

and 18 is 400 to 700 °F. Equation 7 is applicable at normal pressures of less than 3 atm. When eq 7 was tested against values of thermal conductivity obtained by the API Data Book, an average deviation of 3.0% and maximum deviation of 15% were observed for 126 data points. An average deviation of 6.4% was obtained when eq 2 was used. A summary of evaluations for eq 7 and 2 is given in Table III.

Although the accuracy of the proposed correlations for the thermal conductivity of liquids and vapors is not much better than the previously recommended methods, they can predict values of thermal conductivity within the accuracy of experimental measurements. In addition, the proposed correlations are simple and suitable for use by pocket calculator or a large computer. It has been shown that for nonpolar compounds, boiling point and specific gravity are the minimum number of parameters required to predict a transport property such as thermal conductivity. This is the biggest advantage of the proposed equations over the previous correlations, since for compounds which their critical properties are not available, their thermal conductivities can be estimated by only the knowledge of normal boiling points and specific gravities. For polar compounds most probably an additional input parameter indicating the degree of polarity is required.

#### Nomenclature

$A, B, C$  = parameters in eq 15  
 $C_1, C_2$  = parameters in eq 8  
 $a, b, c$  = parameters in eq 3, 4, 5, 7

$A_1, a_1, b_1, c_1, d_1, e_1, f_1$  = parameters in eq 6  
 $C_p$  = isobaric heat capacity, Btu/(lb-mol °F)  
 $k$  = thermal conductivity, Btu/h ft °F  
 $k_0$  = thermal conductivity of liquids at 0 °F, Btu/(h ft °F)  
 $k_{300}$  = thermal conductivity of liquids at 300 °F, Btu/(h ft °F)  
 $M$  = molecular weight  
 $n$  = parameter in eq 1  
 $P_c$  = critical pressure, atm abs  
 $S$  = specific gravity at 60/60 °F  
 $T$  = temperature, °F  
 $t = T/100$   
 $T_b$  = normal boiling point, °R  
 $T_c$  = critical temperature, °R  
 $T_r$  = reduced temperature,  $T/T_c$   
 $V_c$  = critical volume, ft<sup>3</sup>/lb<sub>m</sub>  
 $V_m$  = liquid molar volume at 68 °F, ft<sup>3</sup>/lb-mol  
 $\phi$  = any physical property  
 $\lambda$  = parameter in eq 2,  $T_c^{1/6} M^{1/2} P_c^{2/3}$

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## Analysis of Vapor-Liquid-Liquid Equilibrium in Coal Conversion Processes

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A new framework for analysis of vapor-liquid-liquid equilibrium has been developed. In this framework, the pure liquid fugacity is defined as the reference fugacity for all solvent species, and Henry's constant is defined as the reference fugacity for all solute species. This applies to vapor-liquid (V-L), liquid-liquid (L-L), and vapor-liquid-liquid (V-L-L) equilibrium as well. A data reduction scheme that generates a consistent set of Henry's constant and activity coefficient parameters from isothermal and nonisothermal binary vapor-liquid, liquid-liquid, and vapor-liquid-liquid equilibrium data has been developed. The results of data reduction for several sets of vapor-liquid, liquid-liquid, and vapor-liquid-liquid equilibrium data are presented.

The occurrence of three phases is quite common in coal conversion processes. The major components in coal conversion systems are water, light hydrocarbon liquids, oils, tars, and gases such as hydrogen, carbon monoxide, carbon dioxide, and methane. Minor components include hydrogen sulfide, ammonia, nitrogen, argon, carbonyl sulfide, and hydrogen cyanide. Possible difficulties in the prediction of three-phase equilibria for coal conversion systems are summarized below.

**1. High Temperatures and Pressures.** Coal conversion processes typically operate at high temperatures and pressures. The bulk of the data on systems of interest is at low-to-moderate temperatures and pressures. Often, only nonisothermal gas or mutual solubility data are available. Furthermore, at these high temperatures, most of the light gas components such as hydrogen, carbon monoxide, carbon dioxide, and methane are supercritical. The pure liquid reference fugacity is not readily applicable to supercritical components.

**2. Large Quantities of Water.** Unlike applications in petroleum processing, large quantities of water appear in the gas from the coal conversion reactor. Upon con-

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densation, a second aqueous liquid phase is formed. The phase behavior of water is not adequately handled by most property prediction methods.

**3. Large Quantities of Hydrogen.** Hydrogen is a major constituent of the gas from a coal conversion reactor, and most property prediction methods apply special procedures to it that are not always satisfactory.

**4. Weak Electrolytes.** The gas from coal conversion reactors contains weak electrolyte species such as  $H_2S$ ,  $CO_2$ ,  $NH_3$ , and  $HCN$ . These components ionize in solution, and the ions react chemically. Therefore, property prediction methods that take only physical equilibrium into account are not suitable.

**5. Complex Coal Liquids.** Over the years, the petroleum industry has developed procedures for breaking a "complex" crude assay into cuts or pseudocomponents. The pseudocomponents are usually characterized by the API gravity, normal boiling point, molecular weight, and Watson characterization factor. These parameters can in turn be related to critical properties and the acentric factor. An approach of this type might be possible for coal liquids, but, since coal liquids are highly aromatic and heavier than petroleum products, it is unlikely that petroleum correlations can be applied directly to the characterization of coal liquids.

Phase equilibrium prediction methods rely on two thermodynamic frameworks. One method involves separate descriptions of the vapor and liquid phases, and the other uses a single equation of state to describe both phases. The presence of large quantities of water and weak electrolyte species in coal conversion processes supports the use of a methodology employing separate equations for each phase. Given the highly supercritical nature of the gas phase in coal conversion systems, the pure liquid is not a suitable reference state for a majority of the components. Further, as Prausnitz (1977) has pointed out, weak electrolytes tend to ionize in solution. Ions by definition are nonvolatile, and a pure-liquid reference fugacity does not exist for them. We thus chose to represent VLE for a solute  $j$ -solvent  $i$  binary system by the relationships proposed by Prausnitz and Chueh (1968).

$$H_j \gamma_j^* x_j \exp(P \bar{V}_j^L / RT) = P y_j \phi_j^v \quad (1)$$

$$P_i^\circ v_i^\circ \gamma_i x_i \exp((P - P_i^\circ) \bar{V}_i^L / RT) = P y_i \phi_i^v \quad (2)$$

The asterisk in  $\gamma_j^*$  is a flag that indicates that the activity coefficient is normalized in a symmetric convention. In a recent monograph by Prausnitz et al. (1980), Henry's constants were adopted as the reference fugacity for non-condensable components. However, for liquid-liquid equilibrium, Prausnitz et al. (1980) used the same pure liquid reference fugacity for the component in both liquid phases. Their criterion for liquid-liquid equilibrium is

$$(x_i \gamma_i)^{L_1} = (x_i \gamma_i)^{L_2} \quad (3)$$

If the partially miscible components in binary LLE are normalized in the asymmetric convention, we obtain

$$(P_i^\circ v_i^\circ \gamma_i x_i \exp((P - P_i^\circ) \bar{V}_i^L / RT))^{L_1} = (H_i x_i \gamma_i^* \exp(P \bar{V}_i^L / RT))^{L_2} \quad (4)$$

$$(H_j \gamma_j^* x_j \exp(P \bar{V}_j^L / RT))^{L_1} = (P_j^\circ v_j^\circ \gamma_j x_j \exp((P - P_j^\circ) \bar{V}_j^L / RT))^{L_2} \quad (5)$$

In eq 4 and 5, components  $i$  and  $j$  have different reference states in the two liquid phases.

In eq 4 and 5, the primary temperature effect is accounted for by the vapor pressure and Henry's constant. Therefore, activity coefficients play only a secondary role

in this framework, and quite often they are not necessary in the description of LLE.

Equations 1, 2, 4, and 5 provide a thermodynamic framework for the representation of vapor-liquid and liquid-liquid equilibria. Since the equations are consistent for both types of equilibria, they can be used together to represent vapor-liquid-liquid equilibria (VLLE). We propose therefore the pure liquid fugacity at system temperature and zero pressure for all solvent species and Henry's constant at system temperature and zero pressure for all solute species as reference fugacities for VLLE and its subsets.

The methodology here is applicable to systems for which both liquid phases consist of a solvent and relatively dilute solutes. Solute concentrations must be sufficiently dilute for the solute behavior to be adequately described by Henry's law.

### Pure Component and Binary Properties

Following is a summary of the procedures used in this study for the estimation of vapor pressures, pure component liquid fugacity coefficients, vapor-phase fugacity coefficients, Poynting corrections, Henry's constants, and activity coefficients.

The five-parameter correlation of Yaws (1977) was used to calculate vapor pressures. Pure component liquid fugacity coefficients were estimated from the Lyckman et al. (1965) extension of the Pitzer-Curl correlation.

The De Santis-Breedweld-Prausnitz (1974) equation was used to calculate vapor-phase fugacity coefficients. This equation allows the splitting of the energy parameter  $a$  into a polar and nonpolar contribution. For nonpolar components, the equation reduces to the Redlich-Kwong equation.

Poynting corrections were calculated by using the modification of the Rackett equation proposed by Spencer and Danner (1972) to estimate saturated liquid molar volumes.

Henry's constants were represented by the equation

$$\ln H = A + B \ln T + C/T + DT \quad (6)$$

The coefficients were determined as part of the data reduction procedure.

The UNIQUAC as modified by Anderson and Prausnitz (1978) containing two binary parameters was used in the asymmetric representation to correlate activity coefficients. The following assumptions were employed. (1) There is only one solvent species in each liquid phase. (2) All interactions between the solute species in the liquid phase are ideal. The activity coefficient of solvent  $i$  in the asymmetric convention for a multicomponent system is

$$\ln \gamma_i = \ln \frac{\Phi_i}{x_i} + \left( \frac{Z}{2} \right) q_i \ln \frac{\theta_i}{\Phi_i} + l_i - \frac{\Phi_i}{x_i} \sum_j^N x_j l_j - q'_i \ln \left( \sum_j^N \theta'_j \tau_{ji} \right) + q'_i - q'_i \sum_j^N \frac{\theta'_j \tau_{ij}}{\sum_k^N \theta'_k \tau_{kj}} \quad (7)$$

In the above equations,  $\Phi_i$ ,  $\theta_i$ ,  $\theta'_i$ , and  $l_i$  are obtained as

$$\Phi_i = r_i x_i / \sum_j^N r_j x_j \quad (8)$$

$$\theta_i = q_i x_i / \sum_j^N q_j x_j \quad (9)$$

$$\theta'_i = q'_i x_i / \sum_j^N q'_j x_j \quad (10)$$

The binary parameter  $\tau_{ij}$  is expressed as

$$\tau_{ij} = \exp[-(U_{ij} - U_{ji})/RT] = \exp[-\Delta U_{ij}/RT] \quad (11)$$

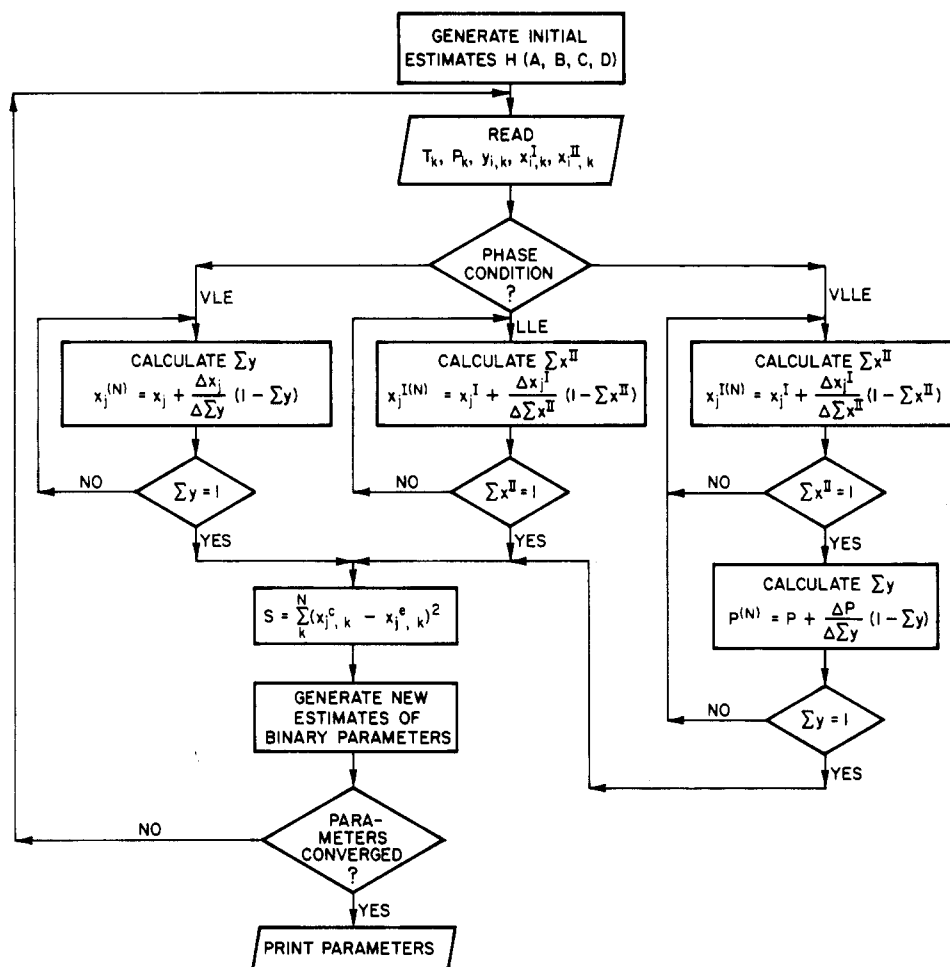


Figure 1. Computational scheme for reduction of three-phase equilibrium data.

Values of the pure component structural parameters  $r$ ,  $q$ , and  $q'$  are reported by Anderson and Prausnitz (1978) and can also be estimated by the group-contribution method of Bondi (1968). The activity coefficient of the solvent component in eq 7 takes account of interactions with all components. The activity coefficient of the solute species in the asymmetric convention for a multicomponent system is

$$\ln \gamma_j^* = \ln \frac{\Phi_j r_i}{x_j r_j} + \left[ \frac{Z}{2} \right] q_j \ln \frac{\theta_j r_j q_i}{\Phi_j r_i q_j} - \Phi_j \left( l_j - \frac{r_j l_i}{r_i} \right) - q'_j \ln \left[ \frac{\theta'_j + \theta'_i \tau_{ij}}{\tau_{ij}} \right] + q'_j \left\{ \tau_{ji} - l + \theta'_i \left[ \frac{\tau_{ij}}{(\theta'_j + \theta'_i \tau_{ij})} - \frac{\tau_{ji}}{(\theta'_i + \theta'_j \tau_{ji})} \right] \right\} \quad (12)$$

The composition variables  $\Phi$ ,  $\theta$ , and  $\theta'$  in eq 12 are computed from eq 8, 9, and 10, respectively, with the provision that the summation in the denominator is over two components only—solvent  $i$  and solute  $j$ . This follows from the second assumption made earlier. The activity coefficient of solute  $j$  in the symmetric and asymmetric conventions are related by

$$\gamma_j^* = \gamma_j / \gamma_j^\infty \quad (13)$$

where  $\gamma_j^\infty$  is the activity coefficient at infinite dilution.

#### Data Reduction

The methodology proposed here is based, in part, on the fact that very little isothermal  $P$ - $x$  data are available for systems of interest in coal conversion processes. There is

almost no V-L-L or multicomponent data available in the literature for these systems. Typically, nonisothermal  $T$ - $x$  gas or mutual solubility data are available. Values for the parameters  $A$ ,  $B$ ,  $C$  and  $D$  in eq 6 for Henry's constant and the parameters  $\Delta U_{ij}$  and  $\Delta U_{ji}$  in eq 11 for activity coefficients are to be determined from experimental data. Our goal was to obtain one consistent set of binary parameters for performing V-L, L-L, and V-L-L equilibrium calculations. This was accompanied by reducing the available V-L-L, V-L, and L-L data simultaneously.

Several objective functions have been proposed for use in the determinations of activity coefficient parameters. Prausnitz et al. (1967) presented several objective functions for reduction of Henry's constant and asymmetric activity coefficient parameters from V-L equilibrium data. One of the objective functions they recommend is

$$S = \sum_k^N (x_{jk}^c - x_{jk}^e)^2 \quad (14)$$

where  $x_j$  is the liquid-phase composition of the solute component. We employed eq 14 in the processing of binary V-L, L-L, and V-L-L equilibrium data. When initial estimates of binary parameters were used vapor, and liquid compositions were computed at the experimental values of  $P$  and  $T$  for VLE and LLE data and at the experimental value of  $T$  for VLLE. Minimizing  $S$  in eq 14 provided the basis for determination of values for binary parameters. The scheme for performing the equilibrium calculations required in the reduction of binary V-L, L-L, and V-L-L data is shown in Figure 1. The computation was carried out by a nonlinear multiple regression algorithm. This algorithm is a slightly modified version of the SHARE

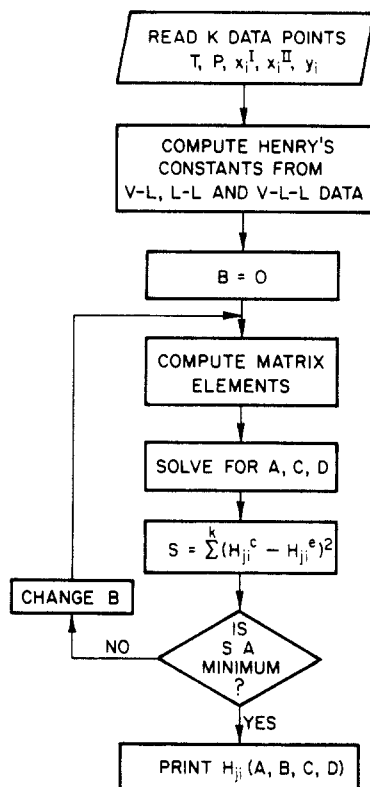


Figure 2. Initial estimates of Henry's constant parameters.

program written by R. S. Gardner and used by Prausnitz et al. (1967).

The UNIQUAC activity coefficient equations contain two parameters  $\Delta U_{ij}$  and  $\Delta U_{ji}$ . Initial estimates of zero were used for both parameters. These estimates were found to be adequate. Since equilibrium calculations are very sensitive to values of Henry's constants, good initial guesses are needed for Henry's constant parameters. The Henry's constant parameters in eq 6 were fitted directly to equilibrium data in a two-step procedure. In the first step, Henry's constants were calculated directly from the experimental data. Values of the parameters in eq 6 were determined by minimizing the objective function

$$S = \sum_k^N (H_{ji}^c - H_{ji}^e)^2 \quad (15)$$

The scheme for obtaining initial estimates of Henry's constant parameters is shown in Figure 2. This scheme was modeled from a procedure presented by Prausnitz et al. (1967) to curve-fit vapor pressures.

## Results and Discussion

**Benzene-Water System.** Henry's constant and activity coefficient parameters were determined from the isobaric LLI data of Thompson and Snyder (1964) over a temperature range of 311.0–477.6 K at 6.99 and 34.57 MPa (1000 and 5000 psig). The Henry's constants of benzene in water,  $H_{C_6H_6O}$ , and the Henry's constants of water in benzene,  $H_{H_2O-H_6}$ , were fitted as functions of temperature according to eq 6. A comparison between experimental and calculated values of  $H$  is shown in Figure 3. The aqueous liquid phase is assumed to be an ideal dilute solution. An ideal dilute is a solution in which the solute obeys Henry's law and the solvent obeys Raoult's law.

The composition of water in the hydrocarbon and aqueous liquid phases, calculated from the reduced values of Henry's constant and activity coefficient parameters, are compared with experimental data in Figure 4.

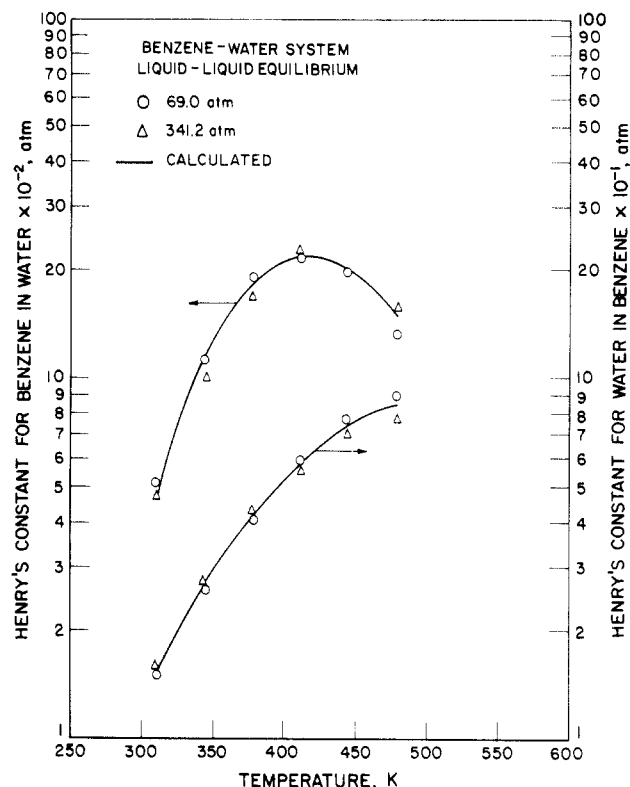


Figure 3. Henry's constants for benzene in water and water in benzene.

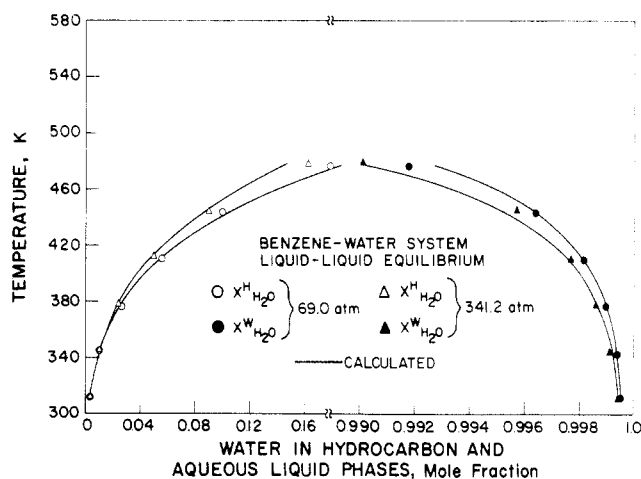


Figure 4. Temperature-composition diagram for water in the hydrocarbon and aqueous liquid phases (benzene-water system).

**Methane-Water System.** Isothermal gas solubility data for the methane-water system from 310 to 444 K was reported by Olds et al. (1942). Since the solubility of methane in water is small, an ideal dilute solution was assumed, and only Henry's constant parameters were determined from data. Figure 5 shows a comparison between calculated and experimentally determined values of Henry's constants for methane in water. Figure 6 is a pressure composition diagram on an expanded scale for methane solubility in water. As may be expected, the solubilities are small and increase approximately linearly with pressure.

**n-Butane-Water System.** Isothermal vapor-liquid-liquid and liquid-liquid equilibrium data for the n-butane-water system over a temperature range of 311–411 K have been reported by Reamer et al. (1952). For each isotherm, the experimental data point at the lowest pressure corresponds to VLLE and was processed ac-

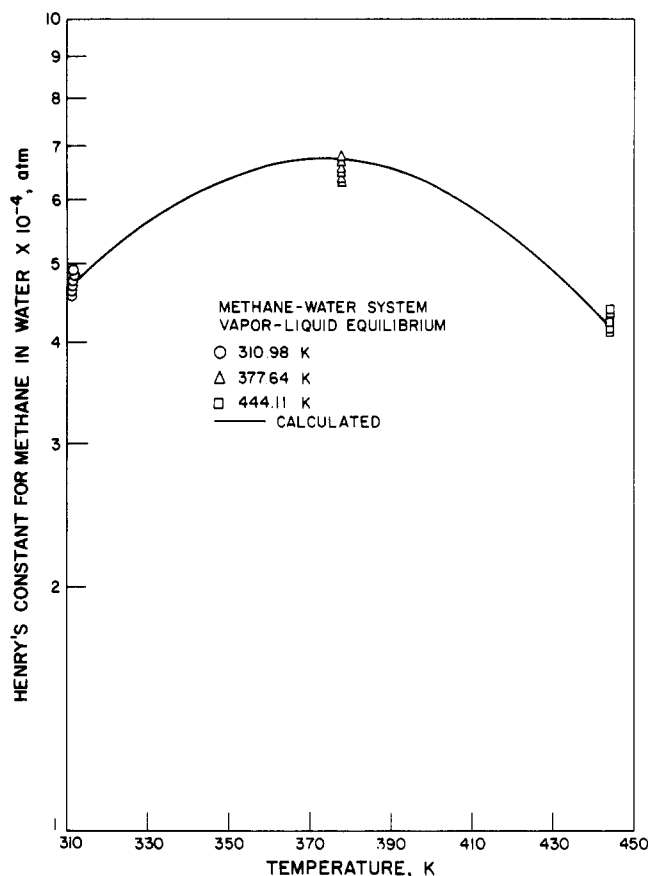


Figure 5. Henry's constant for methane in water.

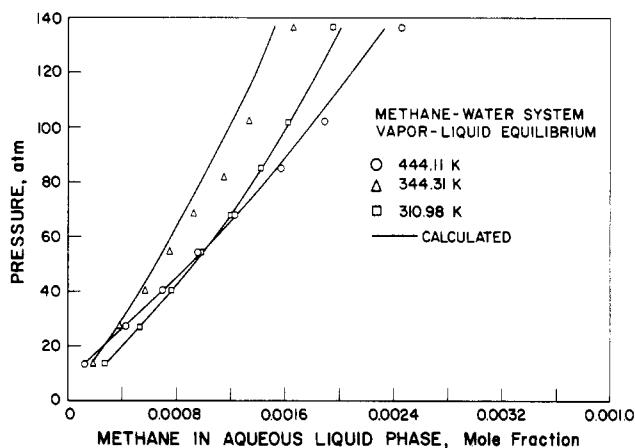


Figure 6. Pressure-composition diagram for methane in the aqueous liquid phase (methane-water system).

cordingly. All other data points correspond to LLE equilibria. Figure 7 shows a fit of Henry's constants of *n*-butane in water and water in *n*-butane. Figure 8 shows pressure-composition diagrams for each isotherm. The calculated and experimental mole fractions in the hydrocarbon and aqueous liquid phases are compared in Figure 8, and the agreement is good.

**Methane-*n*-Butane System.** Isothermal VLE data were reported by Sage et al. (1940) for the methane-*n*-butane system. Experimental data over a temperature range of 311–378 K were employed in this data reduction. The fit of Henry's constants is shown in Figure 9. The experimental values of Henry's constants calculated from  $T$ - $P$ - $x$ - $y$  data show very large scatter. This is believed to be due to inadequacies in the correlations for activity coefficients, vapor-phase fugacity coefficients, and molar volumes. The scatter in the experimental values of Henry's

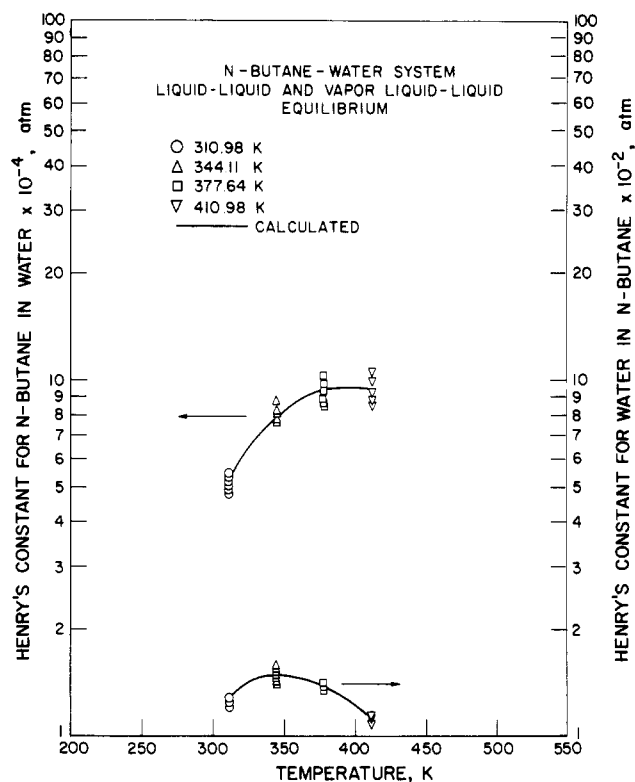


Figure 7. Henry's constant for *n*-butane in water and water in *n*-butane.

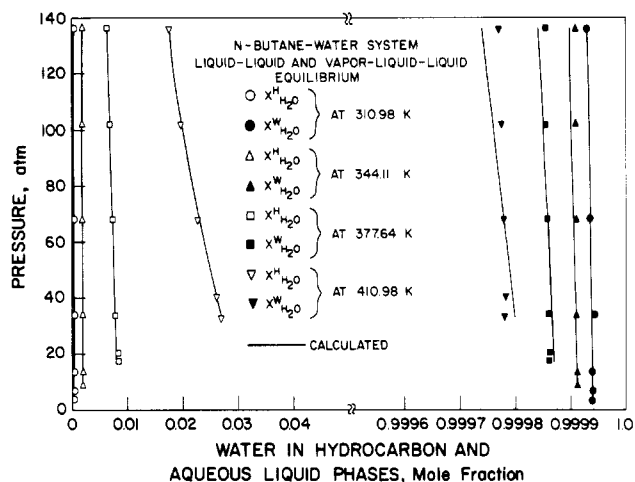


Figure 8. Pressure-composition diagram for water in the hydrocarbon and aqueous liquid phases (*n*-butane-water system).

constants at each isotherm makes it difficult to obtain good estimates of Henry's constant parameters. Pressure-composition diagrams for the family of isotherms in the methane-*n*-butane system are shown in Figure 10. As may be expected, the agreement is good at low pressures, but as pressure increases and approaches the critical point, the agreement becomes progressively worse.

***n*-Tetradecane-Carbon Dioxide System.** The three-phase locus extending from the four-phase equilibrium point to the three-phase critical point has been reported by Hottovy et al. (1979). Figure 11 shows a comparison between calculated and experimentally determined Henry's constants for *n*-tetradecane in carbon dioxide and carbon dioxide in *n*-tetradecane. Figure 12 is a temperature-composition diagram for carbon dioxide in the two liquid phases. Ideal liquid solution behavior is assumed for both liquid phases, and only Henry's constant parameters were determined from data for this system. In this

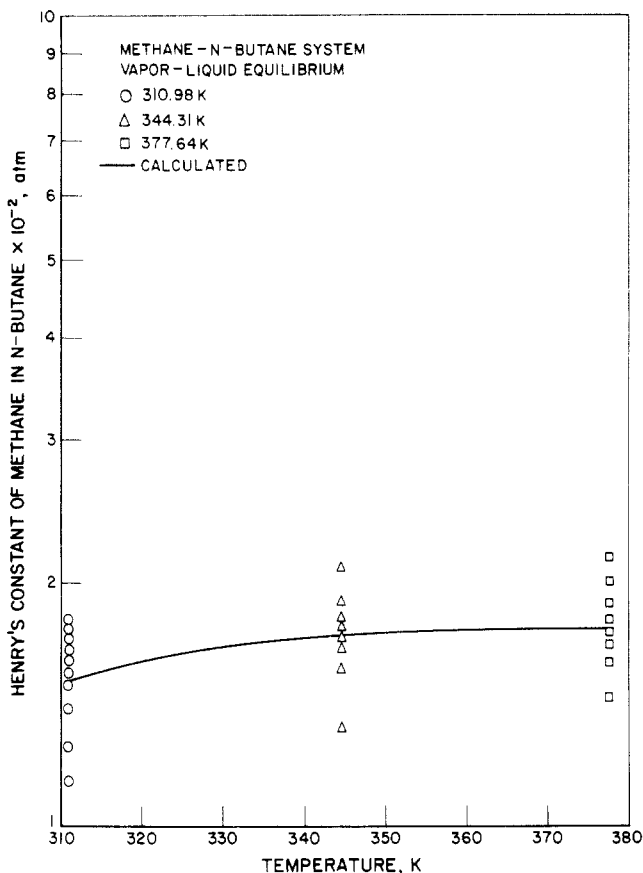


Figure 9. Henry's constant for methane in *n*-butane.

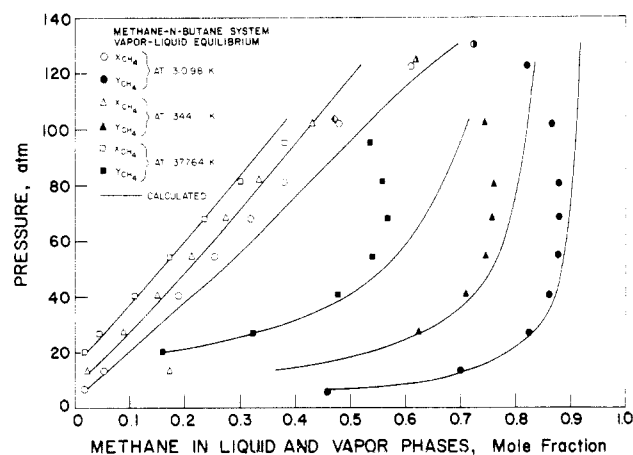


Figure 10. Pressure-composition diagram for methane in the liquid and vapor phases (methane-*n*-butane system).

binary, the UCST at 311 K corresponds to the identity of the vapor phase and the carbon dioxide rich liquid phase. The vapor-phase mole fraction of carbon dioxide is very nearly unity over the entire range of data. Figure 13 is a three-phase temperature-pressure diagram. The pressures were calculated from the fitted Henry's constant and compared with the experimental values. The agreement is good. The experimental data set passes through the critical point of carbon dioxide at 304 K, and this introduced difficulties in the calculation of properties. Although large errors are possible in the vicinity of the critical point, the agreement between data and calculated values was good.

### Concluding Remarks

A thermodynamic framework for calculations of VLE and its subsets has been developed. Based on this

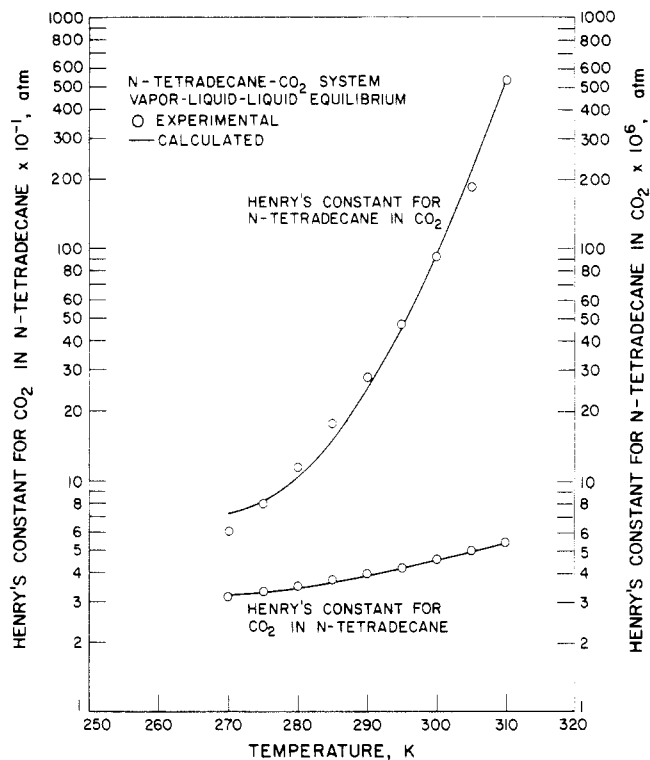


Figure 11. Henry's constants for carbon dioxide in *n*-tetradecane and *n*-tetradecane in carbon dioxide.

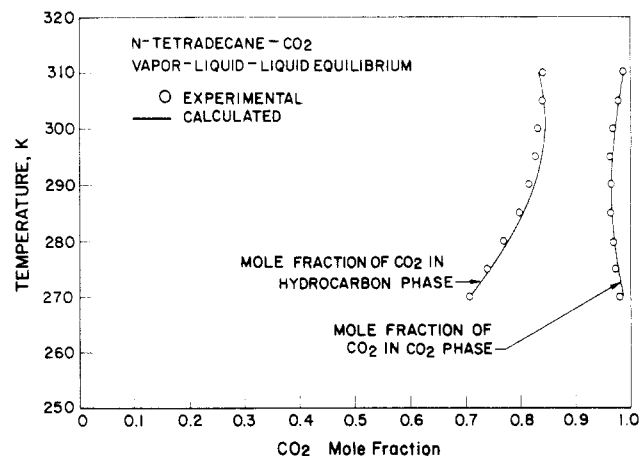


Figure 12. Temperature-composition diagram for carbon dioxide in the hydrocarbon and carbon dioxide liquid phases (*n*-tetradecane-carbon dioxide system).

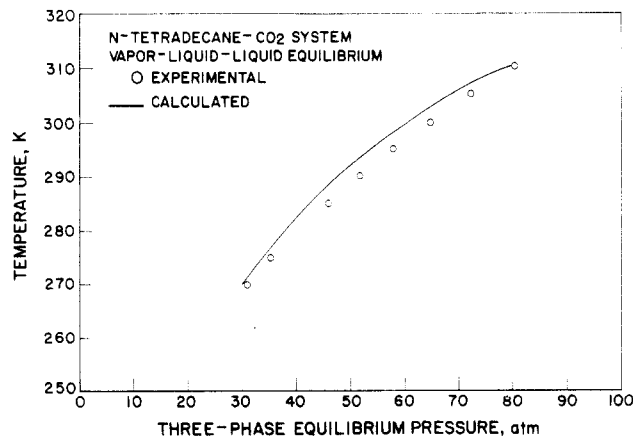


Figure 13. Three-phase temperature-pressure diagram for the *n*-tetradecane-carbon dioxide system.

framework, a data reduction procedure for obtaining Henry's constant and activity coefficient parameters was presented. Binary V-L, L-L, and V-L-L equilibrium data were reduced here by using the data reduction procedure. Agreement was good for both isothermal and nonisothermal data from V-L, L-L, and V-L-L studies. One virtue of this framework and data reduction scheme is that it is applicable and consistent in the treatment of V-L, L-L, and V-L-L equilibrium data. Therefore, one can obtain a consistent set of binary parameters which can then be used to make predictions for all the phase equilibrium conditions. Another major asset of this data reduction procedure is that initial estimates are internally generated.

## Nomenclature

$A, B, C, D$  = Henry's constant parameters (see eq 6)  
 $f$  = fugacity  
 $H$  = Henry's constant  
 $l$  = UNIQUAC parameter (see eq 7)  
 $N$  = total number of components in system or data points  
 $P$  = pressure  
 $q, q'$  = characteristic UNIQUAC surface area parameter defined by eq 9 and 10  
 $r$  = characteristic UNIQUAC volume parameter defined by eq 8  
 $S$  = objective function  
 $T$  = temperature  
 $U$  = UNIQUAC interaction energy parameter  
 $V$  = molar volume  
 $x$  = liquid-phase mole fraction  
 $y$  = vapor-phase mole fraction  
 $Z$  = coordination number in UNIQUAC equations

## Greek Letters

$\gamma$  = liquid-phase activity coefficient  
 $\Delta$  = difference  
 $\theta, \theta'$  = liquid-phase area fraction defined by eq 9 and 10  
 $\nu$  = pure liquid fugacity coefficient  
 $\Sigma$  = sum  
 $\tau$  = UNIQUAC binary parameters defined by eq 11  
 $\varphi$  = vapor-phase fugacity coefficient  
 $\Phi$  = liquid-phase volume fraction defined by eq 8

## Subscripts

$i, j$  = component  
 $k$  = refers to data point

## Superscripts

$c$  = calculated  
 $e$  = experimental  
 $L$  = liquid phase  
 $(N)$  = new guess  
 $^\circ$  = pure liquid reference state  
 $v$  = vapor phase  
 $I, II$  = refers to the liquid phases  
 $\infty$  = infinite dilution state  
 $*$  = normalized in the asymmetric convention  
 $-$  = partial molar quantity

**Registry No.** benzene, 71-43-2; methane, 74-82-8; butane, 106-97-8; tetradecane, 629-59-4; carbon dioxide, 124-38-9.

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# Effect of Liquid Composition on the Slurry Fischer-Tropsch Synthesis. 1. Rate of Reaction

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With a reduced fused magnetite catalyst, the rate of reaction in the presence of phenanthrene is nearly twice that observed in the presence of *n*-octacosane even though the solubility of  $H_2$  and CO is moderately less in phenanthrene. The rate in the presence of triphenylmethane was about the same as in *n*-octacosane. In the presence of a perfluoropolyether, the rate of reaction was markedly reduced, even though  $H_2$  and CO solubilities are much higher than in hydrocarbons. This was attributed to substantial mass transfer resistances through an encapsulating hydrocarbon layer around the catalyst particles. The effect of the nature of a liquid on several other reactions is also discussed.

The objectives of this study were to determine the effect of the nature of an inert liquid on the rate of reaction and selectivity of the Fischer-Tropsch synthesis on a reduced

fused magnetite catalyst, under reaction conditions representative of industrial practice. This is of interest from both a theoretical and practical point of view. Part 2