Correlation of Phase-Separation Data for Coal-Conversion Systems

A multiparameter corresponding-states correlation is applied to describe fossil-fluid vapor/liquid-equilibrium behavior needed to design separation and other process units in coal-liquefaction plants. Data for both defined and undefined fluids pertinent to coal liquefaction are utilized in correlation development. The procurement of these data requires a thorough evaluation and study of the needs for additional data to improve correlations. These needs are systematically outlined in the context of the level of predication capability that can be achieved using the currently available data base.

A conformal-solution model is applied to describe the behavior of many defined binary and ternary coal-solvent systems. The correlation is then extended to undefined systems such as those encountered in the Exxon Donor Solvent process. Correlation results are reported and correlation limits are assessed.

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SCOPE

The methodology for correlating phase-separation data is emphasized. Data requirements for maximum utility in correlation are specified. These include the need for determination of feed composition as well as overhead (e.g., vapor) and bottom (e.g., liquid) compositions so that closure of compositional material balances can be used to provide an evaluation of data consistency. Needs are specified for compositional analysis and characterization in cases of phase-separation data for complex mixtures for which fractions must be treated as pseudocomponents. The multiparameter corresponding-states method using the conformal-solution model for mixtures is used to provide an example of correlation framework and results for coal fluids.

CONCLUSIONS AND SIGNIFICANCE

The information presented herein should provide perspective regarding correlation needs for phase-separation data relevant to coal-conversion systems. Fundamental data are required for correlation development, with binary VLE data playing the central role. Defined-system multicomponent VLE data are required for correlation testing and undefined-system VLE data are required to make the correlations applicable to real process streams. The accuracy of the VLE data utilized is an important factor, as erroneous VLE data can lead to erroneous conclusions.

Accurate predictions for many coal-fluid systems are possible with a three-parameter corresponding-states correlation using a modified Benedict-Webb-Rubin equation of state for thermodynamic properties and the conformal-solution model for property composition dependence. The coal-conversion industry needs a data-procurement program, the development of improved compositional analysis/chemical characterization methods, and further correlation efforts for continued progress towards the capability to describe the VLE and overall thermodynamic behavior of coal fluids.

The design of separation processes in coal-conversion systems requires the capability to accurately predict the vapor/liquid equilibrium (VLE) of coal-derived fluids. The starting point in developing this capability is the fundamental data, including binary VLE data, required to develop accurate thermodynamic-properties correlations. These needs for binary VLE data are discussed herein in the context of the equation-of-state correlation of thermodynamic properties in the framework of the multiparameter corresponding-states method, using the conformal-solution model to describe the composition dependence of properties. The needs for multicomponent VLE data are then discussed in the context of correlation testing and applications to actual plant streams. In order to develop and test thermodynamic correlations, the VLE data used must be as free from errors as possible. Methodologies for the use of component-material-balance relations to detect erroneous VLE data are presented. The availability and needs for coal-fluid VLE data are then discussed. Finally, the capabilities of a three-parameter corresponding-states correlation for predicting coal-fluid VLE are presented.

CORRELATION METHODOLOGY AND NEED FOR BINARY VLE DATA

Historically, VLE data have been the most utilized mixture data for the development of those fluid-mixture thermodynamic-properties correlations that can be applied to both the vapor and liquid phases. To illustrate the need for VLE data, development methodology is presented for CSM-MPCS-EOS correlations. Herein, CSM-MPCS-EOS refers to multiparameter corresponding-states (MPCS) correlations which utilize equations of state (EOS) to define property temperature and density dependence and conformal-solution models (CSM) to define dependence of properties on composition. Figure 1 shows the sequence of steps commonly utilized in developing CSM-MPCS-EOS correlations.

The first step in CSM-MPCS-EOS correlation development is to determine the dependence of P on T and ρ (or v). This is done using data for individual pure fluids in the classes of fluids for

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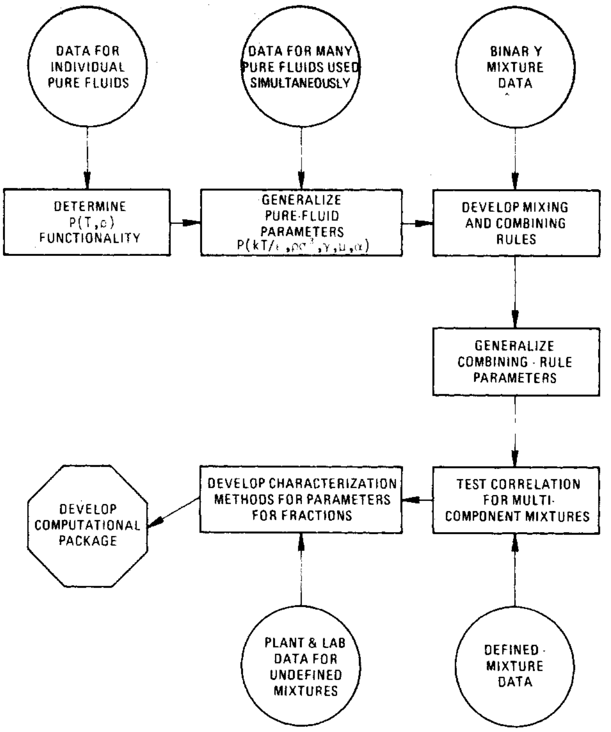

Figure 1. Sequence of steps in properties correlation.

which the correlation is intended. The state-of-the-art procedure is to utilize multiproperty regression analysis of density, enthalpy, vapor pressure and other available thermodynamic data using trial functions which are systematically modified to determine an accurate $P(T, \rho)$ relation (Lin et al., 1972; Starling, 1973). It should be noted that the T, ρ dependence for one particular class of fluid may not be adequate for other classes of fluids. Thus, a hierarchy of $P(T, \rho)$ relations may result from the first step in Figure 1 if several classes of fluids are to be described by the correlation.

The second step in CSM-MPCS-EOS correlation is to generalize the equation of state using multiparameter corresponding-states methodology. The corresponding-states method uses properties-correlation characterization parameters to distinguish the effects of molecular-interaction types on thermodynamic properties, e.g., ϵ for molecular-energy interaction, σ for molecular size and γ for molecular accentricity and other mild anisotropies (Brulé et al., 1979, 1982).

The next step in CSM-MPCS-EOS correlation development clarifies the need for binary VLE data using the conformal-solution model to describe composition dependence (Leland et al., 1968; Smith, 1972). For example, for the 3PCS (three-parameter corresponding-states) correlation used herein (Brulé et al., 1982), the following CSM relations have been studied,

$$\sigma_x^a = \sum\sum x_i x_j \sigma_{ij}^a \tag{1}$$

$$\epsilon_x^b \, \sigma_x^c = \sum\sum x_i x_j \epsilon_{ij}^b \, \sigma_{ij}^c \tag{2}$$

$$\gamma_x^d \epsilon_x^e \sigma_x^f = \sum\sum x_i x_j \gamma_{ij}{}^d \epsilon_{ij}^e \sigma_{ij}^f \tag{3}$$

In these types of relations, commonly referred to as "mixing rules," x_i is the mole fraction of the ith component in the mixture, σ_{ii}, ϵ_{ii}, and γ_{ii} are the values of σ, ϵ, and γ for the ith component and the σ_{ij}, ϵ_{ij}, and γ_{ij} $(i \neq j)$ are the so-called unlike interaction parameters. The exponents a, b, c, d, e and f are so-called mixing-rule exponents, which have been determined from theory (Lee et al., 1977) and empirical methods (Lee et al., 1979). The empirical exponents are $a = 4.5$, $b = 1.0$, $c = 4.5$, $d = 1.0$, $e = 0$, and $f = 3.5$. In principal, values for the unlike-interaction parameters, ϵ_{ij}, σ_{ij}, and γ_{ij} $(i \neq j)$, can be determined from thermodynamic-property data of any type for binary mixtures. However, bulk-property data such as density and enthalpy data for mixtures are much less sensitive to the values of the unlike-interaction parameters than are VLE data. This evidently is because the use of the correlation for prediction of VLE requires the computation of property derivatives with respect to composition, while predictions of density and enthalpy do not require composition derivatives. On this basis, data for properties which involve composition derivatives, such as volume of mixing, enthalpy of mixing, Gibbs free energy of mixing and VLE measurements, are most valuable for correlation of composition effects.

Of these data types, VLE data are the most abundant, are generally the easiest to measure experimentally, and can be made to correspond most closely to actual plant conditions (e.g., separators).

In early applications of conformal-solution methods, use was made of so-called combining rules, which express each unlike-interaction parameter as a function of the pure-component parameters, i.e.,

$$\epsilon_{ij} = f(\epsilon_i, \epsilon_j) \tag{4}$$

The most commonly used combining rules for ϵ_{ij} and σ_{ij} (based in part on theory) are

$$\epsilon_{ij} = (\epsilon_i \epsilon_j)^{1/2} \tag{5}$$

$$\sigma_{ij} = \tfrac{1}{2}(\sigma_i + \sigma_j) \tag{6}$$

where the single subscript refers to the pure-component parameter ($\epsilon_i = \epsilon_{ii}$, $\sigma_i = \sigma_{ii}$). The relation for ϵ_{ij} is a geometric combining rule while the relation for σ_{ij} is an arithmetic combining rule. Although a number of other combining rules for ϵ_{ij} and σ_{ij} have been investigated, entirely satisfactory combining rules have not yet been found. For this reason, more recent practice has been to introduce so-called binary-interaction parameters into one or more of the combining-rule relations, i.e.,

$$\epsilon_{ij} = \zeta_{ij}(\epsilon_i \epsilon_j)^{1/2} \tag{7}$$

where ζ_{ij} is the binary-interaction parameter (BIP). Part of the early rationale for determining BIPs (e.g., ζ_{ij}) instead of unlike-interaction parameters (e.g., ϵ_{ij}) was the fact that the BIPs for similar fluids (e.g., heptane with octane) often were near unity and the deviations of the BIPs from unity was a rough measure of the nonideality of solutions of the mixture pair. Unfortunately, the BIPs deviate markedly from unity when there are large differences in the molecular size, shape, etc. of the molecule pair. Nevertheless, the values of the BIPs for a given light fluid (e.g., hydrogen) with a subclass of heavier fluids (e.g., nonpolar polycyclic aromatics) can be correlated as functions of the characterization parameters for the constituents of the binary pairs. Thus, binary VLE data for only a few fluids from a given subclass of fluids (e.g., paraffins) with a given fluid (e.g., methane) are needed to develop correlations for the BIPs for the given fluid with the subclass.

CORRELATION TESTING AND NEED FOR MULTICOMPONENT VLE DATA

After a correlation framework has been developed and pure-fluid and binary-mixture data have been used to establish the parameters in the correlation, the correlation must be tested using multicomponent thermodynamic properties and/or VLE data to be assured that the correlation can describe complex mixtures which are more typical of the systems encountered industrially.

Correlation testing of a sort different from that discussed above creates a need for data for so-called undefined systems. As used herein, an undefined system is a system for which the system components cannot all be identified as individual compounds or for which the number of components is so large that mixture-properties calculations are impractical (i.e., excessive computer time and cost are incurred). Usually, undefined systems are complex-fluid streams in process plants (e.g., the feed, overhead, and bottoms streams for a separator in a coal-liquefaction plant). The compositional analysis of undefined mixtures (e.g., by distillation or other separation methods) usually results in the determination of the amounts of different fractions which contain many components with similar characteristics (e.g., fractions with 25°C boiling ranges). These fractions are then treated as though they were pure components for the purpose of predicting properties and are therefore referred to herein as pseudocomponents or pseudocomponent fractions. To utilize the CSM-3PCS-EOS correlation for predicting the properties of undefined systems, correlations must be developed for estimating the properties-correlation characterization parameters (i.e., ϵ, σ, γ) for each pseudocomponent fraction. These characterization parameters must be correlated as functions of measurable quantities for the pseudocomponent fractions (e.g., average boiling-point temperature, molecular weight, specific gravity, viscosity, etc. for distillation fractions). These characterization-parameter correlations can be developed from pure-fluid characterization-parameter values and then can be tested and improved using mixture data for undefined systems.

TESTING OF VLE DATA USING COMPONENT MATERIAL BALANCES

One hazard that is ever present in correlation development efforts is the fact that erroneous data will affect the correlation adversely. It is important to detect and eliminate erroneous data. The simultaneous use of data from several investigators sometimes can expose an erroneous individual data set. The simultaneous use of several data types in multiproperty analysis sometimes can expose erroneous data for an individual data type. The use of thermodynamic consistency tests based on the Gibbs-Duhem equation sometimes can expose inconsistent VLE data. Unfortunately, these methods for detecting potentially erroneous data do not provide a method for correcting the erroneous data except through the use of the correlation itself, a procedure which should be avoided at all costs. However, if a step back from the data-correlation level to the data-procurement level is taken, then data smoothing procedures can be used productively to expose erroneous data that should be retaken. An important example is the use of component material balances to test the consistency of VLE data.

If the feed flow rate to a single-stage equilibrium separator is taken to be unity ($F = 1$), the component mole balance is

$$z_i = y_i V + x_i(1 - V) \tag{8}$$

The following useful relation can be obtained by solving Eq. 8 for the quantity y_i/z_i,

$$y_i/z_i = 1/V + (x_i/z_i)(V - 1)/V \tag{9}$$

This is the equation of a straight line when values of y_i/z_i for each component are plotted versus the corresponding values of x_i/z_i. This straight line has a slope of $(V - 1)/V$ and an intercept of $1/V$. Since $0 < V < 1$, the slope of this straight line is always negative. Multicomponent VLE data can be plotted as y_i/z_i vs. x_i/z_i to develop a consistency plot to check closure of the component material balance (Brulé et al., 1981). The greatest value of this quick and easy method is in exposing erroneous data, for if a straight line cannot be passed through all data points, some of the data necessarily are in error. Ordinarily, if early in the data program, VLE data are found to be erroneous, the data usually can be retaken. The consistency plot also provides the opportunity to focus on those components which fall off the data consistency line when the remeasurements are made. These components usually occur in either the vapor or the liquid phase in such small mole fractions that the percentage errors in the measured mole fractions are large. Major errors in the data for heavy components usually occur in the vapor phase. Similarly, for light components which have small mole fractions in the liquid phase, the major errors in the data are expected in the liquid phase. This is helpful information for remeasurements and also provides a guideline for drawing the appropriate straight line and correcting the measured phase mole fractions in the event remeasurements are not possible and the available VLE data must be used. The general rule is to draw the straight line using the data points for those components which are present in appreciable mole fractions in both the vapor and the liquid phases. The corrections should then be made for the smallest component mole fractions in a phase.

Besides its use for the detection and correction of VLE data, the component-material-balance consistency plot can be used to test predictions of the vapor/liquid split using correlations. The plot provides values of V from the intercept (or slope) of the plot. Thus, not only can experimental and predicted component phase compositions and K-values be compared for correlation testing but also the separator vapor/liquid split, which is quite important in design (affects equipment sizes and product yields), can be compared.

VLE PREDICTION CAPABILITIES USING CSM-3PCS-MBWR

The three-parameter corresponding-states modified BWR correlation (CSM-3PCS-MBWR) (Brulé et al., 1982) has 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 (Lee et al., 1979) 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 polycyclic aromatic hydrocarbons (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 to 430°C (374 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 defined 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 BIPs, ξ_{ij} and ζ_{ij}, which are used to account for unlike-component interactions in the combining rules, 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:

$$I = \sum_{i=1}^{k} \left[\frac{(T_i^m - T_i^0)^2}{\sigma_{T_i}^2} + \frac{(P_i^m - P_i^0)^2}{\sigma_{P_i}^2} + \frac{(x_1^m - x_1^0)^2}{\sigma_{x_{1i}}^2} + \frac{(y_1^m - y_1^0)^2}{\sigma_{y_{1i}}^2} + \frac{(K_1^m - K_1^0)^2}{\sigma_{K_{1i}}^2} + \frac{(K_2^m - K_2^0)^2}{\sigma_{K_{2i}}^2} \right] \quad (10)$$

The phase-equilibrium constraints are:

$$\hat{f}_i^v = \hat{f}_i^L \qquad i = 1, 2 \quad (11)$$

expressed explicitly,

$$y_1 \hat{\phi}_1^v (T, P, y_1, y_2) = x_1 \hat{\phi}_1^L (T, P, x_1, x_2) \quad (12)$$

$$y_2 \hat{\phi}_2^v (T, P, y_1, y_2) = x_2 \hat{\phi}_2^L (T, P, x_1, x_2) \quad (13)$$

where $\hat{\phi}_i$ are fugacity coefficients.

BINARY VLE PREDICTION

Table 1 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 2; the overall %AARDs for K_1 are 6.16, 5.64, 3.37, and 3.64, respectively. Figures 2 through 5 provide a visual comparison of the experimental vs. predicted K-values of light gases + PCAHs 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 3.

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. 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 (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

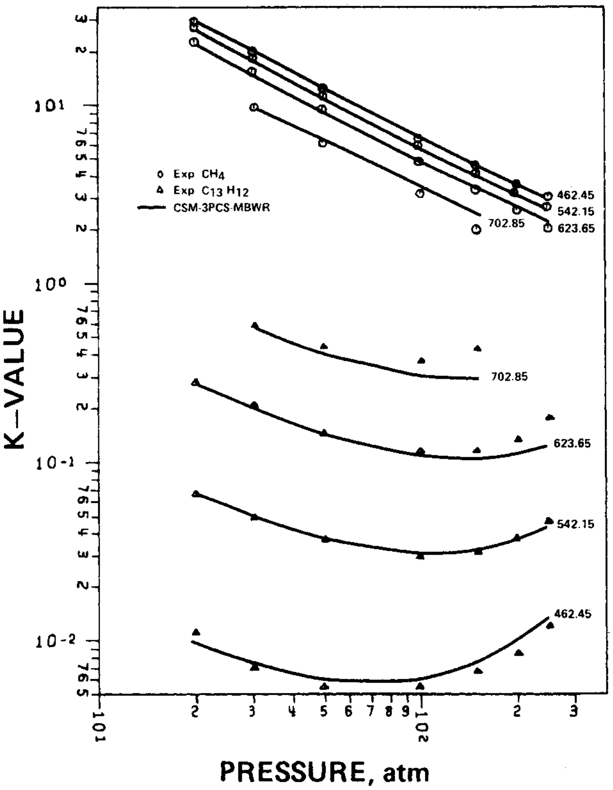

Figure 3. Comparison of methane and diphenylmethane K-values with those predicted by the CSM-3PCS-MBWR correlation.

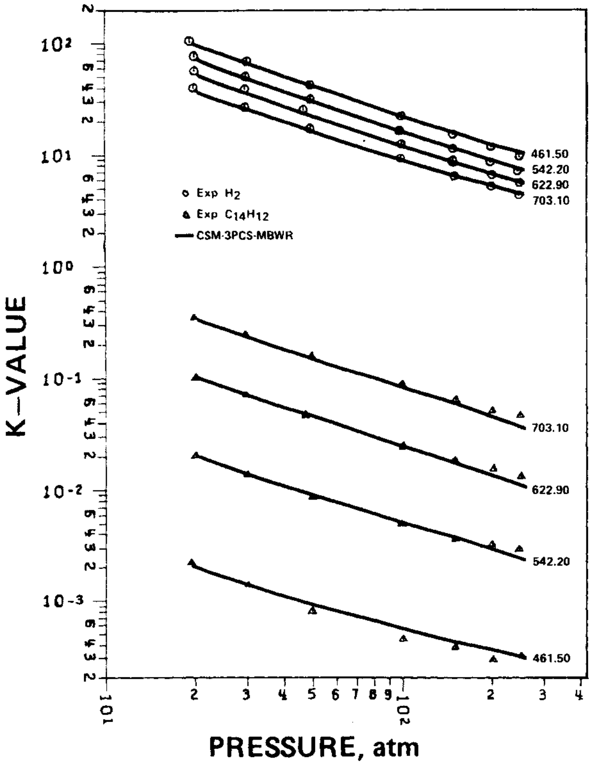

Figure 2. Comparison of hydrogen and 9, 10-dihydrophenanthrene K-values with those predicted by the CSM-3PCS-MBWR correlation.

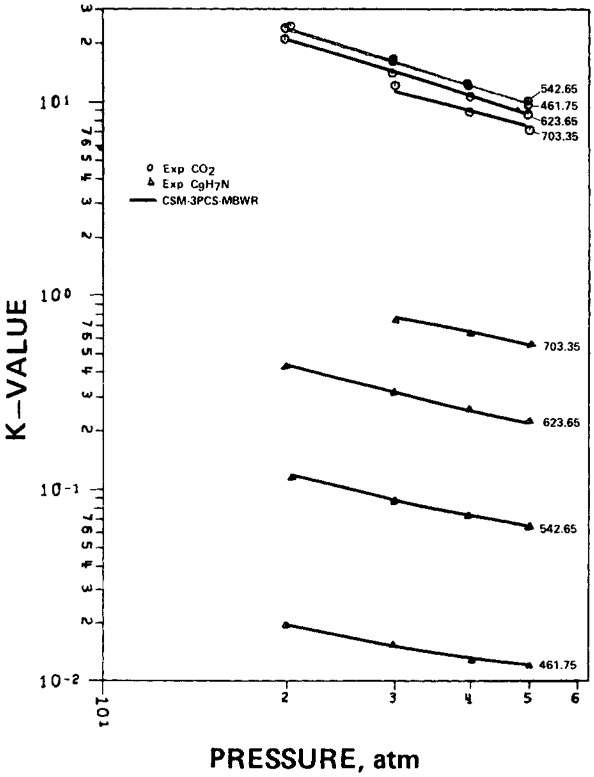

Figure 4. Comparison of carbon dioxide and quinoline K-values with those predicted by the CSM-3PCS-MBWR correlation.

TABLE 1. BINARY-INTERACTION PARAMETERS FOR DEFINED COMPONENTS[1]

	H_2	N_2	CO	CO_2	H_2S	H_2O	Methane
N_2	ξ_{ij} 1.02116						
	1.08378						
CO	ξ_{ij} 1.10974	1					
	0.54651	1					
CO_2	0.98438	1.00715	1				
	1.39935	1.08921	1				
H_2S	1	1.01753	1	1.01396			
	1	1.02279	1	0.92472			
H_2O	0.84649	0.89680	1	0.93949	0.97389		
	1.35568	1.30323	1	1.07950	1.08822		
Methane	1.12777	1.03399	1	0.98933	1.00044	0.74468	
	1.43874	0.96381	1	0.99122	1.00066	0.21272	
Ethane	1.04205	1.01715	1.01526	1.15510	0.99525	1	0.99992
	1.20040	0.92233	0.97647	0.85965	0.94637	1	0.97959
Propane	1.06895	1.03410	1.04531	1.04473	1.06237	1	1.01188
	1.25144	0.88779	0.94447	0.84856	0.88593	1	0.93684
n-Butane	1.07701	1.07661	1	1.05828	(1.062)	0.68169	1.03002
	1.14592	0.91347	1	0.80422	(0.86)	0.25978	0.89247
n-Pentane	(1.087)	1	1	1.06222	(1.062)	1	1.03220
	(1.069)	1	1	0.77926	(0.835)	1	0.86098
Benzene	1.03604	1.04793	1	1.06120	1	1	1.05562
	0.85238	0.84785	1	0.81353	1	1	0.93614
Cyclohexane	1.08337	1	1	(1.033)	1	1	1.04492
	0.96081	1	1	(0.723)	1	1	0.84716
n-Hexane	1.09412	1	1	1.07725	(1.063)	1	1.05049
	0.99088	1	1	0.76891	(0.81)	1	0.83257
Toluene	1.11066	1	1	1.06900	1.05001	1	1.06344
	1.31810	1	1	0.78159	0.85585	1	0.89874
m-Cresol	1.04271	1	1	1.06057	1	1	1.04193
	1.16955	1	1	0.87031	1	1	1.00440
n-Heptane	(1.106)	1.05180	1	1.08024	1.06363	1	1.06234
	(0.987)	0.67961	1	0.75104	0.78620	1	0.81665
m-Xylene	1.08272	1	1	(1.060)	1	1	1.07348
	0.89440	1	1	(0.717)	1	1	0.86740
n-Octane	(1.115)	1	1	(1.094)	(1.084)	1	1.05112
	(0.983)	1	1	(0.730)	(0.776)	1	0.75148
n-Nonane	(1.124)	1	1	(1.097)	1.10474	1	1.07753
	(0.979)	1	1	(0.714)	0.76698	1	0.79909
Tetralin	1.11696	1	1	1.09863	1	1	1.08889
	0.98839	1	1	0.72025	1	1	0.85009
n-Decane	1.13417	1.09018	1	1.11172	(1.124)	1	1.12205
	0.97546	0.71972	1	0.69768	(0.758)	1	0.85972
1-Methylnaphthalene	1.10596	1	1	1.09054	1	1	1.06982
	0.95867	1	1	0.71916	1	1	0.82637
Bicyclohexyl	1.13437	1	1	(1.109)	1	1	(1.090)
	0.90479	1	1	(0.699)	1	1	(0.757)
Diphenylmethane	1.12998	1	1	1.10504	1	1	1.08878
	0.88391	1	1	0.73801	1	1	0.78261
Quinoline	1.07129	1	1	1.07057	1	1	1.05230
	0.86521	1	1	0.77029	1	1	0.87391
Thianaphthene	1.10239	1	1	(1.07)	1	1	(1.072)
	0.83601	1	1	(0.715)	1	1	(0.846)
9,10-Dihydrophenanthrene	1.13893	1	1	(1.113)	1	1	1.09443
	0.77175	1	1	(0.696)	1	1	0.72671
Phenanthrene	1.10910	1	1.07806	1.11066	1	1	0.93799
	0.45423	1	0.59201	0.65852	1	1	0.41165
n-Hexadecane	1.16886	1	1	1.15176	1	1	1.13154
	0.84807	1	1	0.66138	1	1	0.76822

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[1] Parentheses indicate estimated values.

TABLE 2. PREDICTION OF PHASE-EQUILIBRIUM BEHAVIOR OF BINARY MIXTURES USING THE CSM-3PCS-MBWR

				% AARD				
Systems	N	T Range K	P Range atm	Liq. Comp. of 1st Cmpn x_1	Vap. Comp. of 1st Cmpn y_1	K-Value of 1st Cmpn K_1	K-Value of 2nd Cmpn K_2	Data References
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	Hong and Kobayashi, 1981
Ethane	25	172–283	7–272	4.86	2.05	6.00	16.98	Cohen et al., 1967

TABLE 2. *Continued*

				% AARD				
Systems	N	T Range K	P Range atm	Liq. Comp. of 1st Cmpn x_1	Vap. Comp. of 1st Cmpn y_1	K-Value of 1st Cmpn K_1	K-Value of 2nd Cmpn K_2	Data References
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	4.96	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
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	Ng et al., 1980
n-Heptane	28	311–478	6– 94	4.33	1.04	4.87	9.36	Ng 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	Sebastian et al., 1980d
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
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	Gugnoni 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	Ng and Robinson, 1978
n-Heptane	47	311–477	16–131	4.67	0.69	4.53	8.74	Kalra et al., 1978

TABLE 2. *Continued*

Systems	N	T Range K	P Range atm	% AARD Liq. Comp. of 1st Cmpn x_1	Vap. Comp. of 1st Cmpn y_1	K-Value of 1st Cmpn K_1	K-Value of 2nd Cmpn K_2	Data References
Tetralin	15	462–665	20– 51	1.18	0.99	1.44	1.73	Sebastian et al., 1980f
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	Sebastian et al., 1980e
m-Cresol	14	463–665	19– 51	2.02	1.05	2.77	2.48	Sebastian et al., 1980e

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[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 1.

TABLE 3. COMPARISON OF K-VALUE DEVIATIONS[1] FOR COAL-SOLVENT MIXTURES ESTIMATED USING DIFFERENT CORRELATIONS

Systems	Temp. Range °C	Pres. Range atm	CSM-3PCS-MBWR K_1	K_2	Penn State Modified Soave Eq. K_1	K_2	Grayson-Streed Method[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

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[1] $\%AARD = \frac{1}{N}\sum_{1}^{N}\left|\frac{K_{exp} - K_{calc}}{K_{exp}}\right| \times 100$

[2] Frith et al. (1979).

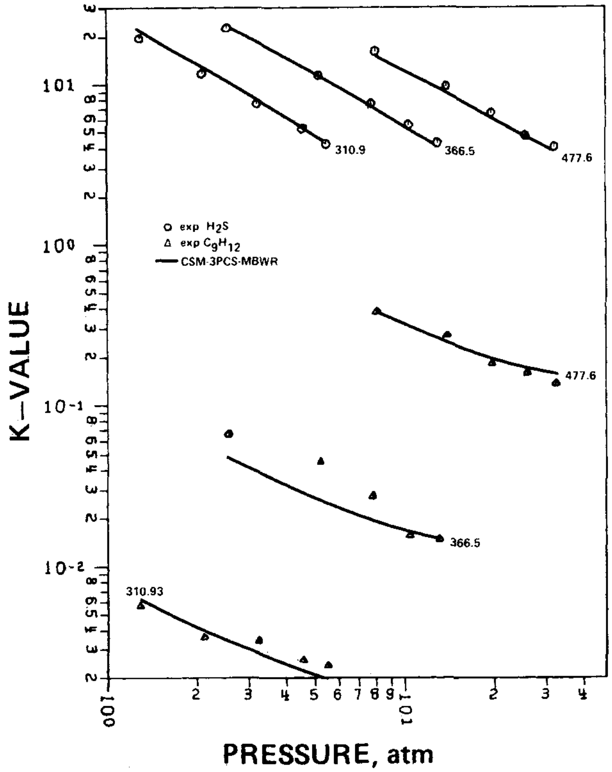

Figure 5. Comparison of hydrogen sulfide and mesitylene *K*-values with those predicted by the CSM-3PCS-MBWR correlation.

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 that may coexist in water + hydrocarbon systems (Watanasiri, 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 difficult systems.

GENERALIZED PREDICTION OF BIPS

To facilitate prediction of VLE for light gases and complex fractions, 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 4. Certain deterioration in the predicted results is incurred when using the generalized BIPs, as shown in Table 5. 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. The generalized BIP correlations should be used with caution beyond the ranges recommended in Table 4.

TERNARY VLE PREDICTION

As was pointed out earlier, because binary VLE data are used in CSM-MPCS-EOS correlation development, predictions for systems containing three or more components provide more stringent tests of the correlation. 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 6. Figures 6 and 7 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 calcu-

TABLE 4. GENERALIZED CORRELATIONS FOR THE BINARY-INTERACTION PARAMETERS OF HYDROGEN, METHANE, AND CARBON DIOXIDE WITH PCAHS

Binary System with	$\xi_{ij} = a + bX$		$\zeta_{ij} = c + dY$		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 5. 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
H_2 + Tetralin	4.72	7.52	5.62	7.58
H_2 + 1-Methylnaphthalene	4.88	9.88	20.10	10.20
H_2 + Diphenylmethane	4.17	10.62	5.52	11.98
H_2 + 9,10-Dihydrophenanthrene	3.53	7.61	9.24	18.50
CH_4 + Tetralin	4.71	9.27	10.90	14.70
CH_4 + 1-Methylnaphthalene	7.23	11.88	11.56	9.90
CH_4 + Diphenylmethane	3.59	8.87	10.17	9.34
CH_4 + 9,10-Dihydrophenanthrene	4.19	6.96	8.68	10.78
CO_2 + Tetralin	1.44	1.73	9.59	6.41
CO_2 + 1-Methylnaphthalene	2.76	2.25	6.47	3.14
CO_2 + Quinoline	2.04	1.37	5.86	4.81

[1] BIPs, ξ_{ij} and ζ_{ij}, determined from VLE data regression.

[2] BIPs determined from generalized correlations in Table 4, K_1 and K_2 are calculated via a flash calculation in which temperature and pressure are specified.

lations. Prediction accuracy for these ternaries 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). Simultaneous regression of both binary and ternary data was undertaken to improve prediction accuracy. 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 better than if only the binary pairs are used individually in the data-reduction process.

PREDICTION OF LIGHT-GAS SOLUBILITY IN COAL LIQUIDS

Lin et al. (1981) 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 ϵ, σ, and γ for each fraction using the characterization equations given by Brulé et al. (1982). Each 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 4. Results of the solubility predictions are summarized in Table 7.

The predicted results are generally satisfactory, especially for the SRC-II fractions with 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. Figure 8 shows the effects, on predicted hydrogen solubility deviations, of molecular weight (M) and distillate-fraction boiling-temperature range (ΔT_b). In Figure 8, the fraction boiling-point-temperature range, ΔT_b (in °C), and average molecular weight, M, are shown in parenthesis (ΔT_b, M) for each data point. The large deviation for the highest average molecular-weight SRC-II fraction ($M = 252$) is possibly due to the fact that this fraction contains some high-molecular-weight compounds, so that the characterization of the fraction is inadequate for the use of correlations for ϵ, σ, and γ. The presence of these diverse compounds in the wide-boiling-range SRC-II distillate fraction possibly weakens the assumption that the fraction can be treated as a pseudocomponent (i.e., as a pure compound). For combinations of fraction boiling-point-temperature ranges below 28°C (50°F) and average molecular weights below 212, hydrogen-solubility deviations are no greater than 10%, which is reasonable for design purposes. It is obvious from this study that work is needed to establish what fraction-boiling-range limitations for analyses are imposed by correlations. Work also is needed to improve capabilities to characterize higher-molecular-weight fractions and to better correlate properties-correlation characterization parameters as functions of measurable quantities for high-molecular-weight fractions.

COAL-FLUID VAPOR/LIQUID-EQUILIBRIUM PREDICTION

VLE data in conjunction with characterization information 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 2,500 psig). The K-values are reported in terms of 10 defined

TABLE 6. 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
$H_2(1)$ + $CH_4(2)$ + Tetralin (3)	462–663	50–252	6.50	5.65	10.16
H_2 + CH_4 + 1-Methylnaphthalene	542–704	50–250	5.63	7.82	8.92
H_2 + CO_2 + Tetralin	543–663	50–250	7.52	5.37	6.66
H_2 + CO_2 + 1-Methylnaphthalene	543–704	50–252	7.49	7.04	7.52
H_2 + CO_2 + Quinoline	543–704	50–252	8.06	6.36	9.29
H_2 + Tetralin + m-Xylene	462–582	20–250	5.19	9.19	8.22
H_2 + Tetralin + Diphenylmethane	461–701	20–250	6.77	10.82	10.33

[1] See Chao et al., 1980.

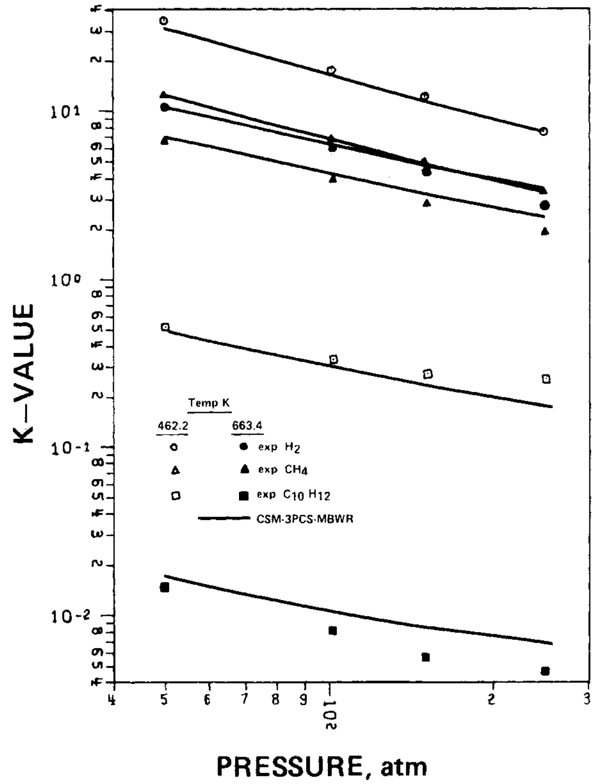

Figure 6. Comparison of hydrogen, methane, and tetrlin *K*-values with those predicted by the CSM-3PCS-MBWR correlation.

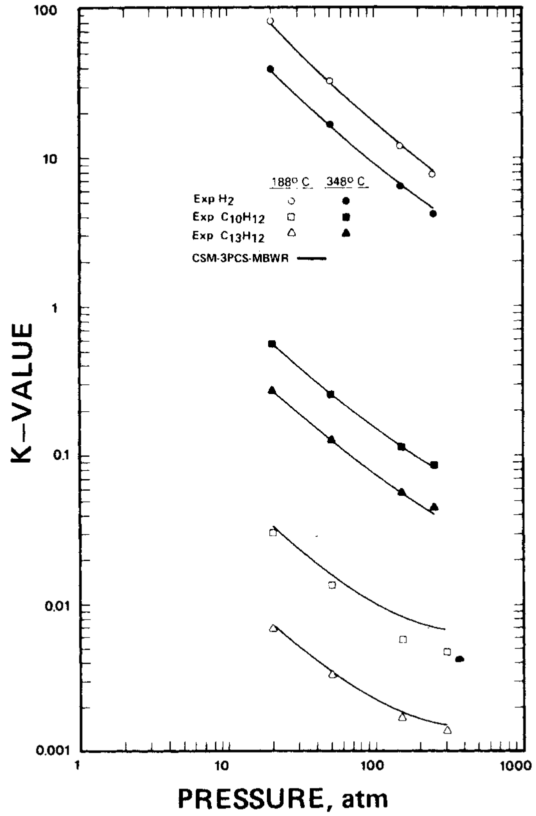

Figure 7. Comparison of hydrogen, tetralin, and diphenylmethane *K*-values with those predicted by the CSM-3PCS-MBWR correlation.

TABLE 7. PREDICTION OF THE SOLUBILITY OF HYDROGEN AND METHANE IN EDS AND SRC-II COAL LIQUIDS

System[1]	Coal-Liquid Boiling Point Range (°C) T_b	Avg. mol wt. M	% AARD
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

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[1] See Lin et al. (1981).

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 was used to estimate the characterization parameters ϵ, σ, and γ of each fraction (using methods of Brulé et al., 1982). The BIPs for defined + defined binary pairs are those reported in Table 1. The BIPs for defined + undefined boiling fractions are calculated from the generalized BIP correlations given in Table 4. The BIPs for all remaining binary pairs are taken to be unity. Predicted K-values using the CSM-3PCS-MBWR are compared with the experimental data in Table 8.

The accuracy of the predictions are good for some of the components (e.g., hydrogen and methane), but 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 residua overextends the range of validity of the

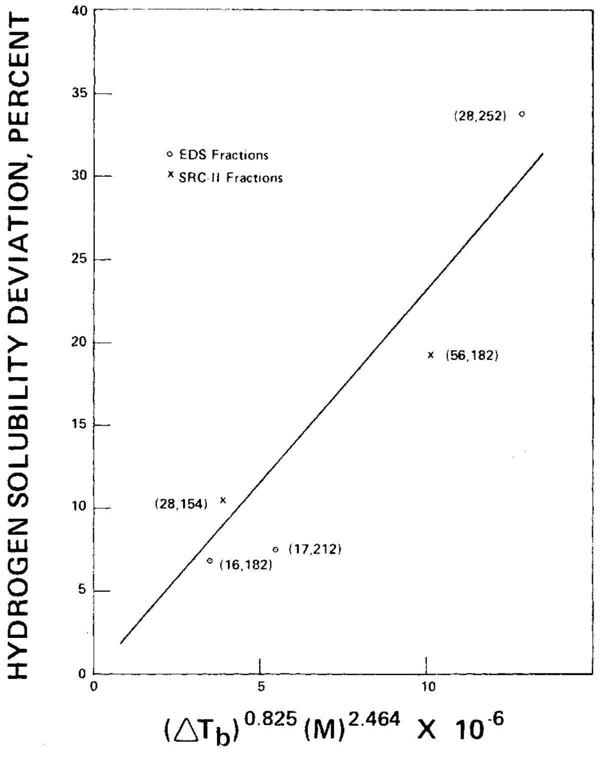

Figure 8. Deviations of predicted hydrogen solubility as functions of EDS and SRC-II distillate fraction molecular weight and boiling temperature range.

TABLE 8. PREDICTION OF K-VALUES, FOR COMPONENTS IN THE STREAMS FROM THE H-COAL PROCESS HOT SEPARATOR, USING THE CSM-3PCS-MBWR

Component	Molecular weight	Gravity API	K-Value[2] Exp.	K-Value[2] 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 + Residuum	550.	−20.	0.0	0.000

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[1] See IGT (1980).

[2] Pressure = 171 atm (2,500 psi).
Temperature = 706.5 K (812°F).

characterization correlations. However, only when more data are measured for heavier fluids can characterization correlations be developed for residua present in 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.

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NOTATION

$\hat{f}_i$ = fugacity of component i
K_i = equilibrium vaporization ratio y_i/x_i
M = fraction average molecular weight
S = specific gravity
T = absolute temperature
T_b = normal boiling temperature
v = molar volume
V = molar flow rate of overhead vapor
x_i = liquid-phase mole fraction
y_i = vapor-phase mole fraction
z_i = mole fraction of the ith component in feed stream

Greek Letters

ϵ = characteristic molecular-energy parameter
γ = molecular orientation parameter
ρ = molar density
σ = characteristic molecular-size parameter
ξ_{ij} = molecular-size binary-interaction parameter
ζ_{ij} = molecular-energy binary-interaction parameter
ϕ_i = fugacity coefficient of component i
σ^2 = variance of experimental data

Superscripts

L = liquid phase property
m = measured variable
o = estimate of the true value of the variable
V = vapor phase property

Subscripts

i = component i
ij = binary pair, ij
x = mixture property

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Approximate Solutions to Explosion Kinetics

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Stiffness in combustion models is quite different from that in more conventional kinetic descriptions. The steady-state approximation, so useful in other contexts, cannot be applied in the usual *ad hoc* manner but can be applied with attention to its origins in singular perturbation analysis. The magnitude and time scaling on the equations representing the isothermal kinetics of hydrogen combustion reveal distinct regions of the transient to which this approximation may naturally and successfully be made to reduce computation time. The steady-state approximation is found to apply to some free radicals, but not all, and these can change between regions. An analytical solution to an important section of the transient is found and illustrates dramatically the power of the approach. The analysis may be applied *a priori* and leads to a stagewise efficient numerical solution.

SCOPE

Great strides have been made in the development of fast methods for the numerical solution of stiff differential equations. These methods for the most part certainly apply to mass action kinetics with its simple nonlinearitives and sparse structure. They are not always sufficient, however, for mass action kinetics modeling combustion processes in which there is an explosion. (See Aiken, 1981c, for a definition of an explosion.) One reason for this is the severe efficiency demands placed on the kinetics integration routine when included in a much larger program that models a real non-homogeneous combustor; the kinetics set must be solved many times for each spacial grid. Another and more fundamental reason for the special computational problems for combustion kinetics is associated with the fact that the narrow region of the domain containing the fast dynamics is often of interest, unlike for most kinetic descriptions. This "flamezone" does not occur initially in the solution as the more common "boundary layer" but internal to the time domain (or space if this is the independent variable). Thus, we want to take large steps before and after the flame heart but not within, and this is not necessarily compatible with stiff software designed to cover the domain with nothing but big steps. Recognition of time scales and examination of the solution behavior therein is performed nicely by singular perturbation analysis used here. In particular, the power of the steady-state approximation may be used to significantly reduce computation time while preserving all required solution information.

CONCLUSIONS AND SIGNIFICANCE

Combustion kinetic data is becoming more readily available with much improved experimental technique and funding encouraged by the energy crisis. Optimal design and operation of real combustors can undoubtedly be better approached with analysis as has their simpler chemical reactor counterparts. Because of the model complexity required, however, improvements in computation speed must be found first. Even a small improvement in the efficiency of calculating the kinetic step is significant in this regard. A very significant simplification for stiff dynamic systems is found in the steady-state approximation. This approximation has not heretofore been successfully applied to combustion systems; the reasons for this are examined here. Chemical knowledge may be used through these approximations to arrive at a simpler model that is not stiff and thus does not have the associated computational problems. The analysis presented here for the hydrogen-oxygen reaction is completely applicable to other, larger problems where its effect should be more dramatic. The insights obtained through this technique also provide fundamental modeling information useful in parameter estimation and planning of experiments.

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