapidly develop practical properties-prediction capability for the coal demonstration-plant program.

The three-parameter corresponding-states correlation presented herein is shown to accurately describe the thermodynamic behavior of a number of pure coal fluids and mixtures for which the mixture constituents are known (so-called defined mixtures).

Characterization techniques are outlined for converting analyses of undefined mixtures (with composition available in terms of broad fractions) into representative pseudocomponents. Empirical correlations have been developed to estimate pseudocomponent characterization parameters and ideal-gas thermodynamic properties for use with the equation of state.

CONCLUSIONS AND SIGNIFICANCE

Multiparameter corresponding-states (MPCS) correlation of coal-fluid thermodynamic properties has been demonstrated. A three-parameter corresponding-states correlation, based on perturbation theory (Pople 1954, Pitzer *et al* 1955, Starling *et al* 1978) can be applied to predict the thermodynamic properties of pure coal chemicals (Brulé *et al* 1979). Less accurate estimates are obtained for polar compounds. In most cases, results are sufficiently accurate to carry out constructive process design.

A conformal-solution model (CSM) (Leland *et al* 1968, Smith 1972, Lee *et al* 1979) is applied to describe the VLE behavior of many defined binary and ternary coal-solvent systems. Both the accuracy and computational speed of K-value predictions have been improved by implementing the CSM.

Finally, this MPCS correlation is able to reliably predict the density, enthalpy, and VLE of undefined distillable coal fluids. Pseudocomponent characterization parameters are estimated using empirical correlations which are functions of fraction average measurable properties such as normal boiling point and specific gravity. The degree of accuracy is apparently related to the amount of characterization data available.

MPCS METHODOLOGY

The corresponding-states method used in this work is based on the concept of conformality. A reduced property is said to be conformal with the same reduced property of a second fluid if the reduced-property values for the two fluids are nearly equal at equivalent reduced temperature and density (Pitzer *et al* 1955, Rowlinson and Watson 1969). The classical example of conformality is provided by the thermodynamic behavior of monatomic fluids. For example, the compressibility factor of argon is almost the same as that of krypton at equal values of reduced temperature, T^* , and reduced density, ρ^* .

$$Z(T^*, \rho^*)_{Ar} \cong Z(T^*, \rho^*)_{Kr} \quad (1)$$

Polyatomic-fluid compressibility factors are generally not conformal. However, the compressibility factors (and other reduced properties) of many nonpolar, polyatomic fluids can be correlated using the expression,

$$Z(T^*, \rho^*) = Z_0(T^*, \rho^*) + \omega Z_\omega(T^*, \rho^*) \quad (2)$$

where ω is Pitzer's acentric factor (Pitzer *et al* 1955, Pitzer 1977). In eqn (2), Z_0 and Z_ω are universal functions of T^* and ρ^* ; i.e., Z_0 and Z_ω are conformal for many nonpolar, polyatomic fluids.

For polar, polyatomic fluids, compressibility factors can be correlated using the relation,

$$Z(T^*, \rho^*) = Z_0(T^*, \rho^*) + \omega Z_\omega(T^*, \rho^*) + \mu^{*4} Z_\mu(T^*, \rho^*) \quad (3)$$

where μ^* is the reduced dipole moment. Other polarity parameters, such as Stiel's polarity factor (Halm and Stiel 1971), can also be used. In eqn (3), Z_0 , Z_ω , and Z_μ are universal functions of (T^*, ρ^*) and therefore are conformal. Expansion of eqn (3) with the use of higher-order terms in ω and μ^* , as well as other corresponding-states characterization parameters, allows thermodynamic-properties correlation for fluids with virtually any intermolecular effects (e.g., London dispersion forces, dipoles, quadrupoles, octupoles, etc...). For fluids with mild dipole moments (~ 2 D), and other effects in addition to those due to molecular shape and size, a convenient three-parameter approximation is possible:

$$Z(T^*, \rho^*) = Z_0(T^*, \rho^*) + \gamma Z_\omega(T^*, \rho^*) \quad (4)$$

where γ is an orientation parameter, similar to acentric factor but including other nonideal intermolecular effects such as weak steric and multipole anisotropies (Lee *et al* 1977, Starling *et al* 1978). Although relations of the type presented in eqns (2) and (3) can be derived from theoretical arguments (e.g., Gubbins *et al* 1977), herein theory is used merely to provide a framework and starting

point for the MPCs correlation of fluid thermodynamic behavior. In fact, an alternate, more empirical and usually simpler approach to MPCs correlation is to consider that reduced thermodynamic properties can be expressed by a generalized equation of state:

$$Z = Z(T^*, \rho^*, \{R\}, \{E\}) \quad (5)$$

where $\{E\}$ is a set of parameters, $E_1, E_2, \dots$, which are dependent on corresponding-states characterization parameters. The set $\{R\}$ comprises those characterization parameters used to reduce (and sometimes to further modify, e.g., Fisher and Leland 1970) T and ρ (or P),

$$\{R\} = (\epsilon, \sigma, \dots; \text{ or } T_c, P_c, \rho_c, \dots) \quad (6)$$

The set of equation-of-state parameters $\{E\}$ are generalized with respect to different fluids:

$$\{E\} = E_i(\{K\}, \{C\}) \quad (7)$$

One method to accomplish the generalization is to use a set of universal constants, $\{C\} = (a_i, b_i, c_i, \dots)$, to calculate equation-of-state parameters $\{E\}$ as generalized functions of fluid characteristic properties $\{K\} = (\gamma, \mu^*, Q^*, \dots)$. For example, E_i could be of the form corresponding to eqn (3),

$$E_i = a_i + \omega b_i + \mu^{*4} c_i \quad (8)$$

The selection of characterization parameters is usually made with some basis in theory. The intermolecular potential energy is considered herein to involve a molecular-energy parameter, ϵ , a molecular-size

parameter, σ , an orientation parameter, γ . Fluid conditions, T and ρ , can be reduced by isotropic-reference-fluid force constants, ϵ and σ , in the following manner:

$$T^* = kT/\epsilon \quad (9)$$

$$\rho^* = \rho\sigma^3 \quad (10)$$

The values of ϵ and σ can be estimated from critical properties when available,

$$\epsilon = kT_c/1.2593 \quad (11)$$

$$\sigma^3 = 0.3189/\rho_c \quad (12)$$

These approximations are based on the values of ϵ and σ for monatomic fluids when the Lennard-Jones (12-6) intermolecular-potential function is assumed to be the intermolecular potential. The parameters ϵ and σ are used to establish the isotropic contribution, Z_o , to the real-fluid compressibility, Z . The orientation parameter accounts for the anisotropic contribution, γZ_ω , to Z .

Casting the MPCs correlation in terms of molecular parameters, rather than the customary engineering parameters (e.g., T_c , ρ_c , P_c , etc. . .) has unique advantages. Both

thermodynamic and transport properties can be simultaneously and self-consistently correlated using the same characterization parameters, since all properties are interrelated on the molecular level (Starling *et al* 1978). Molecular parameters also prove useful for characterizing complex, high-molecular-weight hydrocarbons when critical properties used in conventional equations of state have not or cannot be measured (Brule *et al* 1979).

Equation of State for Thermodynamic Properties

The equation of state used in this study is a modified Benedict-Webb-Rubin (MBWR) equation (Starling 1973) cast with a conformational-solution model for mixture-properties prediction (Starling *et al* 1978). Actually, any equation of state can be cast into the MPCS framework presented herein. Likewise, the CSM can be applied for prediction of the properties of mixtures using any equation of state that has been cast in the MPCS framework. The MBWR was selected because of its proven capability in accurately predicting both liquid- and vapor-phase thermodynamic properties at relative reduced temperatures as low as $T_r = 0.3$ and relative reduced densities as high as $\rho_r = 3$ (Starling 1973). The CSM was implemented to improve the accuracy and speed of VLE predictions over most previous BWR formulations (*e.g.*, Han and Starling 1972). Thus, one correlation can be used to predict not only VLE for separation-equipment design, but also the enthalpies for heat-exchanger rating and densities

for equipment sizing. Multiparameter corresponding states and conformal-solution model—MPCS and CSM—are generic methods used to build the framework. MBWR is a specific equation of state to which these general methods have been applied. The combined methodology is thus indicated as CSM-MPCS-MBWR to illustrate the different levels on which the correlation is formulated. Further, the terms 3PCS, 4PCS, etc... (three-parameter, four-parameter) can be used to specifically indicate how many MPCS parameters have been used to formulate the equation of state.

The MBWR equation is:

$$\begin{aligned}
 Z = 1 + \rho^* (E_1 - E_2 T^{*-1} - E_3 T^{*-3} + E_9 T^{*-4} - E_{11} T^{*-5}) \\
 + \rho^{*2} (E_5 - E_6 T^{*-1} - E_{10} T^{*-2}) + \rho^{*5} (E_7 T^{*-1} + E_{12} T^{*-2}) \quad (13) \\
 + E_8 \rho^{*2} T^{*-3} (1 + E_4 \rho^{*2}) \exp(-E_4 \rho^{*2})
 \end{aligned}$$

The use of the following relation for the coefficients E_i in eqn (13) corresponds to eqn (7) for nonpolar fluids and casts eqn (13) into the 3PCS form of eqn (4):

$$E_i = a_i + \gamma b_i \quad (14)$$

The values of the universal constants, a_i and b_i , are listed in Table 1. The orientation parameter γ was forced to be equal to the acentric factor ω when determining the values of a_i and b_i from multiproperty regression analysis

of experimental density, vapor pressure, and enthalpy data (Lin *et al* 1972) for the normal paraffins methane through decane (Starling *et al* 1978).

Use of eqn (13) allows the calculation of thermodynamic properties of a single-phase nonpolar or slightly polar fluid given the three characterization parameters, ϵ (or T_c), σ (or ρ_c), and γ for the fluid. This correlation has also been extended using a 4PCS formulation (eqn 3) to describe the thermodynamic behavior of a number of pure halocarbons, with dipole moments up to 2.3 debyes (Milani 1978).

Conformal-Solution Model

For mixtures, the conformal-solution formalism assumes that the mixture properties are the same as those of a hypothetical pure fluid characterized by parameters σ_x , ϵ_x , and γ_x . The following semiempirical mixing rules are used to obtain these three mixture characterization parameters as functions of composition (Lee *et al* 1979):

$$\sigma_x^{4.5} = \sum_{ij} x_i x_j \sigma_{ij}^{4.5} \quad (15)$$

$$\epsilon_x \sigma_x^{4.5} = \sum_{ij} x_i x_j \epsilon_{ij} \sigma_{ij}^{4.5} \quad (16)$$

$$\gamma_x \sigma_x^{3.5} = \sum_{ij} x_i x_j \gamma_{ij} \sigma_{ij}^{3.5} \quad (17)$$

The pair characterization parameters, σ_{ij} , ϵ_{ij} , and γ_{ij} , are functions of the pure-fluid characterization parameters σ , ϵ , and γ of components i and j , and are calculated using the following combining rules:

$$\sigma_{ij} = \xi_{ij} (\sigma_i \sigma_j)^{1/2} \quad (18)$$

$$\epsilon_{ij} = \zeta_{ij} (\epsilon_i \epsilon_j)^{1/2} \quad (19)$$

$$\gamma_{ij} = \frac{1}{2} (\gamma_i + \gamma_j) \quad (20)$$

The binary-interaction parameters (BIPs), ξ_{ij} and ζ_{ij} , essentially account for deviations from ideal-solution behavior. BIPs are normally determined from regression analysis of binary-mixture thermodynamic data or can be correlated in terms of mixture-component characteristics (e.g., see Table 7).

The density is calculated implicitly by solving eqn (13). Other thermodynamic properties can be derived by the classical thermodynamic relations (see, e.g., Reid *et al* 1977). The following is the expression, derived from eqn (13), for the enthalpy departure, $H - H^0$,

$$\begin{aligned} \frac{(H-H^0)}{R(\epsilon_x/k)} = & \rho^* [E_1 T^* - 2E_2 - 4E_3 T^{*-2} + 5E_9 T^{*-3} - 6E_{11} T^{*-4}] \\ & + \rho^{*2} [E_5 T^* - 1.5E_6 - 2E_{10} T^{*-1}] \\ & + 0.2\rho^{*5} [6E_7 + 7E_{12} T^{*-1}] \\ & + E_8 [3 - (3 + 0.5E_4 \rho^{*2} - E_4^2 \rho^{*4}) \exp(-E_4 \rho^{*2})] E_4^{-1} T^{*-2} \end{aligned} \quad (21)$$

where H is the enthalpy of the fluid and H^0 is the ideal-gas-state enthalpy of the fluid at the system temperature. The ideal-gas enthalpy must be calculated to obtain the enthalpy. The expression for the entropy departure, $S - S^0$, is

$$\begin{aligned} \frac{(S - S^0)}{R} = & -\ln[\rho^*RT^*\epsilon_X/k\sigma_X^3] \\ & - \rho^*[E_1 + 2E_3T^{*-3} - 3E_9T^{*-4} + 4E_{11}T^{*-5}] \\ & - 0.5\rho^{*2}[E_5 + E_{10}T^{*-2}] + 0.2E_{12}\rho^{*5}T^{*-2} \\ & + 2E_8[1 - (1 + 0.5E_4\rho^{*2})\exp(-E_4\rho^{*2})]E_4^{-1}T^{*-3} \end{aligned} \quad (22)$$

where S is the entropy of the fluid and S^0 is the ideal-gas entropy of the fluid at system temperature and unit pressure (1 atm, 1 kPa, etc ...).

The fugacity, $\hat{f}_i$, of the i th component in a mixture is

$$\begin{aligned} \ln\left(\frac{\hat{f}_i}{x_i f_i^0}\right) = & (1 + \bar{V}_i) \frac{H-H^0}{RT} - \frac{S-S^0}{R} + (\bar{R}_i - \bar{V}_i)(Z - 1) \\ & + \rho^*[\bar{E}_{1,i} - \bar{E}_{2,i}T^{*-1} - \bar{E}_{3,i}T^{*-3} + \bar{E}_{9,i}T^{*-4} - \bar{E}_{11,i}T^{*-5}] \\ & + \frac{\rho^{*2}}{2}[\bar{E}_{5,i} - \bar{E}_{6,i}T^{*-1} - \bar{E}_{10,i}T^{*-2}] + \frac{\rho^{*5}}{5}(\bar{E}_{7,i}T^{*-1} + \bar{E}_{12,i}T^{*-2}) \\ & + \bar{E}_{8,i}T^{*-3}[1 - e^{-E_4\rho^{*2}}] - \frac{1}{2}E_4\rho^{*2}e^{-E_4\rho^{*2}}/E_4 \end{aligned} \quad (23)$$

where f_i^0 is the standard-state reference fugacity, taken to be unity.

The derivatives in eqn (23) are

$$\begin{aligned}\bar{E}_{j,i} &\equiv \left. \frac{\partial E_j}{\partial n_i} \right|_{T,V,n_{k \neq i}} \\ &= b_j \gamma_x \left[2 \left(\frac{\sum_m x_m \gamma_{mi} \sigma_{mi}^{3.5}}{\gamma_x \sigma_x^{3.5}} - 1 \right) - \frac{3.5}{3} \bar{R}_i \right]\end{aligned}\quad (24)$$

$$\begin{aligned}\bar{R}_i &\equiv \left. \frac{1}{\sigma^3} \frac{\partial \sigma^3}{\partial n_i} \right|_{T,V,n_{k \neq i}} \\ &= \frac{6}{4.5} \left[\frac{\sum_m x_m \sigma_{mi}^{4.5}}{\sigma_x^{4.5}} - 1 \right]\end{aligned}\quad (25)$$

$$\begin{aligned}\bar{V}_i &\equiv - \left. \frac{1}{T^*} \frac{\partial T^*}{\partial n_i} \right|_{T,V,n_{k \neq i}} \\ &= 2 \left[\frac{\sum_m x_m \epsilon_{mi} \sigma_{mi}^{4.5}}{\epsilon_x \sigma_x^{4.5}} - 1 \right] - \frac{4.5}{3} \bar{R}_i\end{aligned}\quad (26)$$

ESTIMATION OF THE THERMOPHYSICAL PROPERTIES OF DEFINED PURE AND MIXTURE HYDROCARBON FLUIDS

Application of any property correlation to pure coal chemicals and defined hydrocarbon mixtures is of limited practical use in coal-liquefaction-process design *per se*. However, properties calculations for known-component systems are necessary to develop and test correlations before applying them to undefined fluids.

For applying MPCS correlations to undefined coal fluids, average properties of pseudocomponent fractions making up the coal fluid are often used to estimate correlation parameters. Characterization correlations must be developed to relate these measurable properties to MPCS characterization parameters. One strategy for developing characterization correlations is to first develop a data set consisting of MPCS parameters (*e.g.*, critical temperature or pressure) *vs* measurable properties (*e.g.*, ASTM inspection data - such as average boiling point, specific gravity, *etc.*...) for selected pure and defined-mixture systems representative of those in coal liquefaction. Using this known-component-data base, generalized correlations can be developed for estimating MPCS characterization parameters from undefined-fraction inspection data. The development of the characterization-data base begins with establishing the capability of the correlation to predict pure-compound as well as defined-mixture properties.

Pure Coal Chemicals

To calculate the thermophysical properties of pure coal chemicals using the CSM-3PCS-MBWR correlation, critical temperature, critical molar density (or inversely, volume), and the orientation parameter are required. A list of characterization parameters for selected coal-related chemicals is given in Table 2. The light gases listed in Table 2 are some of those usually included in a material-balance slate for a coal-liquefaction plant. Table 2 also includes polycyclic aromatic hydrocarbons (PAHs) for which values of γ were determined using multiproperty analysis. For the PAHs and other coal chemicals shown, the cumulative average absolute deviation (%AARD as defined in Table 2)

is 1.83% for vapor pressure, 1.58% for density, and 2.33% for enthalpy departure. A more detailed compendium including other coal chemicals is also available (Brulé *et al* 1979).

Critical temperature and density for the light gases are experimental values. For heavier compounds with no critical data, T_c and ρ_c are estimated empirically, *e.g.*, Lydersen's method (Reid *et al* 1977). The orientation parameter can be determined via multiproperty analysis. A good estimate of γ can also be obtained using only one vapor-pressure datum, which can conveniently be the normal boiling point, the boiling point at 1333 Pa (10 mm Hg), or another reference vapor pressure. Sensitivity analysis rather than regression has to be used when dealing with only the one point. This technique is effective as shown in

Table 3. Using only a three-parameter formulation, some properties of highly polar and/or hydrogen-bonding compounds such as ammonia and water are not well predicted over an extended range of temperature and pressure (such as in the cryogenic region where many hydrogen and ammonia data are reported). For these problem fluids, the value of ω can usually be substituted for that of γ in order to make a calculation. Although densities for these compounds may be poorly predicted, other properties, such as vapor pressure are sufficient for making VLE or enthalpy calculations for coal fluids in which the concentrations of these components are relatively small and mostly in the vapor phase.

Defined Coal-Fluid Mixtures

The CSM-3PCS-MBWR has also been applied to predict the VLE behavior of many light-gas (hydrogen, methane, carbon dioxide, hydrogen sulfide, etc ...) + defined coal-solvent binary mixtures. Semiempirical mixing rules, *i.e.*, eqns (15) through (17) are used to characterize mixture-component interactions. These mixing rules are computationally efficient; the time requirement is about 15% more than that expended for the Redlich-Kwong-Soave equation of state when used to make a flash calculation for a 17-component mixture (Boston and Mathias 1980).

VLE data of systems involving light gases with model PCAHs typical of coal solvents were measured by Chao, Lin, and others at Purdue University (Chao *et al* 1980). Most of the

data fall in the temperature range 190° C to 430° C (374° F to 806° F) and pressures from 20 to 250 atm (294 to 3675 psia). The Purdue data represent most of the basis presently available for establishing VLE-prediction capability for distillable coal fluids. Systems of lighter components produced in coal liquefaction were measured in past investigations not directly connected with synfuels development. Many such investigations have been reported over the years; systems that might be accounted for when making a material balance for a coal-liquefaction plant were selected for study. Much of these data are in the cryogenic region, far removed from the extreme temperature- and pressure-operating conditions encountered in coal liquefaction. The data are nonetheless of great value in general equation-of-state development for fossil fuels.

Reduction of Phase-Equilibria Data

In correlating the VLE behavior of a binary mixture, the binary-interaction parameters (BIPs), ξ_{ij} and τ_{ij} , which are used to account for unlike-component interactions in the combining rules, eqns (18) through (20), are obtained from regression analysis of experimental VLE data. If available, both binary and ternary data should be used simultaneously in the data-reduction process to determine BIPs.

The generalized least-squares method developed by Britt and Luecke (1973) was used to determine BIPs for each binary pair in the mixture. This data-regression method, based on maximum-likelihood estimation, subjects all experimental measurements, including temperature and pressure, to random experimental errors. Consequently, the method provides more statistically meaningful parameters for the model to be fitted (Britt and Luecke 1973).

In the data-regression analysis of binary VLE mixture data, the BIPs obtained are those which minimize the maximum-likelihood objective function. This function represents the weighted sum of squares of the differences between the experimental data and the estimates of the true values of the variables predicted by the CSM-3PCS-MBWR correlation, subject to a set of phase-equilibrium constraints. The objective function is:

$$I = \sum_{i=1}^k \left[\frac{(T_i^m - T_i^0)^2}{\sigma_{T_i}^2} + \frac{(P_i^m - P_i^0)^2}{\sigma_{P_i}^2} + \frac{(x_{1i}^m - x_{1i}^0)^2}{\sigma_{x_{1i}}^2} + \frac{(y_{1i}^m - y_{1i}^0)^2}{\sigma_{y_{1i}}^2} + \frac{(K_{1i}^m - K_{1i}^0)^2}{\sigma_{K_{1i}}^2} + \frac{(K_{2i}^m - K_{2i}^0)^2}{\sigma_{K_{2i}}^2} \right] \quad (27)$$

where superscript m indicates a measured value, superscript o indicates an estimate of the true value of the variable, and subscript i denotes the ith data point. The σ^2 is the variance (measure of experimental error) of each variable, and the summation is over all k data points. The objective function, eqn (27), is minimized subject to the following phase-equilibrium constraints:

$$\hat{f}_i^V = \hat{f}_i^L \quad i = 1, 2 \quad (28)$$

Expressed explicitly,

$$y_1 \hat{\phi}_1^V(T, P, y_1, y_2) = x_1 \hat{\phi}_1^L(T, P, x_1, x_2) \quad (29)$$

$$y_2 \hat{\phi}_2^V(T, P, y_1, y_2) = x_2 \hat{\phi}_2^L(T, P, x_1, x_2) \quad (30)$$

The fugacity coefficients, $\hat{\phi}_i$, are calculated using eqn (23).

Table 4 summarizes the BIPs for all binary mixtures studied. The predicted results for binary systems of defined coal solvent with hydrogen, methane, carbon dioxide, and hydrogen sulfide are presented in Table 5; the overall %AARDs for K_1 are 6.16, 5.64, 3.37, and 3.64 respectively. Figures 1 through 4 provide a visual comparison of the experimental vs predicted K-values of light gases most typical of those dissolved in coal-liquefaction recycle solvents. Comparisons of the accuracy of VLE predictions for the CSM-3PCS-MBWR correlation and other methods are given in Table 6.

As was observed for the pure components, systems with appreciable amounts of ammonia and water, especially in the liquid phase, are very difficult to predict. For one, these systems are complicated by the formation of ionic solutions. Other problems also exist; e.g., hydrogen sulfide and ammonia readily react to form ammonium sulfide— an operational problem for heat exchangers in coal-liquefaction plants as well as a calculational problem when predicting properties for reacting components. Some correlations have evolved for predicting phase behavior for

aqueous ionic systems representative of refinery sour-water streams (see, e.g., API 1978). In this work, the BIPs for systems involving water have been determined over rather narrow ranges of temperature and pressure; these BIPs are found to be highly temperature dependent. The water systems studied were limited only to the vapor—liquid region; the more general problem also encompasses predicting phase behavior of water—hydrocarbon systems which exhibit liquid—liquid immiscibility. Valuable efforts to correlate this behavior have involved provisional equation-of-state modifications such as using different sets of BIPs for the different phases which may coexist in water—hydrocarbon systems (Watanasiri and Boston 1979, Erbar *et al* 1980). No attempt was made herein to pursue these approaches; future work will undoubtedly focus on extending rather than just modifying the correlation framework to handle these tough-to-predict systems.

Generalized Prediction of BIPs

The BIPs for hydrogen, methane, and carbon dioxide with heavy hydrocarbons (C_6 and heavier) have been generalized as functions of the critical molar volumes of each of the components making up the binary pair. The generalized correlations for the BIPs are summarized in Table 7. As expected, some deterioration in the accuracy of the predicted results is incurred when using the generalized BIPs, as shown in Table 8. BIPs for other light-gas plus heavy-hydrocarbon systems were not generalized since there are not enough data for these systems to carry out the generalization.

Application of the CSM-3PCS-MBWR equation to predict

the VLE behavior of defined multicomponent systems requires only the BIPs for each possible binary pair of components present in the multicomponent mixture. For unlike heavy-hydrocarbon + heavy-hydrocarbon pairs, the BIPs are taken to be unity.

VLE predictions were made for five ternary systems involving two light gases with a single PCAH. Two more systems made up of one light gas and two PCAHs were also studied. Results for all ternary systems are summarized in Table 9. Figures 5 and 6 show the experimental vs predicted K-values of the systems hydrogen + methane + tetralin and hydrogen + tetralin + diphenylmethane. The PCAH + PCAH BIPs were taken to be unity in these calculations. Prediction accuracy is commensurate with that obtained for the binaries.

A key system applicable to hydrotreater design, the hydrogen + methane + tetralin ternary is one of the most important studied by the Purdue group (Simnick *et al* 1980). As a special effort to achieve prediction accuracy, simultaneous regression of both binary and ternary data was undertaken. Data for hydrogen + methane, hydrogen + tetralin, methane + tetralin, and finally hydrogen + methane + tetralin were all used simultaneously in determining the BIPs for each of the possible combinatorial pairs. This approach allowed the development of parameters that satisfy the ternary-data set more than if only the binary pairs are used individually in the data-reduction process.

CORRELATION OF CORRESPONDING-STATES CHARACTERIZATION PARAMETERS WITH FRACTION AVERAGE MEASURABLE PROPERTIES

To obtain reliable estimates of MPCs characterization parameters for undefined, distillable coal-fluid fractions, correlations have been developed in the manner commonly practiced in dealing with petroleum fractions. Most established correlations for distillable fluids are based on petroleum hydrocarbons (e.g., Riazi and Daubert 1980, Sim and Daubert 1980). In order to be successful for coal fluids, these correlations must be re-evaluated and modified using a data base which includes PCAHs typical of coal fluids.

For most of the distillable coal chemicals for which data are available, the average normal boiling point T_b and specific gravity S are the typically reported inspection data (Lin *et al* 1980a,b,&c). Additional inspection data such as viscosity could potentially improve correlation accuracy; e.g., petroleum fluids and coal fluids with the same Watson characterization factor can have very different viscosities at ambient temperature and pressure. Average molecular weight M is apparently needed for characterizing high-molecular-weight fluids, as heavy-hydrocarbon S changes only slightly as M increases (however, *molar* density continues to decrease uniformly as M increases). M is also needed to distinguish between homocyclic and heterocyclic compounds; a heterocyclic with T_b about the same as that of a homocyclic can have a much lower M than the homocyclic.

Unfortunately, additional inspection data such as

viscosity and M have not generally been available, and thus, most of the empirical formulas presented herein express corresponding states parameters as functions of only T_b and S . These characterization correlations are based on data for more than 130 pure homocyclic aromatic hydrocarbons as well as NOS (nitrogen, oxygen, sulfur) heterocyclics. Using these correlations, estimates can be obtained for critical temperature T_c , critical molar volume V_c , and orientation parameter γ — the characterization parameters used for the 3PCS correlation presented herein. Note that these correlations are generally not applicable to nondistillables, which must be treated using different procedures (Brulé *et al* 1980).

Average Critical Temperature, Critical Volume, Orientation Parameter, and Molecular Weight

The equation used for many years in the petroleum industry (Cavett 1962) has been modified for predicting T_c of distillable coal-fluid fractions:

$$\begin{aligned}
 T_c = & 429.138 + 0.886861 T_b - 4.596433 \times 10^{-4} T_b^2 \\
 & - 2.410089 \times 10^{-3} \text{API} \times T_b + 1.630489 \times 10^{-7} T_b^3 \\
 & - 9.323778 \times 10^{-7} \text{API} \times T_b^2 - 1.430628 \times 10^{-8} \text{API}^2 \times T_b^2
 \end{aligned} \quad (31)$$

where T_c is in kelvins, $T_b = 1.8 T_b(^{\circ}\text{C}) + 32$ or $T_b = T_b(^{\circ}\text{F})$, and $\text{API} = 141.5/S - 131.5$. This correlation is based on $S @ 20/20^{\circ}\text{C}$ ($68/68^{\circ}\text{F}$) since most PCAH specific-gravity data

reported in the literature are usually for fluids at 20° C, rather than the U.S. customary reference temperature of 60°F (15.6°C). The difference between S for most aromatic hydrocarbons at the two reference temperatures is small, ca 0.3 %, and therefore can be neglected for most engineering calculations. The behavior of the correlation for T_c vs T_b at different S is shown in Figure 7.

Hall and Yarborough's correlation for V_c (1971) has been modified using a coal-PCAH data base:

$$V_c = 3.01514 M^{1.02247} S^{-0.054476} \quad (32)$$

where V_c is in cm^3/gmol . Figure 8 illustrates the trends using eqn (32) for V_c vs M , at different S . If M is not available, M can be estimated using eqn (34).

Estimates for γ can be obtained from

$$\begin{aligned} \gamma = & 333.333 + 151.244(T_c/T_b) - 519.841(T_b/T_c) \\ & + 38.9063(T_b/T_c)^4 + 1255.01 \log_{10}(T_b/T_c) \end{aligned} \quad (33)$$

where both T_b and T_c are in the same absolute units, i.e., in kelvins or degrees Rankine. Figure 9 gives a plot of γ vs the relative reduced normal boiling temperature $T_{br} = T_b/T_c$ generated from eqn (33).

The expression given by Kesler and Lee (1976) for

calculating M for petroleum fractions has been modified for coal fluids:

$$\begin{aligned}
 M = & -12421.7 + 9316.25 S + (7.753212 - 5.362614) T_b \\
 & + (1.0 - 0.753344 S - 0.0173543 S^2)(1.42072 \\
 & - 405.3994/T_b)(5.5556 \times 10^6/T_b) + (1.0 - 0.888972 S \\
 & + 0.118591 S^2)(1.66192 - 46.75250/T_b)(1.714678 \times 10^{14}/T_b^3)
 \end{aligned} \tag{34}$$

where T_b is in kelvins. Equation (34) has been used to generate a plot of M vs T_b , at different S , as shown in Figure 10.

Equations (31), (32), (33), and (34) have been successfully used to estimate the characterization parameters for distillable coal-fluid fractions in calculations of thermophysical properties. Caution should be exercised when extrapolating beyond a boiling temperature of about 350°C; little data were available for correlation development beyond this temperature.

Ideal-Gas Heat Capacity, Enthalpy, and Entropy

For calculating heat capacity, enthalpy, or entropy changes during a real process, the ideal-gas heat capacity is required. The Kesler-Lee correlation (Kesler and Lee 1976), which is designed to calculate the ideal-gas heat capacities for petroleum fluids, has been modified for distillable coal fluids. Most of the data used are from the API-44/TRC Data Project (1978). The expression for heat capacity, which serves as the base equation for deriving other ideal-gas properties, is

$$\begin{aligned}
C_p^0 = m_1 \{ & c_1 + c_2 K + (c_3 + c_4 K + c_5 K^2) T \\
& + c_6 T^2 + [c_7 (\frac{c_8}{K} - 1) (\frac{c_9}{K} - 1)]^2 \\
& \times [c_{10} + c_{11} S + (c_{12} + c_{13} S) T + (c_{14} + c_{15} S) T^2] \}
\end{aligned} \tag{35}$$

The ideal-gas enthalpy, $H_T^0 - H_0^0$, is obtained by integrating the ideal-gas heat capacity, eqn (35), over temperature:

$$\begin{aligned}
H_T^0 - H_0^0 = m_2 \{ & c_1 T + c_2 K T + (c_3 + c_4 K + c_5 K^2) T^2 / 2 \\
& + c_6 T^3 / 3 + [c_7 (\frac{c_8}{K} - 1) (\frac{c_9}{K} - 1)]^2 \\
& \times [(c_{10} + c_{11} S) T + (c_{12} + c_{13} S) T^2 / 2 + (c_{14} + c_{15} S) T^3 / 3] \}
\end{aligned} \tag{36}$$

where H_0^0 is the constant of integration. Note that the constant of integration cancels when making difference calculations between two state points of a process. For making isentropic-compression or -expansion calculations, the ideal-gas entropy is needed. Dividing eqn (35) by T and integrating yields the difference in the ideal-gas entropy at temperature T , S_T^0 , and the ideal-gas entropy at temperature T_{ref} , $S_{T_{ref}}^0$,

$$\begin{aligned}
S_T^0 - S_{T_{ref}}^0 = m_1 \{ & (c_1 + c_2 K) \ln \frac{T}{T_{ref}} + (c_3 + c_4 K + c_5 K^2) (T - T_{ref}) \\
& + c_6 (T^2 - T_{ref}^2) / 2 + [c_7 (\frac{c_8}{K} - 1) (\frac{c_9}{K} - 1)]^2 \\
& \times [(c_{10} + c_{11} S) \ln (\frac{T}{T_{ref}}) + (c_{12} + c_{13} S) (T - T_{ref}) \\
& + (c_{14} + c_{15} S) (T^2 - T_{ref}^2) / 2] \}
\end{aligned}
\tag{37}$$

In eqns (35), (36), and (37), K is the Watson characterization factor defined as $1.2164 T_b^{1/3} / S$, T_b and T are both in kelvins, $m_1 = 4.1868$ and $m_2 = 2.326$, and coefficients c_i are given in Table 10. Heat capacity and entropy are in $\text{kJ}/(\text{kg K})$; enthalpy is in kJ/kg . For U.S. customary units of $\text{Btu}/(\text{lb}_m \text{ } ^\circ\text{R})$ and Btu/lb_m , respectively, use $K = T_b^{1/3} / S$ and T_b and T in $^\circ\text{R}$, and set $m_1 = m_2 = 1$.

CALCULATION OF THE THERMODYNAMIC PROPERTIES OF UNDEFINED, DISTILLABLE COAL FLUIDS

Application of the 3 PCS thermodynamic correlation presented herein, to distillable coal fluids, requires the use of the characterization parameters for the undefined fluid. The characterization parameters, T_c , V_c , and γ , as well as M , can be estimated using eqns (31) through (34). For a given coal-fluid fraction, all the information required to estimate the parameters, i.e., T_b ,

S , and M , may not always be available. The following procedures are recommended for these cases:

When T_b , S , and M are available, use eqns (31), (32), and (33) to estimate T_c , V_c , and γ .

When only T_b and S are available, use eqn (34) to estimate M . Then use the estimated M and eqns (31), (32), and (33) to calculate T_c , V_c , and γ .

Depending on what inspection data are available, the coal fluid may be treated either as a single pseudocomponent or as a mixture. Generally more pseudocomponents need to be specified when calculating properties for multiphase systems rather than for bulk (single-phase) systems. When the T_b , S , and M for just the whole fluid are given, the fluid can be treated as a single pseudocomponent having characterization parameters estimated by using the procedures prescribed above. If the whole coal fluid is characterized by separating it into different TBP fractions, with inspection data for each fraction, the fluid can be treated as a mixture with each fraction represented as a pseudocomponent. Characterization parameters for each

pseudocomponent in the mixture are estimated by using the above prescribed procedures if T_b , S , and/or M are available. If S of each fraction is not available, but S of the whole fluid is given, use the whole-fluid S to calculate the M of each fraction using eqn (34); then estimate T_c , V_c , and γ from M and eqns (31), (32), and (33). The mole fraction of each pseudocomponent in the coal-fluid mixture can be estimated by various procedures depending on the available information:

If the weight percent (wt%) and M of each fraction are given, then

$$x_i = \frac{\text{wt}\%_i / M_i}{\sum_j (\text{wt}\%_j / M_j)} \quad (38)$$

If only the wt% of each fraction is available, but not M , use T_b and S to estimate M using eqn (34). Then calculate x_i per eqn (38).

If percent volume distilled, $v\%$, S , and T_b of each fraction distilled are given, which is the usual inspection data included in an ASTM-distillation analysis, use T_b and S to estimate M using eqn (34). Then the mole fraction, x_i , is calculated by

$$x_i = \frac{v\%_i S_i / M_i}{\sum_j (v\%_j S_j / M_j)} \quad (39)$$

If $v\%$ and T_b of each fraction and S of the whole fluid before analysis are given, use the whole-fluid S for all the fractions. The x_i can then be estimated by using eqn (39).

Coal-Liquid Density Prediction

The CSM-3PCS-MBWR has been used in conjunction with characterization equations (31) through (34) to predict the density of several coal liquids. The experimental data

reported were measured at conditions ranging from 21 to 454 °C and 6.8 to 218 atm (70 to 850 °F and 100 to 3200 psia) (Hwang et al 1980). The T_b and M for each liquid are given.

An approximate S was extrapolated from the density

data. Each coal fluid was treated as a single pseudocomponent (not as a mixture), with characterization parameters calculated using eqns (31), (32), and (33). The density predictions summarized in Table 11 are for 7 coal liquids without hydrogen and 6 liquids with hydrogen. The 6 systems of coal liquid + hydrogen were each treated as binary mixtures in equation-of-state calculations.

The good prediction results corroborate the previous assertion that bulk thermodynamic properties are not strongly dependent on the resolution of the coal fluid to pseudocomponents.

Prediction of Light-Gas Solubility in Coal Liquids

Chao and coworkers (1980) have reported the solubility of hydrogen and methane in two narrow-boiling distillate cuts from the Exxon Donor Solvent (EDS) process, and three narrow-boiling distillate cuts from the Solvent-Refined-Coal (SRC-II) process. The data were obtained at the bubble-point condition of the mixture (distillate

fraction with hydrogen or methane). Each boiling fraction is characterized by an average T_b , M , and S . This information is used to estimate T_c , V_c , and γ for each fraction. The coal-liquid fraction is treated as a binary mixture in flash calculations to predict the solubility of hydrogen or methane in the coal liquid. The BIPs for hydrogen or methane, with each fraction, are estimated from the generalized BIP correlations given in Table 7. Results of the solubility predictions are summarized in Table 12.

The predicted results are generally satisfactory, especially for the SRC-II fractions that have a narrow boiling-temperature range. Agreement between calculated and experimental values deteriorates as the boiling range for the fraction widens; such is the case for the EDS 260-316 °C (500-600 °F) fraction. This is probably due to a breakdown in the assumption that the pseudocomponent fraction has been narrowed down enough so as to approach the behavior of an individual compound.

Coal-Fluid Vapor/Liquid-Equilibrium Prediction

VLE data for full-range coal-fluid systems are extremely scarce in the open literature. One single VLE datum point was found— K-values of components in the overhead and bottoms streams from the hot separator following the reactor in the H-Coal pilot plant (IGT 1980). The system conditions are 433°C and 170 atm (812°F and 2500 psia). The K-values are reported in terms of 10 defined components including H_2 , C_1 - C_6 , H_2S , CO_2 , and water, and

also 10 undefined fractions boiling from 66 to 524 °C (150 to 975°F including about 17 wt% residuum. The measured inspection properties for the fractions are T_b , S , and M ; this information is needed to estimate the characterization parameters of each fraction by using eqns (31) through (33). Predicted K -values using the CSM-3PCS-MBWR are compared with the experimental data in Table 13. The BIPs for defined—defined binary pairs are those reported in Table 4. The BIPs for defined—undefined boiling fractions are calculated from the generalized BIP correlations given in Table 7. The BIPs for all remaining binary pairs were taken to be unity.

The accuracy of the predictions are good for some of the components (*e.g.*, hydrogen and methane)—not good for others. For the lighter undefined EDS and SRC-II liquids discussed above, results were quite good when the characterization equations were applied to these fluids. One reason is that the majority of these fluids are in the boiling-temperature and molecular-weight ranges over which the characterization correlations were developed. When the characterization equations are applied to heavier fractions, such as those present in this H-Coal system, prediction accuracy suffers. The presence of residuum certainly overextends the range of validity of the characterization correlations. Predicting properties of water also overstretches the limits of capability of a three-parameter corresponding-states correlation. As first discussed herein, the equation of state can be extended, within the MPCS framework, to handle polar and associative fluids such

as ammonia and water. But—only when more data are measured for heavier fluids can characterization correlations be developed for full-range coal fluids. The only substantive conclusion that can thus be drawn from this single VLE datum point is that more data are needed to aid in correlation development.

Coal-Fluid Enthalpy Prediction

Predicting the enthalpies of coal fluids is important as nearly forty percent of the coal-liquefaction-plant cost is attributed to heat-transfer equipment. Experimental enthalpy-difference data for 6 coal fluids are reported by Kidnay and Yesavage (1979). The data fall in the temperature range from 50 to 360 °C (120 to 680 °F) and pressures from 3.4 to 100 atm (50 to 1500 psia). Each coal fluid was fractionated into pseudocomponents by ASTM distillation. For most of these fluids, the °API of each whole coal fluid, before resolution to pseudocomponent fractions, is reported; however, S for each fraction is not (Kidnay and Yesavage 1979).

For those cases in which only the whole-coal-fluid S is available, each coal-fluid pseudocomponent fraction was assumed to have the same S as that of the whole coal fluid; this S was thus used to estimate pseudocomponent-characterization parameters via eqns (31) through (33). In addition, the mole fraction of each pseudocomponent is estimated using the procedures of eqns (38) and (39). The

BIPs for each binary pair of fractions are taken to be unity.

In the case of Western Kentucky Syncrude, S data were available for each pseudocomponent fraction. The coal fluid has a wide boiling range and an appreciable amount of nondistillable residuum; thus the S of each individual pseudocomponent fraction was used to determine the pseudocomponent-characterization parameters. The assumption can be made that a constant S for all fractions is valid for narrow-boiling fractions.

In addition to the characterization parameters, the prediction of enthalpy differences from MPCs correlations requires the use of the ideal-gas enthalpy for the coal-derived fluid; see eqn (36). The predicted enthalpy differences from the CSM-3PCS-MBWR equation of state with eqn (36) for ideal-gas enthalpies, well agree with experimental measurements as shown in Figures 11 and 12. For SRC-1 naphtha (from the SRC-1 pilot plant at Wilsonville AL), good agreement was obtained even in the two-phase region as shown in Figure 12. Comparison of estimates using other methods is given in Table 14 for six coal-derived fluids. The average absolute deviation (AAD defined in Table 14) of the predicted enthalpy differences from those from experiment is 8.9 kJ/kg (3.8 Btu/lb), while the AAD from other correlations are all more than 35 kJ/kg (15 Btu/lb). Figure 13 shows an SRC-1 naphtha enthalpy—temperature diagram generated from the CSM-3PCS-MBWR correlation.

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NOMENCLATURE

<u>Roman</u>	
API	$^{\circ}\text{API} = 141.5/S - 131.5$
C_p°	Heat capacity in ideal-gas state
E_i	Generalized ith equation-of-state parameter
a_i, b_i	Universal constants in expression for E_i
$\hat{f}_i, f_i^{\circ}$	Fugacity of component i, standard-state reference fugacity
$H - H^{\circ}$	Specific enthalpy departure of fluid
H°	Specific enthalpy of fluid in ideal-gas state, $H^{\circ} = H_T^{\circ} - H_0^{\circ}$
i, j	Subscript denoting binary pair
k	Boltzmann constant (1.38054×10^{-23} J/K)
K	Watson characterization factor
K_i	Equilibrium vaporization ratio y_i/x_i
M	Fraction average molecular weight
P	Absolute pressure
P_c	Critical pressure
P_s	Vapor pressure
Q^*	Reduced quadrupole moment
S	Specific gravity
$S - S^{\circ}$	Specific entropy departure of fluid
S°	Specific entropy of fluid in ideal-gas state, $S^{\circ} = S_T^{\circ} - S_0^{\circ}$
T	Absolute temperature
T^*	Reduced temperature, $T^* = kT/\epsilon$
T_b	Normal boiling temperature
T_{b_r}	Relative reduced normal boiling temperature, $T_{b_r} = T_b/T_c$
T_c	Critical temperature
T_r	Relative reduced temperature, $T_r = T/T_c$

$v\%$	Average volume percent distilled
V_c	Critical volume
x	Subscript denoting mixture
x_i	Liquid-phase mole fraction
y_i	Vapor-phase mole fraction
Z	Fluid compressibility factor
Z_o	Isotropic-reference-fluid compressibility factor
Z_ω	First-order perturbation contribution to compressibility factor

Greek

ϵ	Characteristic molecular-energy parameter
γ	Molecular orientation parameter
μ^*	Reduced dipole moment
ρ	Density
ρ_c	Critical density
ρ^*	Reduced number density, $\rho^* = \rho \sigma^3$
ρ_r	Relative reduced density, $\rho_r = \rho / \rho_c$
ω	Acentric factor
σ	Characteristic molecular-size parameter
ϵ_{ij}	Molecular-size binary-interaction parameter
τ_{ij}	Molecular-energy binary-interaction parameter
$\hat{\phi}_i$	Fugacity coefficient of component i
σ^2	Variance of experimental data

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Table 1. Universal constants a_i and b_i for obtaining parameters E_i for the CSM-3PCS-MBWR

$$E_i = a_i + \gamma b_i$$

i	a_i	b_i
1	1.45907	0.32872
2	4.98813	-2.64399
3	2.20704	11.3293
4	4.86121	0
5	4.59311	2.79979
6	5.06707	10.3901
7	11.4871	10.3730
8	9.22469	20.5388
9	0.094624	2.76010
10	1.48858	-3.11349
11	0.015273	0.18915
12	3.51486	0.94260

Table 2
Prediction of Thermodynamic Properties Using
Generalized 3PCS-MBWR Equation of State¹

Coal Chemicals		Characterization parameters ³					No. of Data pts	Range		SAARD	Data References
Emp form.	Fluid name	Mol wt	Crit temp T _c K	Crit vol V _c cm/mol	Orient. param γ	Prop.		Temp °C	Pres kPa		
H2	Hydrogen ²	2.016	32.95	64.14	0.	—	—	—	—	—	Yaws 1978
N2	Nitrogen	28.016	126.17	90.10	0.0263	P _S	19	-184~-147	200~3392	0.90	Canjar & Manning 1967
CH4	Methane	16.042	190.69	99.50	0.01289	H-H ^o	79	-184~-10	1379~17237	2.02	Douslin et al 1964 Vennix 1966 Yesavage 1968 Reid et al 1977
						P _S	30	-199~-82	1~4613	0.68	
						ρ	41	-148~350	889~16030	0.65	
						H-H ^o	35	-157~-10	1724~13789	1.34	
H2O	Water ⁴	18.015	647.3	56.0	0.344	—	—	—	—	—	—
CO	Carbon monoxide	28.011	132.89	93.04	0.04385	P _S	25	-203~-143	20~3039	1.52	Vargaftik 1975
H2S	Hydrogen sulfide	34.076	373.56	95.00	0.1092	ρ	40	-205~-143	20~3039	1.06	Reamer et al 1950
						P _S	24	-60~101	101~9004	0.72	
CO2	Carbon dioxide	44.01	304.17	94.00	0.2093	ρ	41	4~171	689~13789	1.85	Canjar & Manning 1967
						P _S	33	-56~29	517~7115	0.76	
						H-H ^o	41	-30~140	1517~31923	0.65	
CO2	Carbon dioxide	44.01	304.17	94.00	0.2093	ρ	39	-30~140	3041~50678	3.16	—
CO2	Carbon dioxide	44.01	304.17	94.00	0.2093	H-H ^o	39	-30~140	3041~50678	3.16	—
CO2	Carbon dioxide	44.01	304.17	94.00	0.2093	P _S	23	-103~106	2~6349	1.22	Robinson & Senturk 1979
CO2	Carbon dioxide	44.01	304.17	94.00	0.2093	P _S	37	16~283	8~4895	0.53	API-44/TRC Project
CO2	Carbon dioxide	44.01	304.17	94.00	0.2093	ρ	36	132~289	396~4923	3.75	Chao 1978
CO2	Carbon dioxide	44.01	304.17	94.00	0.2093	P _S	26	10~270	6~3565	0.72	API-44/TRC
CO2	Carbon dioxide	44.01	304.17	94.00	0.2093	ρ	9	10~80	6~99	0.16	—
CO2	Carbon dioxide	44.01	304.17	94.00	0.2093	H-H ^o	112	149~360	1379~9653	1.59	—
CO2	Carbon dioxide	44.01	304.17	94.00	0.2093	P _S	42	60~316	19~4068	1.45	Vargaftik 1975
CO2	Carbon dioxide	44.01	304.17	94.00	0.2093	ρ	23	0~110	1~99	0.91	API-44/TRC
CO2	Carbon dioxide	44.01	304.17	94.00	0.2093	H-H ^o	84	10~371	346~17237	3.03	—
CO2	Carbon dioxide	44.01	304.17	94.00	0.2093	P _S	20	100~432	2~4550	0.74	Kudchadker et al 1978a
CO2	Carbon dioxide	44.01	304.17	94.00	0.2093	ρ	25	58~433	0.1~4557	7.26	—
CO2	Carbon dioxide	44.01	304.17	94.00	0.2093	P _S	43	-68~258	0.004~2413	0.75	API-44/TRC
CO2	Carbon dioxide	44.01	304.17	94.00	0.2093	ρ	41	-68~238	101~21243	0.65	—
CO2	Carbon dioxide	44.01	304.17	94.00	0.2093	H-H ^o	16	267~374	545~16292	2.13	—
CO2	Carbon dioxide	44.01	304.17	94.00	0.2093	P _S	30	138~343	106~3516	1.53	API-44/TRC
CO2	Carbon dioxide	44.01	304.17	94.00	0.2093	ρ	59	20~275	100~40000	1.20	—
CO2	Carbon dioxide	44.01	304.17	94.00	0.2093	P _S	15	200~434	76~4400	4.04	Kudchadker et al 1978b
CO2	Carbon dioxide	44.01	304.17	94.00	0.2093	P _S	63	-57~293	0.002~2413	1.16	API-44/TRC
CO2	Carbon dioxide	44.01	304.17	94.00	0.2093	ρ	54	-57~266	101~1655	1.18	—
CO2	Carbon dioxide	44.01	304.17	94.00	0.2093	H-H ^o	66	24~316	1379~9653	3.17	—
CO2	Carbon dioxide	44.01	304.17	94.00	0.2093	P _S	29	158~357	19~1060	0.55	Kobayashi 1979
CO2	Carbon dioxide	44.01	304.17	94.00	0.2093	P _S	29	164~428	15~1979	1.16	Wilson et al 1979
CO2	Carbon dioxide	44.01	304.17	94.00	0.2093	ρ	9	100~240	1~107	0.46	Viswanath 1979
CO2	Carbon dioxide	44.01	304.17	94.00	0.2093	P _S	12	35~164	1~101	3.79	API-44/TRC
CO2	Carbon dioxide	44.01	304.17	94.00	0.2093	P _S	26	-49~179	0.001~207	1.46	API-44/TRC
CO2	Carbon dioxide	44.01	304.17	94.00	0.2093	P _S	17	199~371	3~1345	3.37	Kudchadker et al 1978d
CO2	Carbon dioxide	44.01	304.17	94.00	0.2093	ρ	18	218~316	106~586	4.95	—
CO2	Carbon dioxide	44.01	304.17	94.00	0.2093	P _S	22	93~446	3~3296	1.10	Kudchadker et al 1978c
CO2	Carbon dioxide	44.01	304.17	94.00	0.2093	ρ	20	94~400	3~3296	1.89	—
CO2	Carbon dioxide	44.01	304.17	94.00	0.2093	P _S	24	-29~204	0.001~207	0.77	API-44/TRC
CO2	Carbon dioxide	44.01	304.17	94.00	0.2093	ρ	32	38~238	1379~41368	1.09	—

Table 2 (continued)

Coal Chemicals		Characterization parameters					No. of Data pts	Range		%AARD	Data References
Emp form.	Fluid name	Mol wt	Crit temp T_c K	Crit vol V_c cm ³ /mol	Orient. param γ	Prop.		Temp °C	Pres kPa		
C11H10	1-Methylnaphthalene	142.202	772.22	445.91	0.3538	P _s	17	142~246	6~103	1.27	Boublik et al 1973
C12H9N	Carbazole	167.200	900.0	624.28	0.4650	P _s	33	253~358	9~108	3.98	Boublik et al 1973
C12H10	Acenaphthene	154.214	805.56	542.85	0.3759	P _s	11	147~288	3~125	1.70	Boublik et al 1973
C12H10	Biphenyl	154.214	788.89	503.45	0.3022	P _s	11	160~360	7~655	4.38	Vargaftik 1975
						ρ	11	180~360	14~655	1.36	
C12H22	Bicyclohexyl	166.31	731.4	576.97	0.4078	P _s	23	151~304	10~347	1.55	Kobayashi 1979
C13H9N	Acridine	179.211	905.56	542.85	0.4044	P _s	9	166~346	1~101	4.82	McNeill 1965
C13H10	Fluorene	166.225	822.22	594.55	0.4136	P _s	12	161~300	2~108	1.85	Boublik et al 1973
C13H12	Diphenylmethane	168.241	770.22	567.36	0.4358	P _s	30	152~374	4~670	1.17	Kobayashi 1979
C14H10	Phenanthrene	178.236	922.22	524.60	0.3299	P _s	51	199~382	3~200	0.80	Kudchadker et al 1978
						ρ	8	100~320	1~101	0.67	
C14H12	9,10-Dihydrophenanthrene ⁵	180.25	846.1	606.1	0.4181						
C16H10	Pyrene	202.258	938.33	657.14	0.5532	P _s	12	262~444	5~200	5.32	Kudchadker et al 1979
C16H10	Fluoranthene	202.258	979.44	594.55	0.3251	P _s	11	296~494	3~101	4.23	Boublik et al 1973
C16H14	1,2,3,4-Tetrahydrofluoranthene	206.3	954.4	625.5	0.3211	P _s	5	127~196	0.1~1.4	0.34	API-42 1942-1966
C16H34	n-Hexadecane	226.43	717.22	975.44	0.7122	P _s	10	190~280	7~88	0.29	Vargaftik 1975
						ρ	10	190~270	7~70	2.12	
C18H12	Triphenylene	228.296	1013.3	734.45	0.5176	P _s	13	296~494	5~200	4.78	API-42
C18H24	1,2,3,4,5,6,7,8,13,14,14,16-Dodecahydrochrysene	240.4	923.3	781.3	0.4795	P _s	5	149~217	0.1~1.4	0.61	API-42
C20H26	1,2,3,3a,4,5,6,7,8,9,9a,10,11,12-Tetradecahydroperylene	266.4	929.4	889.3	0.6591	P _s	5	184~252	0.1~1.4	1.66	API-42

$$^1 \%AARD = \frac{1}{N} \sum_{i=1}^N |(exp-calc)/exp| \times 100$$

² Parameters estimated for supercritical hydrogen corresponding to typical coal-liquefaction conditions.

³ Some of the compounds listed are components present in the VLE systems studied (see next section). Other coal chemicals shown are in addition to those previously reported by Brulé et al (1979).

⁴ Water exhibits hydrogen bonding and the correlation of water properties within a 3PCS framework is difficult over wide ranges of T and P. For making VLE calculations, γ has been assumed to be the same as ω .

⁵ No pure-fluid data were found with which to determine characterization parameters via multiproperty analysis, so the parameters have been estimated in order to make VLE calculations.

**Table 3. Comparison of Thermodynamic-Property-Prediction Results
Using Orientation Parameters from Vapor-Pressure Data Sets of Varying Sizes**

Orientation Parameter γ from:		P_S = Normal Boiling Point		P_S to 2 atm		P_S to critical		All Properties to Critical	
PCAHs	Properties	γ	% AARD	γ	% AARD	γ	% AARD	γ	% AARD
Toluene	P_S	0.2694	1.80	0.2664	1.44	0.2660	1.46	0.2665	1.45
	ρ		0.86		0.91		0.92		0.91
	H-H°		3.42		3.02		3.00		2.99
Tetralin	P_S	0.3222	1.18	0.3236	1.08	0.3230	1.11	0.3232	1.89
	ρ		1.94		1.99		2.02		1.10
o-Cresol	P_S	0.4401	2.08	0.4394	2.12	0.4417	2.04	0.4478	2.23
Anthracene	P_S	0.55	6.95	0.53	5.20	—	—	—	—
	ρ		3.82		4.03		—		—
Triphenylene	P_S	0.5174	4.85	0.5176	4.78	—	—	—	—

Table 4. Binary-Interaction Parameters for Defined Components¹

	H2	N2	CO	CO2	H2S	H2O	Methane
N2	1.02116 1.08378						
CO	1.10974 0.54651	1 1					
CO2	0.98438 1.39935	1.00715 1.08921	1 1				
H2S	1 1	1.01753 1.02279	1 1	1.01396 0.92472			
H2O	0.84649 1.35568	0.89680 1.30323	1 1	0.93949 1.07950	0.97389 1.08822		
Methane	1.12777 1.43874	1.03399 0.96381	1 1	0.98933 0.99122	1.00044 1.00066	0.74468 0.21272	
Ethane	1.04205 1.20040	1.01715 0.92233	1.01526 0.97647	1.15510 0.85965	0.99525 0.94637	1 1	0.99992 0.97959
Propane	1.06895 1.25144	1.03410 0.88779	1.04531 0.94447	1.04473 0.84856	1.06237 0.88593	1 1	1.01188 0.93684
n-Butane	1.07701 1.14592	1.07661 0.91347	1 1	1.05828 0.80422	(1.062) (0.86)	0.68169 0.25978	1.03002 0.89247
n-Pentane	(1.087) (1.069)	1 1	1 1	1.06222 0.77926	(1.062) (0.835)	1 1	1.03220 0.86098
Benzene	1.03604 0.85238	1.04793 0.84785	1 1	1.06120 0.81353	1 1	1 1	1.05562 0.93614
Cyclohexane	1.08337 0.96081	1 1	1 1	(1.033) (0.723)	1 1	1 1	1.04492 0.84716
n-Hexane	1.09412 0.99088	1 1	1 1	1.07725 0.76891	(1.063) (0.81)	1 1	1.05049 0.83257
Toluene	1.11066 1.31810	1 1	1 1	1.06900 0.78159	1.05001 0.85585	1 1	1.06344 0.89874

Table 4. (continued)

	H ₂	N ₂	CO	CO ₂	H ₂ S	H ₂ O	Methane
m-Cresol	1.04271 1.16955	1 1	1 1	1.06057 0.87031	1 1	1 1	1.04193 1.00440
n-Heptane	(1.106) (0.987)	1.05180 0.67961	1 1	1.08024 0.75104	1.06363 0.78620	1 1	1.06234 0.81665
m-Xylene	1.08272 0.89440	1 1	1 1	(1.060) (0.717)	1 1	1 1	1.07348 0.86740
n-Octane	(1.115) (0.983)	1 1	1 1	(1.094) (0.730)	(1.084) (0.776)	1 1	1.05112 0.75148
n-Nonane	(1.124) (0.979)	1 1	1 1	(1.097) (0.714)	1.10474 0.76698	1 1	1.07753 0.79909
Tetralin	1.11696 0.98839	1 1	1 1	1.09863 0.72025	1 1	1 1	1.08889 0.85009
n-Decane	1.13417 0.97546	1.09018 0.71972	1 1	1.11172 0.69768	(1.124) (0.758)	1 1	1.12205 0.85972
1-Methylnaphthalene	1.10596 0.95867	1 1	1 1	1.09054 0.71916	1 1	1 1	1.06982 0.82637
Bicyclohexyl	1.13437 0.90479	1 1	1 1	(1.109) (0.699)	1 1	1 1	(1.090) (0.757)
Diphenylmethane	1.12998 0.88391	1 1	1 1	1.10504 0.73801	1 1	1 1	1.08878 0.78261
Quinoline	1.07129 0.86521	1 1	1 1	1.07057 0.77029	1 1	1 1	1.05230 0.87391
Thianaphthene	1.10239 0.83601	1 1	1 1	(1.07) (0.715)	1 1	1 1	(1.072) (0.846)
9,10-Dihydrophenanthrene	1.13893 0.77175	1 1	1 1	(1.113) (0.696)	1 1	1 1	1.09443 0.72671
Phenanthrene	1.10910 0.45423	1 1	1.07806 0.59201	1.11066 0.65852	1 1	1 1	0.93799 0.41165
n-Hexadecane	1.16886 0.84807	1 1	1 1	1.15176 0.66138	1 1	1 1	1.13154 0.76822

¹ Parentheses indicate estimated values.

Table 5. Prediction of Phase-Equilibrium Behavior of Binary Mixtures Using the CSM-3PCS-MBWR

Systems	% AARD							Data References
	N	T Range K	P range atm	Liq Comp	Vap Comp	K-Value	K-Value	
				of 1st Cmpn x1	of 1st Cmpn y1	of 1st Cmpn K1	of 2nd Cmpn K2	
Hydrogen with:								
Nitrogen	11	90~95	8~45	1.35	0.28	1.59	0.65	Maimoni 1961
Carbon monoxide	22	273~323	34~136	5.72	2.81	9.55	7.39	Trust and Kurata 1971a
Carbon dioxide	38	220~290	11~200	5.35	4.54	7.82	9.23	Spano et al 1968
Water	9	366~589	14~109	31.40	5.67	35.20	7.60	DeVaney et al 1978
Methane	16	183	39~74	0.64	1.13	0.71	2.21	
Ethane	25	172~283	7~272	4.85	2.05	6.00	16.98	Cohen et al 1967
Propane	16	298~348	34~204	3.79	5.34	7.23	10.02	Trust and Kurata 1971a
n-Butane	60	338~394	11~170	3.84	3.18	5.80	7.27	Klink et al 1975
Benzene	20	339~433	5~680	3.04	0.61	2.80	5.07	Thompson and Edmister 1965
Cyclohexane	16	339~394	7~681	1.91	0.44	2.22	6.93	Thompson and Edmister 1965
n-Hexane	31	344~478	34~238	3.64	1.24	4.90	10.31	Nichols et al 1957
Toluene	25	462~575	20~250	4.03	2.01	5.74	7.32	Simnick et al 1978b
m-Xylene	27	462~582	20~251	2.76	1.83	4.41	8.11	Simnick et al 1979a
Tetralin	24	463~662	20~250	3.53	1.34	4.72	7.52	Simnick et al 1977
n-Decane	31	344~478	34~238	5.75	1.18	7.20	12.62	Sebastian et al 1980b
1-Methylnaphthalene	27	462~702	20~250	3.24	1.68	4.88	9.88	Yao et al 1977
Bicyclohexyl	28	462~702	20~250	6.63	1.90	8.30	10.34	Sebastian et al 1978a
Diphenylmethane	27	463~702	20~250	3.21	1.18	4.17	10.62	Simnick et al 1978a
9,10-Dihydrophenanthrene	28	462~703	19~252	3.50	0.18	3.53	7.61	Chao et al 1980
Phenanthrene	8	544~700	14~109	7.93	0.94	8.15	10.50	DeVaney et al 1978
n-Hexadecane	29	462~664	20~250	8.53	0.80	9.76	20.69	Chao et al 1980
Quinoline	27	462~702	20~250	4.22	0.69	5.01	4.90	Sebastian et al 1978b
m-Cresol	41	462~662	20~251	4.59	2.06	6.59	9.32	Simnick et al 1979a
Thianaphthene	27	461~703	20~250	4.93	0.91	5.11	4.44	Sebastian et al 1978c
Nitrogen with:								
Carbon dioxide	17	233~273	35~137	5.72	2.08	7.20	3.57	Zenner and Dana 1963
Water	11	323~373	25~200	31.52	5.73	-	-	Krichevsky and Kasarnovsky 1935
Methane	13	178~183	31~48	1.35	4.38	3.32	0.44	Stryjek et al 1974a
Ethane	19	172~194	7~120	5.51	2.05	5.31	13.86	Stryjek et al 1974b
Propane	10	248~273	14~136	2.43	1.15	2.82	6.05	
n-Butane	13	311~411	16~167	8.03	3.13	8.26	4.94	Roberts and McKetta 1962
Benzene	15	348~398	61~298	1.17	0.16	1.21	3.38	Miller and Dodge 1940
n-Heptane	8	353~455	69~240	7.85	1.08	7.74	25.07	Akers et al 1954
n-Decane	52	311~411	34~238	7.68	0.06	7.65	19.12	Azarnoosh and McKetta 1963

Table 5. (continued)

Systems	% AARD							Data References
	N	T Range K	P. range atm	Liq Comp	Vap Comp	K-Value	K-Value	
				of 1st Cmpn xl	of 1st Cmpn yl	of 1st Cmpn K1	of 2nd Cmpn K2	
Carbon monoxide with:								
Ethane	18	223~273	9~115	5.04	2.94	6.25	6.95	Trust and Kurata 1971b
Propane	15	275~323	14~136	5.06	2.42	6.99	5.51	Trust and Kurata 1971b
Phenanthrene	8	544~700	14~109	4.67	0.68	5.02	8.19	DeVaney et al 1978
Carbon dioxide with:								
Water	13	348~373	25~300	15.14	0.31	-	-	Wiebe and Gaddy 1939
Ethane	9	222~266	7~28	1.31	3.82	3.56	1.63	Guignoni et al 1974
Propane	28	278~344	14~54	3.05	2.05	4.07	3.29	Reamer, et al 1951
n-Butane	40	311~411	4~68	1.26	1.30	1.92	1.36	Olds et al 1949
n-Pentane	27	311~378	6~88	3.73	0.93	4.02	3.73	Besserer and Robinson 1973
Benzene	17	298~313	9~76	7.48	0.12	8.02	13.28	Ohgaki and Katayama 1976
n-Hexane	20	298~313	4~76	4.56	0.52	4.19	21.76	Ohgaki and Katayama 1976
Toluene	29	311~477	10~151	2.46	0.98	2.87	7.96	Nq and Robinson 1978
n-Heptane	47	311~477	16~131	4.67	0.69	4.53	8.74	Kalra et al 1978
Tetralin	15	462~665	20~51	1.18	0.99	1.44	1.73	Chao et al 1980
n-Decane	16	463~584	14~51	3.23	0.88	3.09	1.46	Sebastian et al 1980a
1-Methylnaphthalene	15	463~704	20~51	2.54	0.56	2.76	2.25	Sebastian et al 1980c
Diphenylmethane	16	463~704	19~50	1.05	0.41	0.81	2.88	Sebastian et al 1980c
Phenanthrene	12	444~700	14~109	4.11	0.43	4.59	17.80	DeVaney et al 1978
n-Hexadecane	16	463~664	20~50	2.10	0.57	2.20	7.57	Sebastian et al 1980a
Quinoline	15	462~703	20~50	1.82	1.08	2.04	1.37	Chao et al 1980
m-Cresol	14	463~665	19~51	2.02	1.05	2.77	2.48	Chao et al 1980

Table 5. (continued)

Systems	% AARD							Data References
	N	T Range K	P range atm	Liq Comp	Vap Comp	K-Value	K-Value	
				of 1st Cmpn x1	of 1st Cmpn y1	of 1st Cmpn K1	of 2nd Cmpn K2	
Hydrogen sulfide with:								
Nitrogen	24	300~344	35~204	0.45	2.61	2.92	8.16	Robinson and Besserer 1972
Carbon dioxide	37	233~361	7~82	0.99	1.75	1.94	5.79	Sobocinski and Kurata 1959
Water	24	344~444	17~119	31.94	0.51	26.63	12.77	Selleck et al 1952
Ethane	11	200~283	1~20	0.15	2.24	2.15	2.87	Robinson and Kalra 1975
Propane	35	218~344	1~27	1.69	4.41	4.43	3.85	Brewer et al 1961
Toluene	27	311~478	2~114	3.66	0.95	4.12	16.50	Nq et al 1980
n-Heptane	28	311~478	6~94	4.33	1.04	4.87	9.36	Nq et al 1980
n-Nonane	15	311~477	1~27	2.47	1.08	2.75	9.41	Eakin and DeVaney 1974
Mesitylene	15	311~477	1~27	5.18	0.85	4.99	13.79	Eakin and DeVaney 1974
Methane with: ¹								
Carbon dioxide	22	219~271	15~75	5.05	2.95	6.34	2.88	Donnelly and Katz 1954
Hydrogen sulfide	41	278~344	14~119	5.62	4.11	6.96	3.25	Sage and Lacey 1955
Water	24	377~444	27~170	13.84	6.92	-	-	Culberson and McKetta 1951
n-Butane	43	194~283	2~109	5.69	0.22	6.56	6.81	Kahre 1974
Benzene	17	421~501	20~200	5.47	4.52	6.41	8.98	Lin et al 1979
Cyclohexane	38	294~344	27~238	3.35	0.32	3.30	10.22	Reamer et al 1958
Toluene	16	262~543	20~227	4.19	2.65	6.15	4.44	Lin et al 1979
m-Xylene	22	461~582	20~199	3.94	1.75	4.94	5.09	Simnick et al 1979c
n-Octane	23	323~423	20~70	4.54	0.15	4.45	5.26	Kohn and Bradish 1964
Tetralin	14	543~665	30~223	3.61	1.86	4.71	9.27	Sebastian et al 1979
n-Decane	11	543~583	50~125	3.46	3.04	3.24	5.28	Lin et al 1979
1-Methylnaphthalene	27	464~704	20~248	3.71	3.37	7.23	11.88	Sebastian et al 1979
Diphenylmethane	25	462~703	20~250	2.43	1.32	3.59	8.87	Sebastian et al 1979
9,10-Dihydrophenanthrene	26	463~703	20~250	4.16	0.30	4.19	6.96	Chao et al 1980
Phenanthrene	8	544~700	14~109	11.03	1.18	11.78	30.48	DeVaney et al 1978
n-Hexadecane	10	543~704	30~200	6.72	0.52	5.84	10.36	Lin et al 1980
Quinoline	27	463~703	20~250	3.79	2.20	6.06	7.62	Simnick et al 1979b
m-Cresol	25	462~663	20~250	5.22	3.48	8.51	13.82	Simnick et al 1979c

¹ See Lee et al (1979) for deviations of predictions for methane + light gases. However, BIPs for these systems are also reported herein in Table 4.

Table 6. Comparison of K-Value Deviations¹ for Coal-Solvent Mixtures
Estimated Using Different Correlations

Systems	Temperature Range °C	Pressure Range atm	CSM-3PCS- MBWR		Penn State Modified Soave Equation		Grayson-Streed Method ²	
			K ₁	K ₂	K ₁	K ₂	K ₁	K ₂
H ₂ + Tetralin	190-430	20-250	4.72	7.52	9.2	10.5	7.0	8.1
H ₂ + Diphenylmethane	190-430	20-250	4.17	10.62	9.6	13.6	7.7	9.3
H ₂ + 1-Methylnaphthalene	190-430	20-250	4.88	9.88	14.6	11.9	7.2	7.3
H ₂ + m-Cresol	190-390	20-250	6.59	9.32	—	—	96.5	11.1
H ₂ + Quinoline	190-430	20-250	5.01	4.90	32.9	21.51	52.2	8.2

$$^1 \text{IAARD} = \frac{1}{N} \sum_{i=1}^N \left| \frac{K_{\text{exp}} - K_{\text{calc}}}{K_{\text{exp}}} \right| \times 100$$

² Frith et al (1979)

Table 7. Generalized Correlations for the Binary-Interaction Parameters of Hydrogen, Methane, and Carbon Dioxide with PCAHs.

Binary System with	$\epsilon_{ij} = a + b X$		$\zeta_{ij} = c + d Y$		Max. T_b Recommended for Use
	a	b	c	d	
Hydrogen	0.852849	0.347961	1.214091	-0.0406321	350 C
Methane	0.965333	0.176491	1.056045	-0.0516114	350
Carbon Dioxide	0.818063	0.403741	0.751148	-0.0084719	300

$$X = |V_{c_i} - V_{c_j}| / (V_{c_i} + V_{c_j})$$

$$Y = V_{c_j} / V_{c_i}$$

where V_{c_j} and V_{c_i} are the critical molar volumes of PCAH and light gas (hydrogen, methane, or carbon dioxide), respectively.

Table 8. Comparison of K-Values %AARD Using Different Sets of BIPs for Light Gases + PCAHs

Systems	%AARD			
	Case A ¹		Case B ²	
	K ₁	K ₂	K ₁	K ₂
H2 + Tetralin	4.72	7.52	5.62	7.58
H2 + 1-Methylnaphthalene	4.88	9.88	20.10	10.20
H2 + Diphenylmethane	4.17	10.62	5.52	11.98
H2 + 9,10-Dihydrophenanthrene	3.53	7.61	9.24	18.50
CH4 + Tetralin	4.71	9.27	10.90	14.70
CH4 + 1-Methylnaphthalene	7.23	11.88	11.56	9.90
CH4 + Diphenylmethane	3.59	8.87	10.17	9.34
CH4 + 9,10-Dihydrophenanthrene	4.19	6.96	8.68	10.78
CO2 + Tetralin	1.44	1.73	9.59	6.41
CO2 + 1-Methylnaphthalene	2.76	2.25	6.47	3.14
CO2 + Quinoline	2.04	1.37	5.86	4.81

¹ BIPs, ϵ_{ij} and ζ_{ij} , determined from VLE data regression.

² BIPs determined from generalized correlations in Table 7. K_1 and K_2 are calculated via a flash calculation in which temperature and pressure are specified.

Table 9. Deviations in Ternary-System K-Value Predictions Using the CSM-3PCS-MBWR Equation of State

Systems ¹	Temp Range K	Pres Range atm	K-Value Dev, %AARD		
			K ₁	K ₂	K ₃
H2(1) + CH4(2) + Tetralin(3)	462~663	50~252	6.50	5.65	10.16
H2 + CH4 + 1-Methylnaphthalene	542~704	50~250	5.63	7.82	8.92
H2 + CO2 + Tetralin	543~663	50~250	7.52	5.37	6.66
H2 + CO2 + 1-Methylnaphthalene	543~704	50~252	7.49	7.04	7.52
H2 + CO2 + Quinoline	543~704	50~252	8.06	6.36	9.29
H2 + Tetralin + m-Xylene	462~582	20~250	5.19	9.19	8.22
H2 + Tetralin + Diphenylmethane	464~701	20~250	6.77	10.82	10.33

¹ See Chao *et al.* 1980.

Table 10

Constants for Generalized Expressions
for Ideal-Gas Properties Given by
Equations (35), (36) and (37)

i	c_i
1	-1.87703×10^{-1}
2	8.16495×10^{-4}
3	2.49514×10^{-3}
4	-2.98252×10^{-4}
5	1.90150×10^{-5}
6	-6.86916×10^{-7}
7	$1. \times 10^2$
8	7.80576
9	1.0056×10^1
10	-1.68224×10^{-1}
11	2.02814×10^{-1}
12	6.63346×10^{-4}
13	-8.45394×10^{-4}
14	-4.87947×10^{-7}
15	6.21045×10^{-7}

Table 11. Comparison of Coal-Fluid Density Data with Prediction via the CSM-3PCS-MBWR Equation of State.

Coal-liquid Designation ¹	N No. of Points	T _b at 50 wt% Distilled	Avg Mol Wt	%AARD
IHS	33	271° C (520°F)	179	1.04
IA-10	32	244 (471)	164	1.58
IA-6	36	260 (500)	172	1.05
IA-3	30	246 (475)	167	4.18
WA-5	30	248 (478)	167	2.93
WA-6	26	253 (488)	169	4.52
WV-1	29	276 (528)	192	4.40
IA-6 + H ₂	18	260 (500)	172	1.61
IA-3 + H ₂	18	246 (475)	167	4.21
WA-5 + H ₂	22	248 (478)	167	8.36
WA-6 + H ₂	30	253 (488)	169	5.05
WV-1 + H ₂	28	276 (528)	192	5.32
WA-2 + H ₂	22	366 (690)	242	8.82

¹
I = Illinois No. 6 coal.
W = Wyoming Wyodak Coal.

Table 12. Prediction of the
Solubility of Hydrogen and Methane in EDS and
SRC-II Coal Liquids

System ¹	Coal-Liquid	Avg Mol Wt M	% AARD
	Boiling Point Range (°C) T _b		
H ₂ + CLPP-A5	204~232	154	10.1
CH ₄ + CLPP-A5			9.4
H ₂ + CLPP-A5	260~316	182	19.4
CH ₄ + CLPP-A5			26.3
H ₂ + SRC-II-5	260~276	182	6.9
CH ₄ + SRC-II-5			11.4
H ₂ + SRC-II-9	316~333	212	7.4
CH ₄ + SRC-II-9			13.2
H ₂ + SRC-II-12	371~399	252	33.7

¹ See Chao *et al* (1980).

Table 13. Prediction of K-Values, for Components in the Streams from the H-Coal Process Hot Separator¹, Using the CSM-3PCS-MBWR

Component	Molecular weight	Gravity API	K-Value ²	
			Exp	Calc
Hydrogen			5.024	5.148
Methane			1.938	1.660
Ethane			1.522	1.052
Propane			1.803	1.153
n-Butane			0.742	1.075
n-Pentane			1.425	1.039
n-Hexane			4.482	0.978
Hydrogen Sulfide			1.622	0.493
Carbon Dioxide			0.423	0.732
Water			1.196	0.192
IBP- 90°C	82.	65.	0.416	0.643
90-150	106.	46.	0.304	0.508
150-200	133.	32.	1.016	0.353
200-260	161.	21.	0.399	0.213
260-316	191.	12.	0.217	0.113
316-370	232.	6.	0.110	0.048
370-430	276.	0.	0.114	0.018
430-480	330.	-4.	0.0	0.006
480-525	385.	-8.	0.0	0.002
525°C+Residium	550.	-20.	0.0	0.000

¹ see IGT (1980)

² Pressure = 171 atm (2500 psig)
Temperature = 706.5 K (812°F)

Table 14. Comparison of Average Absolute Deviations¹ of Enthalpy Differences Predicted Using Different Methods⁴

System ⁴	Number of Data Points	Johnson-Grayson Method	Kesler-Lee Graphical Method	Huang Correlation	Lee-Kesler Equation of State	CSM-3PCS MBWR ²
AAD kJ/kg						
Utah Syncrude Distillate	23	31.7	35.1	25.8	38.1 (43) ³	8.42 (43)
Western Kentucky Light Distillate	23	23.3	26.7	/	33.5 (41)	6.54 (41)
Synthoil Distillate	19	84.7	83.1	75.4	94.4 (42)	6.88 (42)
Western Kentucky Syncrude	21	9.07	9.26	12.8	23.0 (43)	12.84 (43)
SRC-I	55	/	/	/	/	5.12
COL #878	43	/	/	/	/	14.6
Total pts:	184					
Overall AAD for method:		kJ/kg 35.6 (Btu/lb) (15.3)	37.2 (16.0)	36.4 (15.7)	47.2 (20.3)	8.91 (3.83)

$$^1 \text{AAD} = 1/N \sum_{i=1}^N |H_{\text{exp}} - H_{\text{calc}}|$$

² Modified Kesler-Lee Correlation used for Ideal-Gas Heat Capacity

³ Number of data points (in parentheses) used for the method.

⁴ See Kidnay and Yesavage (1979).

Figure 1. Comparison of Hydrogen and 9,10-Dihydrophenanthrene K-Values with Those Predicted by the CSM-3PCS-MBWR Correlation

Figure 2. Comparison of Methane and Diphenylmethane K-Values with Those Predicted by the CSM-3PCS-MBWR Correlation

Figure 3. Comparison of Carbon Dioxide and Quinoline K-Values with Those Predicted by the CSM-3PCS-MBWR Correlation

Figure 4. Comparison of Hydrogen Sulfide and Mesitylene K-Values with Those Predicted by the CSM-3PCS-MBWR Correlation

Figure 5. Comparison of Hydrogen, Methane, and Tetralin K-Values with Those Predicted by the CSM-3PCS-MBWR Correlation

Figure 6. Comparison of Hydrogen, Tetralin, and Diphenylmethane K-Values with Those Predicted by the CSM-3PCS-MBWR Correlation

Figure 7. Critical Temperature vs. Average Boiling Temperature of Distillable Coal-Fluid Fractions at Different Specific Gravities

Figure 8. Critical Volume vs Fraction Average Molecular Weight at Different Specific Gravities

Figure 9. Orientation Parameter vs Reduced Normal Boiling Temperature

Figure 10. Molecular Weight vs Average Boiling Temperature at Different Specific Gravities

Figure 11. Comparison of Enthalpy Differences Predicted, Using the CSM-3PCS-MBWR and Eqn (36) for Ideal-Gas Enthalpy, with Experimental Data for a Synthoil Distillate

Figure 12. Comparison of the Predicted Enthalpy Differences with Experimental Measurements for SRC-1 Naphtha

Figure 13. Enthalpy of SRC-I Naphtha Generated by Using the CSM-3PCS-MBWR

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APPENDIX B

The Most General Density-Cubic Equation Of State: Application To Pure Non-Polar Fluids

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ABSTRACT

Thermodynamic properties of pure non-polar fluids are predicted accurately, over wide ranges of temperature and pressure conditions by the most general density-cubic equation of state. Of particular merit is the accurate prediction of liquid densities and low temperature vapor pressures. The development of the equation of state temperature dependence for non-polar fluids is presented herein. The equation of state is generalized using thermodynamic property data for the normal straight chain paraffin hydrocarbons, methane through n-decane. The generalized equation of state predicts vapor pressure and vapor and liquid densities to within one percent (average) of the experimental values for these fluids. Subsequently, the equation of state is applied to fluids not used in the generalization. These fluids include isobutane, isopentane, ethylene, propylene, carbon dioxide, hydrogen sulfide, nitrogen, benzene, naphthalene, tetralin, quinoline and phenanthrene, respectively. The equation of state prediction of thermodynamic properties of 32 fluids is compared with the predictions by a popular density-cubic equation namely, the Peng-Robinson equation and a popular BWR-type equation of state. According to these comparisons the most general density-cubic equation is superior to the Peng-Robinson equation and is on par with the BWR-type equation of state.

Introduction

Many attempts have been made over the years to describe the thermodynamic behavior of real fluids via equations of state. These equations of state have achieved varying degrees of success, enabling us to divide them into three separate classes. In the first class, we have the equations of state which are cubic in density. A few of the more popular density-cubic equations are the van der Waals equation (1873), the Redlich-Kwong equation (1949), the Soave equation (1972) and the Peng-Robinson equation (1976). The density-cubic equations of state give reasonable descriptions of the thermodynamic behavior of real fluids, with each equation generally being more accurate in the chronological order of appearance in the literature. The Beattie-Bridgeman equation (1928), the Benedict-Webb-Rubin equation (1940) and the Modified Benedict-Webb-Rubin equation (1973) are popular examples of the second class of equations of state. They are non-cubic in density and provide a good description of the thermodynamic behavior of real fluids for all fluid states. In the third class of equations, are the non-analytic equations of state which are highly constrained for specific fluid (Goodwin, 1974) and give a highly accurate description of real fluid behavior.

In most industrial design situations as well as research measurements of derived properties, the unknown variable is density, whereas the easily measurable properties pressure and temperature, are known. Consequently, the first class of equations, namely the density-cubic equations are of particular interest since they provide an analytical solution for the density, as compared to the more complicated non-cubic and non-analytic equations of state, which require time consuming iterative procedures to solve for the density.

The presently available popular density-cubic equations of state like the Soave and the Peng-Robinson equations provide good descriptions of real fluid behavior in the two phase region and in the gas phase, but in the compressed liquid region they lack by far the accuracy levels attainable using the second class of equations of state.

When we look at the form of the density-cubic equations in the chronological order of appearance in the literature, we find that in general the more recent equations have more density dependence (when expressed in a pressure explicit form) than their precedents. For example, the Redlich-Kwong equation has more density dependence than the van der Waals equation, as seen below

$$P = \frac{\rho RT}{1-\rho b} - a\rho^2 \quad (\text{van der Waals})$$

$$P = \frac{\rho RT}{(1-\rho b)} - \frac{aT^{-1/2}\rho^2}{(1+\rho b)} \quad (\text{Redlich Kwong})$$

Similarly, the Peng-Robinson equation of state has more density dependence than the Redlich-Kwong equation

$$P = \frac{\rho RT}{1-\rho b} - \frac{a(T)\rho^2}{(1+2b\rho - b^2\rho^2)} \quad (\text{Peng-Robinson})$$

In general, the overall performance in fluid properties prediction is greatly enhanced when using the Peng-Robinson equation as compared to the Redlich-Kwong equation and the Redlich-Kwong equation in turn is better than the van der Waals equation. Thus, though the temperature dependence of each equation is different it can be projected that at a particular temperature, a higher density dependence leads to a more accurate equation of state. Continuing in the same vein, it can be stated that the most density dependence

(in terms of pressure) that can be introduced into a density-cubic equation will in turn lead to the most accurate cubic equation of state. This fact is very important because if the most general density-cubic equation of state can provide an accuracy level comparable to the second class of equations of state for all fluid states it becomes highly desirable in situations where repetitive calculations for the density are required due to its inherent advantages.

The derivation of the most general density-cubic equation of state has been presented recently by the authors (Kumar and Starling, 1980). The equation of state is expressed as follows

$$Z = \frac{1 + d_1\rho + d_2\rho^2}{1 + d_3\rho + d_4\rho^2 + d_5\rho^3} \quad (1)$$

Equation 1 can be written in a computationally more convenient form by expressing the denominator as a product of a first order term and a quadratic function by setting $d_1 = A_5$, $d_2 = A_2$, $d_3 = A_3 - A_1$, $d_4 = A_4 - A_1A_3$ and $d_5 = -A_1A_4$,

$$Z = \frac{1 + A_5\rho_r + A_2\rho_r^2}{(1 - A_1\rho_r)(1 + A_3\rho_r + A_4\rho_r^2)} \quad (2)$$

where A is the compressibility factor and ρ_r is the reduced density (ρ/ρ_c) and A_1 through A_5 are density independent parameters which can be temperature and composition dependent.

Development of a Provisional Temperature Dependence for the Equation of State

The requirement that the equation of state be cubic in density restricts the density dependence, but the temperature dependence is open for analysis, with practical application of the equation of state being the only criterion restricting the order of the temperature dependence. The evaluation of

polynomials consumes very little computing time as compared to repeated calculations using a do-loop and thus, adding more terms to a polynomial in temperature does not for practical purposes increase the time required for an analytical solution of the cubic equation. In the development of the temperature dependence of the equation of state the goal was to attain a level of accuracy comparable to the second class of equations of state like the Three Parameter Corresponding States Modified Benedict-Webb-Rubin equation of state, hereinafter referred to as 3PCS-MBWR (Brulé, Lee and Starling, 1979).

In order to determine the form of the temperature dependence, the expressions for the second virial coefficient and third virial coefficient were obtained from equation 1 by expanding it into a polynomial in density. The second and third virial coefficients are given by the following equations

$$B = A_5 - A_3 + A_1 \quad (3)$$

$$C = A_2 - A_4 + A_1 A_3 - (A_3 - A_1) A_5 + (A_3 - A_1)^2 \quad (4)$$

where B and C are the second and third virial coefficients, respectively. It is known (Tsonopoulos, 1974) that the second and third virial coefficients can be well represented by reciprocal temperature expansions. Since all the five parameters A_1 through A_5 appear in the expressions for the second and third virial coefficients, reciprocal temperature expansions were chosen for the temperature dependence of the equation of state.

To develop the analytical relations for the temperature dependence of the parameters, thermodynamic property values were used for propane along twenty-five isotherms from Goodwin (1977), covering a wide range of fluid states

from a reduced temperature of 0.24 to a reduced temperature of 1.62 and up to a reduced pressure of 17. At each isotherm, values of density, vapor pressure and the partial derivative of pressure with respect to density $(\partial p / \partial \rho)_T$ were used in multiproperty regression analysis (Cox, Bono, Kwok and Starling, 1971; Wang, Van Deal and Starling, 1976), to determine the optimum set of values for the parameters A_1 through A_5 . In the next step, the temperature dependence of each of the parameters was determined. The parameters A_1 and A_4 were independent of temperature while the parameters A_2 , A_3 and A_5 had the following temperature dependence.

$$A_5 = A_{51} + \frac{A_{52}}{T_r} + \frac{A_{53}}{T_r^2} + \frac{A_{54}}{T_r^3} + \frac{A_{55}}{T_r^4} \quad (5)$$

$$A_2 = A_{21} + \frac{A_{22}}{T_r} + \frac{A_{23}}{T_r^2} + \frac{A_{24}}{T_r^3} \quad (6)$$

$$A_3 = A_{31} + \frac{A_{32}}{T_r} + \frac{A_{33}}{T_r^2} + \frac{A_{34}}{T_r^3} \quad (7)$$

The above temperature dependence was developed using thermodynamic property values for propane, but to provide the basis for the generalization of the equation of state, the parameters A_1 , A_4 and the coefficients of the temperature functions for A_5 , A_2 and A_3 were determined for methane, n-heptane and n-octane, respectively. For each fluid, the thermodynamic properties density, vapor pressure and enthalpy departure were used in multiproperty regression analysis to determine the optimum set of parameters. For the fluids considered, namely methane, propane, n-heptane and n-octane the overall average absolute deviation of predicted density, vapor pressure and enthalpy departure from experimental values was about half a percent. This error in

properties prediction is quite small and thus, the equation of state is amenable to generalization.

Generalization of the Equation of State

In the three parameter corresponding states theory proposed by Pitzer (1955) the compressibility factor, Z can be expressed in a power series in the acentric factor ω , with the expansion truncated after the first order term,

$$Z = Z_0 + Z_1\omega + \dots \quad (8)$$

$$Z_0 = Z_0(T_r, P_r) \quad (9)$$

$$Z_1 = Z_1(T_r, P_r) \quad (10)$$

where $T_r = T/T_c$ and $P_r = P/P_c$.

For simple fluids like argon the acentric factor is zero and the compressibility factor is given by Z_0 . For other fluids the acentric factor is calculated from the following defining relation given by Pitzer,

$$\omega = -\log P_r - 1.000 \quad (11)$$

where P_r is the reduced vapor pressure at $T_r = 0.70$. $(Z_0 + Z_1\omega)$ represents the compressibility factor for fluids which deviate from the simple fluid behavior. This theory has been applied to a wide class of fluids, with success greatest for nonpolar fluids.

The parameter values obtained for methane, propane, n-heptane and n-octane were plotted against acentric factor, ω as shown in Figures 1 to 5. From Figures 1 and 2 it can be inferred that A_1 is a function only

of acentric factor and A_4 is practically a constant. The temperature dependent parameters A_2 , A_3 and A_5 have essentially linear dependence on the acentric factor at each reduced temperature.

With knowledge of the general functional dependence of the parameters from Figures 1 to 5, the analytical dependence was determined through regression analysis of thermodynamic properties data. Experimental density, vapor pressure and enthalpy departure values for the normal straight chain hydrocarbons methane, ethane, propane, n-butane, n-pentane, n-hexane, n-heptane, n-octane, n-nonane and n-decane were used simultaneously in multiproperty regression analysis to arrive at the following generalized equation of state.

$$Z = \frac{1 + A_5 \rho_r + A_2 \rho_r^2}{(1 - A_1 \rho_r)(1 + A_3 \rho_r + A_4 \rho_r^2)} \quad (12)$$

where

$$A_5 = \left(\frac{a_3}{T_r^2} + \frac{a_4}{T_r^3} \right) + \left(\frac{a_8}{T_r} + \frac{a_3}{T_r^3} + \frac{a_5}{T_r^4} + \frac{a_3}{10^3 T_r^8} \right) \gamma$$

$$A_2 = \left(a_7 + \frac{a_1}{T_r} + \frac{a_{12}}{T_r^2} \right) + \left(-\frac{a_2}{T_r} + \frac{10a_4}{T_r^2} + \frac{a_{11}}{10^3 T_r^8} \right) \gamma$$

$$A_1 = a_1$$

$$A_3 = \left(\frac{a_9}{T_r} - \frac{a_4}{T_r^2} \right) + \left(\frac{a_6}{T_r} + \frac{10a_{12}}{T_r^2} + \frac{a_{10}}{T_r^3} + \frac{a_2}{T_r^4} \right) \gamma$$

$$A_4 = -a_1$$

where γ is a parameter referred to herein as the orientation parameter. The orientation parameter was set equal to the acentric factor for the regression to determine the parameters a_1 through a_{12} .

The value of the acentric factor, ω for a particular fluid depends on the source from which it is obtained. For example, the value of the acentric factor for methane has been quoted as 0.0072, 0.008 and 0.0115, respectively, in three sources (Passut and Danner, 1973, Reid et. al., 1977 and Henry and Danner, 1978). This discrepancy is probably due to the fact that the accuracy of the value of the acentric factor depends upon the accuracy of the vapor pressure value at a reduced temperature of 0.7 and the accuracy of the critical temperature and the critical pressure of the fluid. In general, the vapor pressure at the reduced temperature of 0.7 is not measured and hence, this vapor pressure value is either interpolated from values at other temperatures or it is obtained from a vapor pressure equation. In any case, the accuracy in predicted property values obtained from a generalized empirical equation of state depends on the use of the acentric factor value which is consistent with the value used in the development of the equation of state. Thus, in order to make the value of the acentric factor compatible with the equation of state, an orientation parameter, γ which in most cases is equal to the former was determined from regression analysis of thermodynamic property data. The values of the orientation parameter, γ for the fluids studied in this work are presented in Table 1 along with the other characterization parameters, critical temperature and critical density. For other fluids, the orientation parameter can either be replaced by the value of the acentric factor or more preferably, it can be determined from regression analysis of thermodynamic property data.

The numerical values for the set of generalized parameter a_1 through a_{12} occurring in equation 12 are presented in Table 2. To use equation 12 to calculate a pure fluid thermodynamic property, only the values of the critical temperature, the critical density and the orientation parameter are required.

Equation 12 predicts density and vapor pressure values for methane, ethane, propane; n-butane, n-pentane, n-hexane, n-heptane, n-octane, n-nonane and n-decane covering wide ranges of temperature and pressure conditions to within one percent of the experimental values on the average (Tables 4 and 5). The enthalpy departure values for methane, ethane, propane, n-butane, n-pentane, n-heptane and n-octane are predicted with 3.95 kJ/kg average absolute deviation (Table 6). Values of the orientation parameter, γ were determined for 22 additional fluids to ascertain the applicability of the equation of state for fluids not used in the generalization. These fluids are isobutane, isopentane, ethylene, propylene, carbon dioxide, hydrogen sulfide, nitrogen, benzene, naphthalene, tetralin, quinoline, phenanthrene and the straight chain saturated hydrocarbons n-undecane through n-eicosane (Tables 4 and 5).

Comparisons with Other Equations of State

The major literature sources from which the experimental data were obtained for use in the development of the most general density-cubic equation of state and for comparisons with other equations of state, are presented in Table 3. The primary objective behind the development of the most general density-cubic equation of state was to provide a cubic equation which could describe the thermodynamic properties of non-polar fluids, especially liquid densities and low temperature vapor pressures on par with non-cubic equations of state. The non-cubic equation of state chosen for comparison is the three parameter corresponding states Modified Benedict-Webb-Rubin (3PCS-MBWR) equation of state developed by Starling and coworkers (1979). To compare equation 12, a cubic equation, the Peng-Robinson equation of state was chosen as it is one of the most popular cubic equations used in industry today.

The comparisons are presented on a relative basis, percent average absolute deviation

$$\text{A.A.D.}\% = \frac{1}{n} \sum_{i=1}^n \left| \frac{\text{exp} - \text{calc}}{\text{exp}} \right|_i \times 100$$

for density and vapor pressure and on an average absolute deviation basis for the enthalpy departure defined by

$$\text{A.A.D.} = \frac{1}{n} \sum_{i=1}^n |\text{exp} - \text{calc}|_i$$

where i indicates the i th data point, n is the total number of data points, exp and calc refer to the experimental and calculated values of the data point, respectively.

Density. The average absolute deviations of equation of state predictions of the densities of thirty fluids, the number of data points used and the temperature and pressure ranges of the data as presented in Table 4. In general, other cubic equations have relatively large deviations for liquid densities compared to non-cubic equations. This is shown to be true for the Peng-Robinson equation (P-R) in comparison with the three parameter corresponding states modified BWR equation (3PCS-MBWR) in Table 4. However, the most general density-cubic equation (eq. 12) is on par with the 3PCS-MBWR equation.

Vapor Pressure. In the development of the Peng-Robinson equation of state, vapor pressure data from the normal boiling point up to the critical point were used (Peng and Robinson, 1976). In the present work, when the Peng-Robinson equation was used to calculate vapor pressures over the full range of temperature for comparison purposes, the relative errors in the calculated vapor pressures were quite large at temperatures below the normal boiling point. In the range of the normal boiling point to the critical point the

vapor pressures are predicted quite accurately, as reported (Peng and Robinson, 1976). Due to the relatively large deviations at low temperatures, the overall deviation for the full range was rather high and hence, vapor pressures comparisons were not appropriate for the Peng-Robinson equation.

Vapor pressure predictions for thirty-two fluids using equation 12 are compared with predictions using the 3PCS-MBWR equation of state in Table 5. The range of fluids for which the comparisons are presented include components of natural gas, petroleum and coal. In most cases low temperature vapor pressure data were included for comparison. It can be seen from the comparisons presented in Table 5 that the most general density-cubic equation of state predicts vapor pressures quite well and as accurately as the 3PCS-MBWR equation of state.

Enthalpy Departures. Enthalpy departure predictions for eleven fluids are presented in Table 6. Here, equation 12 is compared with the Peng-Robinson equation and the three parameter corresponding states Modified Benedict-Webb-Rubin equation. According to these comparisons the most general density-cubic equation of state is more accurate than the Peng-Robinson equation and compares quite well with the 3PCS-MBWR equation of state.

Conclusions

This work presents, for non-polar fluids, the development of the temperature dependence of the most general density-cubic equation of state. The generalized equation of state, which has been developed thus far in a three parameter corresponding states framework for non-polar fluids can be extended to polar and associative fluids if adequate characterization is provided for the effects of polarity and hydrogen bonding. This leads to a multiparameter corresponding states framework where the equation of state, and in turn the parameters in the cubic equation can be expressed as

$$A_1 = A_{11}(T_r) + A_{12}(T_r, \gamma) + A_{13}(T_r, \mu^*) + A_{14}(T_r, \alpha) + \dots$$

where μ^* is the reduced dipole moment and α is a measure of associative effects.

The generalized equation of state was applied to thirty-two pure fluids consisting mainly of non-polar hydrocarbons. Where comparisons have been made, equation 12 is superior to the Peng-Robinson equation of state and is as accurate as the three parameter corresponding states Modified Benedict-Webb-Rubin equation of state. Finally, the most general density-cubic equation has been shown to perform as well as a non-cubic equation such as the 3PCS-MBWR equation in the overall fluid states.

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Appendix

Expressions for the derived thermodynamic properties for equation 12 were converted into reduced form in terms of the variables $\rho_r = \frac{\rho}{\rho_c}$ and $T_r = \frac{T}{T_c}$. The classical relationships in reduced form for enthalpy departure, entropy departure, internal energy departure, Helmholtz free energy departure, entropy departure, Gibbs free energy departure and fugacity coefficient for a pure fluid are as follows

$$\frac{H-H^0}{RT_c} = T_r(Z-1) - T_r^2 \int_0^{\rho_r} (\partial Z / \partial T_r) \rho_r d \ln \rho_r \quad A.1$$

$$\frac{S-S^0}{R} = - \int_0^{\rho_r} (Z-1) d \ln \rho_r - T_r \int_0^{\rho_r} (\partial Z / \partial T_r) \rho_r d \ln \rho_r - \ln P/Z \quad A.2$$

$$\frac{U-U_c^0}{RT_c} = -T_r^2 \int_0^{\rho_r} (\partial Z / \partial T_r) \rho_r d \ln \rho_r \quad A.3$$

$$\frac{A-A_c^0}{RT_c} = T_r \int_0^{\rho_r} (Z-1) d \ln \rho_r + T_r \ln P/Z \quad A.4$$

$$\frac{G-G_c^0}{RT_c} = T_r \int_0^{\rho_r} (Z-1) d \ln \rho_r + T_r \ln P/Z + T_r (Z-1) \quad A.5$$

$$\ln (f/P) = \int_0^{\rho_r} (Z-1) d \ln \rho_r - \ln Z + (Z-1) \quad A.6$$

when the integrals $\int_0^{\rho_r} (Z-1) d \ln \rho_r$ and $\int_0^{\rho_r} (\partial Z / \partial T_r) \rho_r d \ln \rho_r$ are evaluated from the equation of state, all of the above properties can be determined. The equation of state expressions for the two integrals are given below. Let us define

$$F = \frac{A_1^2 + A_5 A_1 + A_2}{A_1^2 + A_3 A_1 + A_4}$$

$$K = \frac{A_4 F - A_2}{A_1}$$

$$Q = A_3^2 - 4A_4$$

$$X = 1 + A_3 \rho_r + A_4 \rho_r^2$$

$$Y = \frac{1}{\sqrt{Q}} \ln \left(\frac{2 + \rho_r (A_3 + \sqrt{Q})}{2 + \rho_r (A_3 - \sqrt{Q})} \right)$$

Then

$$\int_0^{\rho_r} (Z-1) d \ln \rho_r = \frac{(F-1)}{2} \ln X - F \ln (1 - A_1 \rho_r) + Y(K + A_3(F-1)/2) \quad A.7$$

$$\begin{aligned}
\int_0^{\rho_r} \left(\frac{\partial Z}{\partial T_r} \right)_{\rho_r} d \ln \rho_r &= \frac{dF}{dT_r} \ln \left(\frac{\sqrt{X}}{1-A_1 \rho_r} \right) - \frac{1}{Q} \frac{dA_3}{dT_r} \left[(F-1-K\rho_r)(A_3+2A_4\rho_r)/X + \right. \\
&\quad \left. A_3(1-F) \right] + Y \left\{ \frac{dF}{dT_r} \frac{(A_3 A_1 + 2A_4)}{2A_1} - \frac{1}{A_1} \frac{dA_2}{dT_r} + \right. \\
&\quad \left. \frac{1}{Q} \frac{dA_3}{dT_r} \left[2A_4(1-F) - A_3 K \right] \right\}
\end{aligned}$$

A.8

Nomenclature

A = Helmholtz free energy

A_i ($i = 1, 5$) = equation of state parameters

a = attraction parameter

a_i ($i = 1, 12$) = generalized parameters in equation 12

B = second virial coefficient

b = van der Waals co-volume

C = third virial coefficient

d_i ($i = 1, 5$) = parameters in equation 1

f = fugacity

F, K, Q, X, Y = symbols defined in appendix

G = gibbs free energy

H = enthalpy

P = pressure

R = universal gas constant

S = entropy

T = temperature

U = internal energy

Z = compressibility factor

Greek Letters

α = association factor

γ = orientation parameter

μ = dipole moment

ρ = molar density

ω = acentric factor

Superscript

0 = ideal gas state

$*$ = reduced

Subscript

r = reduced property

c = critical property

i = parameter index

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Figure 1. Plot of parameter A_1 versus acentric factor, ω

Figure 2. Plot of parameter A_4 versus acentric factor, ω

Figure 3. Plot of the parameter A_5 versus acentric factor, ω at various reduced temperatures

Figure 4. Plot of the parameter A_2 versus acentric factor, ω at various reduced temperatures

Figure 5. Plot of the parameter A_3 versus acentric factor, ω at various reduced temperatures

Table 1. Characterization Parameters for Use With Equation 12

Fluid	Critical Temperature, °K	Critical Density, kg mole/M ³	Orientation Parameter, Y
Methane	190.69	10.0500	0.0115
Ethane	305.39	6.7566	0.0980
Propane	369.80	4.9600	0.1520
i-Butane	407.85	3.9053	0.1831
n-Butane	425.19	3.9213	0.1947
i-Pentane	460.37	3.2469	0.2246
n-Pentane	469.49	3.2149	0.2467
n-Hexane	507.23	2.7167	0.2967
n-Heptane	540.29	2.3467	0.3467
n-Octane	568.59	2.0568	0.3949
n-Nonane	594.54	1.8421	0.4468
n-Decane	617.54	1.6611	0.4880
n-Undecane	638.80	1.5153	0.5350
n-Dodecane	658.30	1.4026	0.5801
n-Tridecane	675.80	1.2821	0.6213
n-Tetradecane	694.00	1.2049	0.6565
n-Pentadecane	707.00	1.1363	0.7154
n-Hexadecane	717.00	1.0598	0.7860
n-Heptadecane	733.00	1.0000	0.8071
n-Octadecane	745.00	0.9430	0.8492
n-Nonadecane	756.00	0.8937	0.8965
n-Eicosane	767.00	0.8495	0.9427
Ethylene	283.05	8.0653	0.0995
Propylene	365.04	5.5248	0.1475
Hydrogen Sulfide	373.54	10.5257	0.1083
Nitrogen	126.15	11.0992	0.0399
Carbon Dioxide	304.15	10.6378	0.2109
Benzene	562.16	3.8662	0.2133
Naphthalene	748.35	2.4186	0.2998
Tetralin	720.15	2.2692	0.3196
Quinoline	782.15	2.4853	0.2580
Phenanthrene	873.15	1.8066	0.4641

Table 2. Generalized Parameters Used in Equation 12

i	a_i	i	a_i
1	0.262524	7	-0.178144
2	0.236048	8	0.549559
3	-1.096720	9	0.579249
4	0.042057	10	-1.297180
5	0.196828	11	0.278052
6	-1.589350	12	0.250865

Table 3. Data References

Fluid(s)	Major Data Sources
Methane	Douslin, 1964, Jones, 1963, Matthews, 1946, Van Itterbeck, 1963, Vennix, 1966, Yesavage 1968.
Ethane	API, 1953, Canjar, 1967, Sage, 1950.
Propane	Goodwin, 1977, Yesavage, 1968.
i-Butane	Beattie, 1950, Sage, 1950, Waxman, 1979, Connolly, 1962, Zwolinski, 1971.
n-Butane	API, 1953, Canjar, 1967, Sage, 1950.
i-Pentane	Schumann, 1942, Silberberg, 1959, Vohra, 1959, Willingham, 1945.
n-Pentane	API, 1953, Canjar, 1967, Sage, 1950.
n-Hexane	API, 1953, Stewart, 1954, Canjar, 1967.
n-Heptane	API, 1953, Gilliland, 1942, Kay, 1938, Stuart, 1950.
n-Octane	API, 1953, Felsing, 1942, Mundel, 1913, Young, 1900, Lenoir, 1968.
n-Nonane	API, 1953.
n-Decane	API, 1953, Sage, 1950.
n-Undecane to n-Eicosane	Vargaftik, 1975.
Ethylene	Canjar, 1967, Michels, 1936, Rossini, 1953, Tickner, 1951.
Propylene	Canjar, 1967, Michels, 1953, Rossini, 1953, Tickner, 1951.
Hydrogen Sulfide	Kay, 1953, Lewis, 1968, Reamer, 1959, West, 1948.
Nitrogen	Canjar, 1967, Friedman, 1950, Mage, 1963, Streett, 1968.
Carbon Dioxide	Canjar, 1967, Din, 1961.
Benzene	API, 1953.
Naphthalene	API, 1978a, Wilson, 1981.
Tetralin	API, 1978b, Wilson, 1981.
Quinoline	API, 1979a, Wilson, 1981.
Phenanthrene	API, 1979b, Wilson, 1981.

Table 4. Comparisons of Density Predictions

Fluids	No. of Data Points	Temperature Range, °K	Pressure Range, bars	A.A.D. %		
				P-R	3-PCS-MBWR	Eq. 12
Methane	41	114.5 ~ 623.2	8.9 ~ 160.3	5.33	0.65	1.17
Ethane	46	133.5 ~ 427.6	1.0 ~ 551.6	5.35	1.23	1.69
Propane	70	90.0 ~ 600.0	1.1 ~ 733.3	3.84	1.01	0.62
i-Butane	354	185.4 ~ 573.3	0.1 ~ 344.7	3.70	0.87	0.94
n-Butane	40	144.3 ~ 494.3	1.0 ~ 482.6	3.65	0.55	0.54
i-Pentane	116	124.9 ~ 473.1	0.01 ~ 184.4	2.52	1.77	1.25
n-Pentane	41	144.3 ~ 510.9	1.0 ~ 689.5	3.14	1.15	0.84
n-Hexane	41	177.6 ~ 410.9	1.0 ~ 205.5	1.59	0.53	0.33
n-Heptane	41	205.4 ~ 510.9	1.0 ~ 212.5	1.47	0.65	0.53
n-Octane	50	216.5 ~ 538.7	1.0 ~ 16.5	3.92	1.18	1.25
n-Decane	32	310.9 ~ 510.9	13.8 ~ 413.7	4.71	1.09	0.43
n-Dodecane	17	323.2 ~ 483.2	0.001 ~ 0.871	7.80	0.54	2.22
n-Tridecane	17	343.2 ~ 503.2	0.001 ~ 0.934	7.58	1.66	2.78
n-Tetradecane	14	393.2 ~ 523.2	0.01 ~ 0.934	7.76	1.66	2.78
n-Pentadecane	14	413.2 ~ 543.2	0.01 ~ 0.99	8.95	2.03	3.97
n-Hexadecane	9	463.2 ~ 543.2	0.07 ~ 0.696	10.28	2.12	3.47
n-Heptadecane	13	433.2 ~ 553.2	0.01 ~ 0.613	13.41	—	4.31
n-Octadecane	13	453.2 ~ 573.2	0.02 ~ 0.696	17.14	3.57	4.32
n-Nonadecane	12	463.2 ~ 573.2	0.02 ~ 0.5	20.11	4.60	4.72
Ethylene	41	116.5 ~ 399.8	1.0 ~ 138.0	3.19	2.73	1.87
Propylene	61	227.6 ~ 505.4	1.1 ~ 202.6	2.51	1.58	1.44
Hydrogen Sulfide	41	277.6 ~ 444.3	6.9 ~ 137.9	3.57	1.85	2.06
Nitrogen	41	77.6 ~ 388.7	1.0 ~ 616.1	4.24	0.27	1.40
Carbon Dioxide	41	243.1 ~ 413.1	15.2 ~ 304.1	1.99	0.65	0.83
Benzene	60	513.2 ~ 613.2	25.8 ~ 598.1	3.17	2.57	1.84
Naphthalene	18	360.0 ~ 1000.0	1.0 ~ 20.0	1.48	2.89	2.65
Tetralin	17	300.0 ~ 1000.0	1.0 ~ 100.0	6.82	2.91	2.66
Quinoline	17	320.0 ~ 1000.0	1.0 ~ 100.0	1.82	4.34	4.22
Phenanthrene	7	373.2 ~ 573.2	0.00 ~ 0.7	8.45	0.26	4.65

Table 5. Comparisons of Vapor Pressure Predictions

Fluids	No. of Data Points	Temperature Range, °K	A.A.D. %	
			3-PCS-MBWR	Eq. 12
Methane	29	111.66 ~ 190.64	0.68	0.98
Ethane	46	138.71 ~ 305.38	1.10	1.07
Propane	21	120.0 ~ 369.80	0.46	0.94
i-Butane	64	186.11 ~ 407.85	1.61	0.49
n-Butane	38	202.59 ~ 425.16	0.53	0.48
i-Pentane	64	217.17 ~ 460.39	0.86	0.34
n-Pentane	50	179.60 ~ 469.77	1.03	1.19
n-Hexane	53	219.86 ~ 407.87	0.98	0.89
n-Heptane	44	192.74 ~ 531.59	0.75	0.64
n-Octane	47	218.71 ~ 549.82	1.16	1.18
n-Nonane	24	223.75 ~ 452.59	1.46	1.56
n-Decane	24	243.50 ~ 477.59	0.77	1.40
n-Undecane	19	347.04 ~ 499.82	0.44	0.56
n-Dodecane	22	323.15 ~ 659.17	0.56	0.71
n-Tridecane	19	343.17 ~ 677.17	0.97	0.65
n-Tetradecane	16	393.17 ~ 695.0	0.58	0.67
n-Pentadecane	14	413.17 ~ 553.17	0.71	0.30
n-Hexadecane	10	463.17 ~ 553.17	0.29	0.19
n-Heptadecane	16	433.15 ~ 583.17	1.51	0.32
n-Octadecane	15	453.17 ~ 593.17	0.77	0.14
n-Nonadecane	16	463.15 ~ 613.17	1.24	0.76
n-Eicosane	17	473.15 ~ 767.00	--	2.77
Ethylene	36	133.15 ~ 283.05	2.08	2.00
Propylene	28	146.93 ~ 364.93	0.69	1.10
Hydrogen Sulfide	24	212.93 ~ 373.54	0.72	1.21
Nitrogen	19	88.71 ~ 125.93	0.90	0.92
Carbon Dioxide	33	216.48 ~ 304.26	0.76	0.81
Benzene	36	280.30 ~ 553.17	0.69	0.51
Naphthalene	15	441.32 ~ 727.61	6.36	3.07
Tetralin	16	450.17 ~ 710.94	3.63	2.44
Quinoline	8	533.17 ~ 727.61	5.12	5.58
Phenanthrene	12	481.0 ~ 727.61	9.37	4.64

Table 6. Comparisons of Enthalpy Departure Predictions

Fluids	No. of Data Points	Temperature Range, °K	Pressure Range bars	A.A.D., KJ/KG		
				P-R	3-PCS-MBWR	Eq. 12
Methane	38	116.48 ~ 283.15	31.03 ~ 137.9	5.58	3.23	4.67
Ethane	98	166.48 ~ 427.59	13.79 ~ 241.3	3.74	2.28	3.88
Propane	39	116.48 ~ 394.26	34.47 ~ 137.9	8.37	3.37	3.04
i-Butane	24	311.11 ~ 522.22	17.24 ~ 206.8	4.10	1.77	2.58
n-Butane	39	310.93 ~ 494.26	13.79 ~ 344.7	3.16	1.16	1.45
n-Pentane	39	310.93 ~ 510.93	13.79 ~ 689.5	4.16	1.23	2.41
n-Heptane	17	539.98 ~ 594.0	5.43 ~ 162.9	2.46	1.72	2.74
n-Octane	68	297.04 ~ 588.72	13.79 ~ 96.53	6.58	4.30	6.69
Ethylene	38	188.71 ~ 399.82	6.89 ~ 137.9	6.58	4.58	3.39
Nitrogen	79	88.71 ~ 283.15	13.79 ~ 172.4	2.42	1.12	1.15
Carbon Dioxide	39	243.15 ~ 413.15	30.41 ~ 506.7	7.21	6.25	4.99