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VAPOR/LIQUID EQUILIBRIA OF CONSTITUENTS FROM COAL GASIFICATION IN REFRIGERATED METHANOL

by

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ABSTRACT

A thermodynamic framework was established for the development of a model of the phase equilibria of mixtures of methanol and the major constituents found in gases produced from coal. Two approaches were used to model the equilibrium behavior. In one, an equation of state was used to describe both gas and liquid phases, and in the other an equation of state was used to describe the gas while a solution model involving activity coefficients was used to describe the liquid. The approach chosen for each species was based on the component volatility.

The equation of state used in this work was an extended Soave-Redlich-Kwong (SRK) equation; four-suffix Margules, Wilson, and UNIQUAC equations were used to express activity coefficients. Vapor-liquid equilibrium data obtained in the present study and from the literature were used to obtain parameters in the extended SRK equation and Margules, Wilson, and UNIQUAC equations.

The SRK equation and associated sets of parameters obtained by fitting equilibrium data on binary mixtures can be used to describe the vapor-liquid equilibrium behavior of a multicomponent system in the composition, temperature, and pressure ranges found in an absorption-stripping process coupled with a coal gasifier. A gas solubility calculation using the equation greatly simplifies an equilibrium calculation without significantly distorting the capability of the equation.

The parameters for the Four-Suffix Margules, Wilson, and UNIQUAC equations, which are used to describe the liquid phase nonideality, were obtained for many binary systems formed from constituents of coal gas and methanol. The liquid reference state fugacities were calculated from various sources. When using this approach to describe the liquid phase, the SRK equation of state is used to describe the vapor phase.

An exerimental apparatus was constructed to obtain data against which the model predictions could be tested. The apparatus was evaluated by comparison of experimental P-T-x data on mixtures of carbon dioxide and methanol with those from the literature. The comparison was favorable. P-T-x-y data on mixtures of carbon dioxide, methanol and water, and mixtures of carbon dioxide, nitrogen and methanol at temperatures in a range of -30 to 25° C and pressures up to 54 atm were obtained. Comparisons of the calculated and measured values of bubble point pressures and/or liquid compositions of the dissolved gases were satisifactory.

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INTRODUCTION

Since the energy crisis of 1973, much attention has been given to coal utilization. In 1978, North Carolina State University (NCSU) began a study of the environmental aspects of coal gasification under the sponsorship of the Environmental Protection Agency. One of the main objectives of the project was to study processes by which the synthetic gas was cleaned. The gas produced from coal gasification contains carbon dioxide, hydrogen sulfide and other sulfur gases, in addition to the desired gases: carbon monoxide, hydrogen and methane. The acid gases lower the heating value of the product gas and are toxic and corrosive; the sulfur gases also have an offensive odor. Removal of these acid gases is carried out in an acid gas removal system (AGRS) that involves absorption-stripping operations which utilize either a physical or chemical solvent.

Physical solvents have been shown to be good bulk removers of acid gases (Rivas and Prausnitz, 1979), and have a better capacity than chemical solvents when the acid gases are at high concentrations or high partial pressures. Also, physical solvents are easier to regenerate and cost less than chemical solvents. A physical solvent that has shown promise is methanol; it has been used in the NCSU acid gas removal system and several commercial coal gasification facilities.

Absorption of acid gases in methanol is favored at low temperatures and high pressures, while stripping methanol of acid gases must be accomplished at elevated temperatures and reduced pressures. The NCSU acid gas removal system operates in a temperature range from 230 K to 300 K and a pressure range from 1 to 35 atm (1 atm = 101 kPa). Table 1 lists a typical composition of the crude gas produced from the NCSU fluidized bed gasifier when using a Texas Lignite coal and operating at 795°C.

The primary difficulty associated with conditioning gases having a composition similar to that shown in Table 1, is the significantly greater amounts of carbon dioxide, sulfur gases, hydrocarbons, and nitrogen compounds than usually found in natural gas. In addition, the water, hydrocarbons, and nitrogen compounds may alter the behavior of the solvent, especially if it is methanol. This alteration in properties may cause product gas contamination and may complicate the separation of sulfur compounds from carbon dioxide in an absorption operation. Also, hydrocarbons tend to accumulate in

- 1 -

the solvent (Rousseau *et al.*, 1981b) and cause potential problems with methanol regeneration in a stripping operation.

TABLE 1

COMPOSITION OF GAS FROM NCSU FLUIDIZED BED GASIFIER TEXAS LIGNITE COAL

Compound	Mole % Dry Basis
	or ppm
H ₂	34.28%
CÔ	13.58
CO ₂	26.87
N ₂	19.42
	4.99
H ₉ S	1608 ppm
cõs	35
Methyl Mercaptan	31
Thiophene	17
$C_{2}H_{4}$	1612
C_2H_6	2909
C ₃ H ₆	777
C ₃ H ₈	390
C ₄ H ₈	359
Benzene	566
Toluene	179
o-Xylene	15
m-Xylene	30
p-Xylene	6
Ethylbenzene	13

The phase equilibrium behavior of mixtures consisting of methanol and compounds produced in the gasification of coal is the fundamental information required for design and analysis of the components of an AGRS using methanol as a solvent. A mathematical model of each component of the operation can be used to predict the effects of varying feed composition, temperature, and pressure with considerable reliability, and the model can be used to avoid an inefficient over-design. Moreover, other economically important factors, such as the solubility of sweet gas (including H_2 , CO, and CH_4) in methanol and the solubility of methanol in the sweet or stripping gas (Lazalde-Crabtree et al., 1979), can be evaluated with a properly constructed model of the system. Although processes and associated equipment using refrigerated methanol in an acid gas removal system have been designed successfully by some companies (for example, the Rectisol process by Lurgi GmbH) much of the experience and data required for design remain proprietary. Despite the availability of gas solubility data, little information has been published on vapor-liquid equilibria for multicomponent systems which contain methanol (Weber and Knapp, 1980; Weber, 1981; Rousseau *et al.*, 1981a; Takeuchi *et al.*, 1983). As a result, the available equilibrium correlations have been found inadequate for describing the phase equilibrium behavior between refrigerated methanol and the coal gas constituents at elevated pressures. Thus, vaporliquid equilibrium modeling of constitutents from coal gasification in refrigerated methanol has been initiated at NCSU (Bass, 1978; Matange, 1980), where the search for better methods and further extensions continues.

The work reported here is concerned primarily with the equilibrium behavior of individual gas components in methanol at conditions corresponding to an acid gas removal system. The collected data and resulting correlations characterize the solubilities of each species in methanol over a wide range of temperatures and pressures, and account for all the interactions between the existing species in the system. The goal of the study is to construct models that can be included in a simulation package and used to predict the performance of gas-liquid processing units such as absorbers, strippers, and flash tanks. These models are to be based on a limited amount of vapor-liquid equilibrium data and correlations of pure-component data, and they are to be tested against experimental multicomponent vapor-liquid equilibrium data. In addition to these very important and practical benefits, the information obtained and evaluated in this study may be of fundamental importance in understanding the factors that influence phase equilibria and the models that describe such behavior.

In the sections that follow a review of the fundamentals of the thermodynamic relationships that exist between coexisting phases is presented. These principles are formulated to provide two types of expressions relating temperature, pressure, and composition of vapor and liquid phases. One uses an equation of state to describe both gas and liquid phases; the other uses an equation of state to describe the gas and a solution model describing a deviation from ideal behavior to describe the liquid. Binary experimental data obtained in the present study and from the literature were used to obtain parameters in both of these model formulations, and to provide the framework for a model that can be used to describe multicomponent phase equilibrium behavior.

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LITERATURE REVIEW

Several thermodynamic approaches may be applied to the phase equilibrium behavior of a coal gas-methanol system. When a single gas component is dissolved in a physical solvent, a conventional gas solubility treatment may be useful. However, description of the behavior of a multicomponent system involving a wide variety of species dictates that a more fundamental approach be taken.

It has been shown (Prausnitz, 1969) that the basic equation relating temperature, pressure, and compositions in coexisting phases at equilibrium is given by equating the fugacities for each component i in these phases. For vapor-liquid equilibrium,

$$f_i^V = f_i^L \tag{1}$$

This equation is not useful, however, until it is known how the fugacity of component i in each phase can be estimated or related to temperature, pressure and composition in that phase. Relationships among these quantities will be developed in the sections that follow.

SOLUBILITIES OF GASES IN A PHYSICAL SOLVENT

Equation 1 is fundamental to gas solubility calculations, which can be greatly simplified by assuming ideality of the gas phase or of both gas and liquid phases. In solubility calculations, Equation 1 is solved for each gas component, and the solvent in the vapor phase is neglected.

Binary Correlations for Gas Solubilities

If the solubility of a gas in a liquid is proportional to its partial pressure in the gas

phase, the system follows Henry's law:

$$f_2^V = f_2^L = y_2 P = H_{2,1} x_2 \tag{2}$$

where subscript 2 refers to the solute, subscript 1 refers to the solvent, and $H_{2,1}$ is the Henry's law constant for the dissolution of component 2 in component 1. For a given solute and solvent, this constant depends only on temperature at low or moderate pressures. Rigorously, the Henry's law constant is defined as

$$H_{2,1} = \lim_{x_0 \to \infty} f_2 / x_2 \tag{3}$$

Equation 2 is not expected to apply when the partial pressure exceeds 10 atm or the solubility exceeds 3 mole%.

The Krichevsky-Kasarnovsky equation (Krichevsky and Kasarnovsky, 1935) represents the effect of pressure on the fugacity of a dissolved solute. It has the form

$$\ln \frac{f_2}{x_2} = \ln H_{2,1}^{p^*} + \frac{v_2^{\infty}}{RT} \left(P - p_1^s \right)$$
(4)

where

 $H_{2,1}^{p_1^*} = Henry's \ law \ constant \ evaluated \ at \ the saturated \ vapor \ pressure \ of \ the \ solvent$ $v_2^{\infty} = partial \ molar \ volume \ of \ solute \ 2 \ at \ infinite \ dilution$ $p_1^s = vapor \ pressure \ of \ solvent \ at \ the \ system \ temperature$

and where 1 denotes solvent and 2 denotes a gas solute.

Equation 4 can be further extended to include an additional "composition effect" term that is embodied in an activity coefficient. When this term is assumed to follow a two-suffix Margules equation, Equation 4 becomes the Krichevsky-Ilinskaya equation (Krichevsky and Ilinskaya, 1945)

$$\ln \frac{f_2}{x_2} = \ln H_{2,1}^{p_1^*} + \frac{A}{RT} \left(x_1^2 - 1 \right) + \frac{v_2^\infty}{RT} \left(P - p_1^s \right)$$
(5)

where A is an empirical constant determined from solubility data. A good example of

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the application of these correlations for a CO_2-H_2O system has been given by Van Ness and Abbott (1982).

In order to find the solubility of a gas in a mixed solvent, the Henry's law constant may be approximated in an ideal mixture as

$$\ln(H_{i,m}) = \sum_{j=1, j \neq i}^{M} x_j \ln(H_{i,j})$$
(6)

Henry's law constant for a gaseous solute in a nonideal solvent mixture is given by O'Connell (1964) as

$$\ln(H_{i,m}) = \sum_{j=1, j \neq i}^{M} x_j \ln(H_{2,j}) - \sum_{j=1, j \neq i}^{M-1} \sum_{k>j, k \neq i}^{M} a_{jk} x_j x_k$$
(7)

where a_{jk} is a binary constant of the jk pair in a two-suffix Margules equation.

Generalized Correlations for Gas Solubilities

A generalized correlation for nonpolar systems was described by Prausnitz and Shair (1961) and a similar correlation has been given by Yen and McKetta (1962). They used the regular solution theory in a symmetrical convention activity coefficient approach. The basic equation has the following form:

$$\frac{1}{x_2} = \frac{f_2^L}{f_2^G} \exp \frac{v_2^L (\delta_1 - \delta_2) \Phi_1^2}{RT}$$
(8)

where

$$\begin{split} \delta_1 &= \text{ solubility parameter of solvent} \\ \delta_2 &= \text{ solubility parameter of solute} \\ \Phi_1 &= \text{ volume fraction of solvent} \\ v_2^L &= \text{ liquid molar volume of solute} \end{split}$$

Using both the liquid molar volumes and the solubility parameters at 25° C, coupled with the solubility data at 1 atm, the fugacities of a hypothetical pure liquid, f_2^L , were calculated and correlated in a corresponding-states plot $(f^L/P_c vs. T/T_c)$. Prausnitz and Shair (1961) have also suggested that an empirical function of the activity

coefficient may be used with a polar solvent instead of using regular solution theory. This gas solubility correlation for a polar solvent has the form

$$\frac{1}{x_2} = \frac{f_2^L}{f_2^G} \gamma_2$$
 (9)

$$\ln \gamma_2 = v_2^L F(T, \delta_2, properties \ of \ solvent) \tag{10}$$

where f_2^L may be the same as in a nonpolar solvent. The correlations are shown in plots of

$$\ln \gamma_2 / v_2^L vs \delta_2$$

in different solvents. If the solution is under high pressure (greater than 1 atm), the Poynting correction $(exp[v_2^L(P-1)/RT])$ should be applied to the pure liquid fugacity f_2^L . The technique of Prausnitz and Shair can be extended readily to mixed solvents by substituting an average solvent solubility parameter for the pure solvent parameter.

Recently, Sebastian, Lin and Chao (1981a, 1981b) developed a solubility parameter-based correlation for the solubility of gases in hydrocarbon solvents that does not require evaluation of the reference state fugacity. Instead, the logarithm of the undefined activity coefficient (f/x) is expressed as

$$\ln (f/x) = \ln (f/x)_{P=0} + P\overline{v}/RT$$
(11)

The zero-pressure activity coefficient is given as a function of the solubility parameter of the solution, $\overline{\delta}$, and the temperature T:

$$\ln(f/x)_{P=0} = A_1 + A_2 T/\overline{\delta} + A_3 T + A_4 T\overline{\delta} + A_5 T^2 \overline{\delta}^2 + A_6 (\overline{\delta}/T)^2$$
(12)

The coefficients in this equation were determined by correlating the Henry's law constants of the gas in various solvents, and the molar volume (\overline{v}) in Equation 11 was determined from high-pressure equilibrium data. This correlation is a form of the Krichevsky-Kasarnovsky equation (Equation 4). A generalized Henry's constant at zero-pressure (Equation 12) was used instead of the individual Henry's constant at the solvent saturated vapor pressure. This correlation has the capability to correlate with reasonable accuracy the solubility of a gas in various hydrocarbon solvents.

The use of a group-contribution method to predict gas solubilities has gained attention recently. When successful, these methods can predict gas solubilities in a varity of solvents using only a few group parameters. Sander *et al.* (1983) has shown that the

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UNIFAC method can be applied to predict the solubilities of gases in pure and mixed solvents at low pressures and low solubilities. Antunes and Tassios (1983) used a modified UNIFAC model for the prediction of Henry's constant. Tochig and Kojima (1982) predicted non-polar gas solubilities in water, alcohol, and aqueous alcohol solutions by a modified ASOG method.

VAPOR-LIQUID EQUILIBRIUM

A rigorous way to describe the phase behavior of a gas-solvent system is by applying a vapor-liquid equilibrium (VLE) approach. This approach applies the fundamental equilibrium relationships to all of the components in the system, including the solvent. The range of pressures that are of interest in gas-liquid equilibria or high pressure vapor-liquid equilibria are from atmosphere pressure to the critical pressure of the system under consideration. Hence, the nonidealities of vapor and liquid phases must be estimated over this range of pressures as a function of temperature, pressure, and compositions of vapor and liquid. An excellent discussion of vapor-liquid equilibria at high pressure has been given by Reid, Prausnitz, and Sherwood (1977).

The vapor-liquid equilibrium working equation has been shown in Equation 1, and for an N-component system, there are N equilibrium relations. There are 2N variables: temperature T, pressure P, vapor-phase mole fractions y_i , and liquid-phase mole fractions x_i . Therefore, N variables must be specified to formulate each of the four types of VLE calculations, which are as follows:

- 1. Bubble point pressure calculation (BUBLP). This calculation obtains P and y_i from given T and x_i . The calculation starts with an initial estimate of system pressure and proceeds iteratively by adjusting pressure until the sum of calculated vapor mole fractions is within a specified tolerance of 1.
- 2. Bubble point temperature calculation (BUBLT). This calculation obtains T and y_i , from given P and x_i . The calculation starts with an initial estimate of system temperature and proceeds iteratively by adjusting temperature until the sum of calculated vapor mole fractions is within a specified tolerance of 1.
- 3. Dew point pressure calculation (DEWP). This calculation obtains P and x_i from given T and y_i . The calculation starts with an initial estimate of system pressure and proceeds iteratively by adjusting pressure until the sum of calculated liquid mole fractions is within a specified tolerance of 1.

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4. Dew point temperature calculation (DEWT). This calculation obtains T and x_i from given P and y_i . The calculation starts with an initial estimate of system temperature and proceeds iteratively by adjusting temperature until the sum of calculated liquid mole fractions is within a specified tolerance of 1.

Thermodynamics provides two methods to calculate the fugacities in Equation 1. The first is based entirely on an equation of state for both the vapor and liquid phases. The second uses an equation of state for the vapor phase, and a solution model that uses activity coefficients to express deviations of the liquid from ideal behavior as defined by either Raoult's or Henry's law. An excellent comparison of these two methods has been given by Prausnitz (1977); the details of the methods are discussed in the next two sections.

Equation-of-State Method (Phi Method)

The application of an equation of state to the description of vapor-liquid equilibria was pointed out a century ago by van der Waals. The first step in such descriptions is rewriting the criterion for vapor-liquid equilibrium, shown in Equation 1, in the form

$$y_i \phi_i^V = x_i \phi_i^L \tag{13}$$

where ϕ_j^V and ϕ_i^V are fugacity coefficients of vapor and liquid phases, respectively. These coefficients may be calculated from the following thermodynamic relationships:

$$\ln \phi_i = \frac{1}{RT} \int_V^\infty \left[\left(\frac{\partial P}{\partial n_i} \right)_{T,V,n_{j\neq i}} - \frac{RT}{V} \right] dV - \ln z$$
(14)

or

$$\ln \phi_i = \frac{1}{RT} \int_0^P \left[\left(\frac{\partial V}{\partial n_i} \right)_{T,P,n_{j\neq i}} - \frac{RT}{P} \right] dP$$
(15)

Equation 14 is more useful than Equation 15 because most equations of state are pressure-explicit. Equation 14 can be used to calculate the fugacity coefficients of a component both in the vapor and liquid phases at equilibrium by substituting the appropriate vapor-phase or liquid-phase volume in the integration. The calculation is done by iterations until the equilibrium criterion is satisfied.

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The most successful equations of state applied to the calculation of vapor-liquid equilibria are the Benedit-Webb-Rubin (BWR) and Redlich-Kwong (RK) modifications. Recently, Soave (1972) and Peng and Robinson (1976) have modified the Redlich-Kwong equation to improve greatly the vapor-liquid equilibrium calculations for hydrocarbons and simple gases. Extensions of these equations to polar and hydrogen-bonding components, such as water, have been tested by few researchers (Wenzel and Rupp, 1978; Won and Walker, 1979; Evelein and Moore, 1976; Peng and Robinson, 1980). The modifications focused on the intermolecular attraction force parameter a in the equations and the binary interaction parameter K_{ij} in the mixing rules. Vidal (1978), and Huron and Vidal (1979), however, using a new mixing rule in a two-parameter cubic equation of state, achieved good correlations of vapor-liquid equilibria of strongly nonideal mixtures, including a methanol-CO₂ system. Recent developments using density-dependent local composition (DDLC) mixing rules (Mollerup, 1981; Whiting and Prausnitz, 1982; Won, 1983; Mathias and Copeman, 1983) offer great promise for the extension of cubic equations of state to highly nonideal mixtures. The DDLC model may be useful in the future for gas mixtures obtained from coal which contain components covering a wide density range.

Calculation of vapor-liquid equilibria from an equation of state is attractive primarily because it avoids the need to estimate a fugacity for a liquid reference state for supercritical components. Secondly, equations of state are readily extended to multicomponent systems. Unfortunately, no truly satisifactory equation of state has been established for all kinds of systems and thermodynamic properties. Simple cubic equations of state with semi-empirical parameters receive more attention because of their accuracy, simplicity, and applicability over a wide range of conditions.

Activity Coefficient Method (Gamma Method)

The use of the activity coefficient method to calculate vapor-liquid equilibria of a system containing gas components at high pressures is an extension of the method applied at low pressure. Liquid and vapor phases are treated separately in this method. The vapor phase fugacity is evaluated from the following equation:

$$f_i^V = \phi_i y_i P \tag{16}$$

The fugacity coefficient ϕ_i is evaluated from an appropriate equation of state, and it expresses the deviation of the vapor from ideal gas behavior.

The liquid phase fugacity is calculated with an activity coefficient that expresses the

deviation of that liquid component from an ideal liquid reference state. When activity coefficients are defined with reference to an ideal solution in the sense of Raoult's law, the liquid phase fugacity can be expressed by

$$f_i^L = \gamma_i x_i f_i^o \tag{17}$$

where γ_i is the activity coefficient of component i in the liquid solution. This activity coefficient is defined so that $\gamma_i \rightarrow 1$ as $x_i \rightarrow 1$. The activity coefficient in the expression is assumed to be a function of temperature and liquid composition, but independent of pressure.

Activity coefficients can be calculated from many activity coefficient equations derived from different solution models, such as the Scatchard-Hildebrand, Van Laar, Margules, Wilson, NRTL and UNIQUAC equations. The Scatchard-Hildebrand equation does not need binary parameters for most simple fluids that form regular solutions. The other model equations contain parameters that are determined from binary phase equilibrium data. The accuracy with which these equations can express equilibrium behavior depends on the equation used and the polar and/or nonpolar species in the solution. A group-contribution method such as ASOG or UNIFAC is particularly useful when no experimental VLE data are available. However, it should not be used in place of good data (Wilcox, 1983).

A pure liquid reference state fugacity f_i^o for a subcritical component can be calculated from an exact thermodynamic relationship:

$$f_i^o = p_i^* \phi_i^* \exp\left[\int_{p_i}^P \frac{v_i^L}{RT} dP\right]$$
(18)

where p_i^* and ϕ_i^* are functions of temperature, and v_i^L is a function of temperature and pressure.

For a supercritical component such as methane or nitrogen, a hypothetical reference state fugacity must be defined. It is common practice to extrapolate pure liquid fugacities to a temperature above the critical (Hoffman *et al.*, 1962). The most common method of extrapolation is to assume that a semi-logarithmic plot of the fugacity versus reciprocal temperature is a straight line. Chao and Seader (1961), Robinson and Chao (1971), and Lee *et al.* (1973) evaluated hypothetical liquid fugacity functions from large sets of binary VLE data containing supercritical components by using an activity coefficient equation derived from the regular solution theory. These empirical equations are expressed as functions of reduced temperature, reduced pressure and a Pitzer acentric factor. The use of these hypothetical liquid fugacity models to evaluate parameters in other activity coefficient equations, however, may be inaccurate.

Another possibly satisfactory method for the use of activity coefficients on supercritical components is to define a reference state in the sense of Henry's law:

$$f_i^L = \gamma_i^* x_i f_i^o \tag{19}$$

where f_i^{o} equals $H_{i,m}$, the Henry's constant of i in solvent m at the system temperature and pressure. The effect of pressure on the Henry's law constant, $H_{i,m}$ can be evaluated from the equation

$$H_{i,m} = H_{i,m}^{*} \exp \left[\int_{P_{ref}}^{P} \frac{v_{i}^{\infty}}{RT} dP \right]$$
(20)

where $H_{i,m}^{*}$ is the Henry's law constant evaluated at pressure P_{ref} and the system temperature. (The Krichevsky-Kasarnovsky equation is a simplified version of Equation 20.) The activity coefficient is defined so that $\gamma_i^{*} \rightarrow 1$ as $x_i \rightarrow 0$, and it must be calculated by using a corrected equation for the original γ_i . For an expression of excess Gibbs free energy g^E , there exists a correction g^{E^*} which yields the correct γ_i^{*} (O'Connell, 1977). The following relationship exists between γ_i and γ_i^{*} :

$$\ln \gamma_i^* = \ln \gamma_i - \lim_{x_i \to 0} \ln \gamma_i \tag{21}$$

Prausnitz and Chueh (1968) successfully used a dilated Van Laar model for hydrocarbons and simple gases, but no work has been done on polar compounds. Although it is relatively easy to use a Henry's law reference state for the solute of a binary mixture (known as the unsymmetrical convention), severe difficulties exist in multicomponent systems. Because Henry's law constants depend on both the solute and the solvent, care must be exercised in the definition of reference states and corresponding activity coefficients when several solvents are present so that they are defined in a thermodynamically consistent way (Prausnitz, 1977). Also, some uncertainties exist on how to define a solute and a solvent, and how to estimate the Henry's law constant in a mixed solvent. Hence, the Henry's law reference state is not yet practically accepted in application to a multicomponent system.

Prausnitz et al. (1980) have developed a computer program that uses the virial equation of state to describe the vapor phase and optional activity coefficient equations such as UNIQUAC, Wilson, NRTL, Margules, and van Laar to describe the liquid phase. The Raoult's law reference state was used when the component was condensible, and an arbitrary function was used when the component was noncondensible. The program gave good multicomponent results when system temperatures were well below the critical temperature of each component. However, when system temperatures were near or above the critical temperature of one or more of the components, the multicomponent predictions were in error, even though data on all the binary pairs were fit well.

Davis and Kermode (1977/1978), using a computer program of Prausnitz *et al.* (1967), evaluated Wilson parameters for systems containing H_2 , N_2 , CO, CO_2 , CH_4 , H_2S , CH_3OH , and H_2O . They suggested that the minor constituents having low solubility might be lumped with the major constituents having low solubility in a cold methanol absorption process. The necessary binary parameters would be reduced greatly to the number of parameters between all the binary combinations of methanol, CO_2 , H_2S and major low-solubility components such as H_2 . Although assumptions were reasonable, no practical calculation was shown.

PHYSICAL PROPERTIES AND BINARY DATA SETS

Physical properties for pure components and binary VLE data are necessary in almost all the vapor-liquid equilibrium calculations. Physical property data and their correlations for gases and liquids are well presented by Reid *et al.* (1977), and by Yaws (1977). Critical P-V-T properties, the Pitzer acentric factor, the solubility parameter, liquid molar volume, and vapor pressure are some of the important physical properties in vapor-liquid equilibrium correlations. Wichterle, Linek and Hala (1973/1983) have compiled four volumes of the "Vapor-Liquid Equilibrium Data Bibliography" which list the VLE literature published before 1983.

Many efforts have been devoted to binary systems involving methanol, carbon dioxide, nitrogen, hydrogen, carbon monoxide, sulfur gases, hydrocarbon gases, and water. Most of the methanol-gas and water-gas binary mixtures provide P-T-x data or solubility data. Excellent discussions of converting solubility data to a useful form of vaporliquid equilibrium data are given by Friend and Adler (1957), and Adler (1983a, 1983b). Unfortunately, there is no way to check the thermodynamic consistency of these data. Although some sources of data report vapor-phase compositions, methanol and water concentrations in the gas are usually very low and often inaccurately measured. Discrepancies between the data of different laboratories are often found, and selection of data from the literature is achievied primarily by eliminating obviously erroneous information. Table 2 gives a list of binary mixtures formed from species present in most acid gas removal systems that process gases from coal. Binary data for each of these binary mixtures are required for model development, and Table 2 shows those systems for which such data were found in the literature.

MeOH X		MeOH	C02	H ₂ S	N ₂	COS	CH4	H ₂	CO	C2H6	СзНа	H20	C2H4.	CH3SH	CH3SCH3	C2H5SH
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	МеОН		x	x	x	x	+	x	+	0	0	x	X	X	X	X
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	C02			х	х		х	X	X	х	х	х	х			
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	H2Ŝ				x		- X	X	x	X	X	X	х	х		
COS x x x x CH ₄ x x x + H ₂ x x + CO x x + CO x x + C2H ₆ x + x C3H ₈ x x + H ₂ O - + - C2H ₄ - - + C4H ₃ SH - - + C4H ₅ SH - - -	N ₂						х	х	х	X	х	+	х			
CH4 x	CÔS						Х				X	+				
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	CH4							. X	х	х	х	+	х			
C0 x x + x C2H6 x + x C3H8 x + x H20 x + C2H4 + C2H4 CH3SH CH3SCH3 C9H5SH	H2								х	X	х	+	x			
С2H6 x + x C3H8 x x H2O + C2H4 CH3SH CH3SCH3 C9H6SH	C0									х	х	. +	X			
С3H8 H2O C2H4 CH3SH CH3SCH3 C2H6SH	C2H6										х	+	х			
H2U C2H4 CH3SH CH3SCH3 C2H5SH	C3H8											х	X			
С2H4 CH3SH CH3SCH3 C2H5SH	H20												+			
CH3SH CH3SCH3 C2H6SH	C2H4															
CoHaSH	CH351	1														
	C-11-5	2113														
	021153															

Table 2. Check List of Binary Data Sets Including Major Components from Coal Gasification.^a

PRINCIPLES OF BINARY VLE DATA REDUCTION

Vapor-liquid equilibrium calculations, either by the equation-of- state method or by the activity coefficient method, require binary parameters in most of the models to predict multicomponent behavior. The binary parameters must be obtained from experimental VLE data fit by an appropriate model. Poor fit of a model to binary data can result from three possible sources: (1) inaccurate data, (2) an inappropriate model, (3) the method of reducing the data. There are various ways to reduce VLE data, ranging from simple curve fitting to the application of sophisticated statistical principles. Prausnitz (1977) has pointed out that the procedure used to obtain model parameters from limited experimental data was often more important than details within the model. However, Van Ness and Abbott (1982) have a different point of view. They recognize that the improvement of parameters from a sophisticated data reduction method still depends on the quality of data and the appropriateness of the model.

A static equilibrium cell is often used in measuring vapor-liquid equilibrium data. Because direct sampling of the vapor phase in such systems usually upsets the equilibrium condition, vapor-phase data are often neglected in the literature. The Gibbs-Duhem theorem allows the use of a set of P-T-x data to calculate corresponding values of y. The method of Barker (1953) uses this thermodynamic theorem, and it is it is easy to use, efficient, and in some cases the only way to correlate binary vapor-liquid equilibrium data for the system of interest. For these reasons, the Barker method was adopted in the present work

Originally, Barker (1953) introduced a procedure to evaluate activity coefficient model parameters in the Scatchard equation from total pressure measurements. The two essentials of the Barker method are (1) only P-T-x data are necessary, and (2) a least squares routine is applied. Others, such as Orye and Prausnitz (1965), Renon and Prausnitz (1968), Holmes and Winkle (1970), and Nagahama, Suzuki and Hirata (1971), used the Barker method with different objective functions and P-T-x-y data to evaluate van Laar, Margules, Wilson or NRTL parameters. Abbott and Van Ness (1975) did a series of vapor-liquid equilibrium parameter searches on the Margules equation with both numerical and Barker method. They concluded that reliable P-x data only were required to provide reliable VLE relationships. Moreover, the use of the reported yvalues along with P-x data in the data reduction process distorted the correlation of both P-x and y-x relationships.

In recent years, VLE data reduction has focused on the maximum likelihood principle (see Fabries and Renon, 1975; Peneloux *et al.*, 1976; Sutton and Macgregor, 1977; Anderson *et al.*, 1978; Nean and Peneloux, 1981; 1982; Kemeny *et al.*, 1982; Patino-Leal and Reilly, 1982). This statistical principle considers errors in all measured variables and it weights the data properly. The estimated deviation method and the observed deviation method are both based on the maximum likelihood principle. These two methods lead to the same model parameters and the values do not depend on the fitting functions when an appropriate weighting method is used (Nean and Peneloux, 1981). The observed deviation method has advantages over the estimated deviation method, one of which is that it is easier to implement. Actually, the application of the maximum likelihood principle is achieved by calculating the appropriate weighting factor for every measured variable of each data point in an objective function. The validity of the techniques rests on the presumptions that the data set is free of systematic error and that the correlating equation does not itself introduce error (Van Ness and Abbott, 1982); random error is corrected by system statistics. However, the presumptions in these statistical treatments are often not met by VLE data.

RESEARCH SYSTEMS, APPROACHES, AND OBJECTIVES

The compounds, shown in Table 1, found in an acid gas removal system used to condition gases from a coal gasifier can be classified according to volatility into three groups. The first group contains the supercritical components hydrogen, nitrogen, carbon monoxide, and methane; the second group contains gases that are condensable at the system conditions, such as carbon dioxide, hydrogen sulfide, carbonyl sulfide, ethylene, ethane, propane, etc.; the third group includes components that are typically liquids at system conditions, such as methanol, water, mercaptans, and aromatic hydrocarbons. Figure 1 shows this arbitrary classification in terms of fluid density and molecular interactions. The most important interactions in the liquid of an acid gas removal system are those between methanol and the rich components having high solubilities. followed by those between methanol and the lean components with high solubilities and rich gaseous components with low solubilities. Although the interactions between the gaseous solutes in the liquid will be relatively less important than other interactions, a rigorous model includes all interactions in both the liquid and vapor phases. Methanol. carbon dioxide, hydrogen sulfide and other sulfur species may be considered the key components in an acid gas removal system because they are the primary subjects in the process. Because there are no chemical reactions and no electrolyte species present. only physical interactions between component molecules in the vapor and liquid phases were considered in developing a model of mixtures containing these components.

Both the equation-of-state and the activity coefficient approaches were used to describe the equilibrated systems containing methanol. An extended Soave-Redlich-Kwong equation of state was chosen for use in the first approach because of its simplicity and its capability in describing hydrocarbons and gases. The equation has been further extended to describe systems containing polar components. UNIQUAC, Wilson, and Four-Suffix Margules equations were used in the second approach. These equations are well known for their capabilities in handling strongly nonideal liquid mixtures and require well-defined liquid reference states. All of the components in Group III and some components in Group II can be handled by an activity coefficient equation.

The primary objective of this research is to develop generalized thermodynamic models to describe the vapor-liquid equilibrium behavior of systems containing methanol and the constituents from coal gasification. The specific tasks of this study are as follows:





- 1. Develop parameter estimation methods for the extended SRK equation of state and for the activity coefficient equations.
- 2. Collect the necessary binary VLE data and evaluate the binary model parameters.
- 3. Develop multicomponent bubble point calculation programs with both the equation-of-state and the activity coefficient methods, and compare the model calculations with the binary and ternary VLE data.
- 4. Formulate a gas solubility calculation using the extended SRK equation of state that will be a practical and useful method for the estimation of solubility of each component in methanol or a mixed solvent.
- 5. Design and construct a high-pressure vapor-liquid equilibrium apparatus.
- 6. Test the apparatus and experimental procedure by measuring VLE data for methanol-carbon dioxide mixtures and comparing with data from the literature.
- 7. Obtain ternary methanol-carbon dioxide-nitrogen P-T-x-y data at 243.15 and 273.15 K to evaluate the mixed gas solubility calculation.
- 8. Obtain the ternary methanol-carbon dioxide-water P-T-x data at 243.15, 258.15, 273.15, and 298.15 K to evaluate the bubble pressure calculation and the gas solubility calculation in a mixed solvent.

MODELING PHASE EQUILIBRIA WITH AN EQUATION OF STATE

An equation of state that can be used to describe all fluid phases has many advantages in phase equilibrium calculations. Most importantly, it eliminates the troublesome necessity of defining a reference state for a multicomponent mixture that includes one or more supercritical components. Simple cubic equations of state, such as the Soave-Redlich-Kwong (Soave, 1972) and the Peng-Robinson (1976), have been useful in phase equilibrium calculations. The SRK equation of state was originally developed to describe the phase equilibrium behavior of hydrocarbons, and the inclusion of a binary interaction parameter in the equation has extended its range to include nonhydrocarbons. Incorporating a temperature dependence of the binary interaction parameters and/or a polar correction factor may further extend its application to systems containing polar compounds (Evelein and Moore, 1976; Chang et al., 1983; Mathias, 1983). An extended SRK equation of state with a Mathias (1983) polar correction factor was employed in this work. It is described in the following section.

THE EXTENDED SRK EQUATION OF STATE

The SRK equation of state has the form

$$P = \frac{RT}{(v-b)} - \frac{a}{v(v+b)}$$
(22)

For any pure component, the constants a and b are found at the critical point to be

$$a(T_c) = a_c = \frac{0.42747 R^2 T_c^2}{P_c}$$
(23)
$$b = \frac{0.08664 R T_c}{P_c}$$
(24)

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Soave (1972) expressed a as a function of temperature and held b constant, so that

$$a(T) = a_c \alpha(T) \tag{25}$$

where the quantity α is a function of temperature. An expression used here is given by Mathias (1983) as

$$\alpha_{0.5} = 1 + m(1 - T_r^{0.5}) - p(1 - T_r)(0.7 - T_r)$$
(26)

The first and second terms on the right side of Equation 26 were introduced by Soave to correlate m as a function of the acentric factor and reproduce the vapor pressures of nonpolar hydrocarbons. Graboski and Daubert (1978a) used a regression program to evaluate m based on a large API vapor pressure data set for hydrocarbons and gases to obtain

$$m = 0.48508 + 1.55171 \ \omega - 0.15613 \ \omega^2 \tag{27}$$

Although use of the Soave α temperature function calculates vapor pressures of hydrocarbons and gases accurately, it can not do the same for vapor pressures of polar compounds such as water and alcohols. Mathias (1983) introduced the third term on the right side of Equation 26 for this purpose; it uses a correction term p that is obtained by fitting the equation to the vapor pressure data of the system component. This polar correction factor uses only one temperature-independent parameter and enables accurate calculation of the vapor pressures of the polar compounds.

The extended Soave-Redlich-Kwong equation can be applied to mixtures using the mixing rules

$$a = \sum_{i=1}^{N} \sum_{j=1}^{N} x_i x_j a_{ij}$$
(28)

and

$$b = \sum_{i=1}^{N} \sum_{j=1}^{N} x_i x_j b_{ij}$$
(29)

where the cross parameters are given by

$$a_{ij} = (a_i a_j)^{0.5} (1 - K_{ij})$$
(30)

$$b_{ij} = \frac{(b_i + b_j)}{2} (1 - C_{ij})$$
(31)

and K_{ij} and C_{ij} are interaction parameters.

In a previous study (Chang et al., 1983), K_{ij} was expressed as a function of temperature for systems containing methanol:

$$K_{ij} = K_{ij}^{0} + K_{ij}^{1}T(K)$$
(32)

Mathias (1983) has suggested that C_{ij} should also be expressed as a function of temperature:

$$C_{ij} = C_{ij}^{0} + C_{ij}^{1}T(K)$$
(33)

The evaluation of fugacity coefficients from the SRK equation of state is made easier with the definitions

$$z = \frac{Pv}{RT} \tag{34}$$

$$A = \frac{aP}{R^2 T^2} \tag{35}$$

$$B = \frac{bP}{RT} \tag{36}$$

Equation 22 then can be written as

$$z^{3} - z^{2} - (A - B - B^{2})z - AB = 0$$
(37)

A generalized treatment of the system allows evaluation of the fugacity coefficient of any component in a mixture from Equation 14

$$\ln \phi_i = \frac{1}{RT} \int_V^\infty \left[\left(\frac{\partial P}{\partial n_i} \right)_{T, V, n_{j \neq i}} - \frac{RT}{V} \right] - \ln z$$
(14)

Using the extended SRK equation in Equation 14 gives

$$\ln \phi_i = \frac{b_i(z-1)}{b} - \ln (z-B) - \frac{A \ln (1+B/z)}{B} \left[\sum_{j=1}^N \frac{x_j a_{ij}}{a} - \frac{b_i}{b} \right]$$
(38)

Equation 38 can be used to calculate the fugacity coefficients of a component in both liquid and gas phases at equilibrium. In these calculations, the compressibility factor z is obtained by solving Equation 37. The largest root of Equation 37 is used to evaluate gas-phase fugacity coefficients; the smallest root is used to evaluate liquidphase fugacity coefficients. The advantage of solving Equation 37 rather than using Equation 22 is that the compressibility factor is, in most cases, between 0 and 1, while the volume, v, is unbounded. Equation 37 can be solved by a Newton convergence technique with initial estimates of the compressibility factor being set at 1 for the gas phase and 0 for the liquid phase. The iteration proceeds until the absolute value of the left side of Equation 37 is less than 10^{-14} . This tight tolerance is essential for calculation of liquid phase behavior where compressibility is very small (< 0.03).

EVALUATION OF THE POLAR CORRECTION FACTOR

Successfully predicting multicomponent VLE behavior begins with a procedure for accurately calculating pure-component vapor pressures. Soave (1972) introduced a generalized temperature function in the SRK equation that forces the equation to correlate accurately the vapor pressures of nonpolar and slightly polar substances. Mathias (1983) added a polar correction term in the Soave temperature function. Although this term has only one temperature-independent polar correction factor, p, Mathias was unable to correlate this factor with other molecular properties. Therefore, this polar correction factor must be evaluated for each polar component in the system of interest before applying the extended SRK equation to binary or multicomponent systems.

The polar correction factor can be evaluated by matching the calculated vapor pressures from the equation with vapor pressure data of the polar compound. Figure 2 shows a logic flow diagram for evaluating this factor. An optimized value of p can be obtained by minimizing an objective function of the sum of vapor pressure variances for n temperatures using a Fibonacci search technique. As the polar correction factor is expected to be close to zero, setting p equal to zero is an excellent place to start the search for this quantity. A vapor pressure calculation corresponds to evaluating a pure-component vapor-liquid equilibrium condition; this is done by adjusting pressure until the ratio of liquid-phase fugacity coefficient to vapor-phase fugacity coefficient is one. A computer program ASAIN (see Chang 1984) is available for the polar correction factor evaluation.



Figure 2. Logic Flow Chart for Polar Correction Factor Evaluation.

Table 3 lists several values of p for polar components of interest for this study. The vapor pressure data were calculated from the Antoine equation with constants from Reid *et al.* (1977). Table 3 also lists the values of p for methanol and water that were given by Mathias (1983). The polar correction factors are large for methanol and water, and the improvements in fitting their vapor pressures are significant. However, the polar correction factor is relatively small for methyl mercaptan. The p values for ethyl mercaptan and dimethyl sulfide are near zero, so that the correction to the SRK equation may not be necessary for these two compounds. The polar correction factors for hydrocarbons and other gases are assumed to be zero because the SRK equation calculates their vapor pressures very well.

Compound	Optimal p Value		Temp. Range	Avg	% Dev.*
Mathias		This Work	K	p=0	p fitted
MeOH	0.2359	0.2208	213 - 513	11.92	1.16
H ₂ O	0.1277	0.1262	273-643	7.18	1.05
С́Н _а SH	-	0.0237	200-300	3.83	1.65
С, н ₋ SH	-	0.0010	225-330	1.05	1.03
сӊ ₃ šсн ₃	-	-0.0012	225-330	0.95	0.98

TABLE 3POLAR CORRECTION FACTOR

* Where the average % deviation is defined by,

$$Avg Dev = \sum_{1}^{n} \frac{|P_e - P_{cal}|}{n}$$

and n equals the number of data points.

BINARY PHASE EQUILIBRIUM AND INTERACTION PARAMETER EVALUATION

The use of the SRK equation to perform binary vapor-liquid equilibrium calculations for a hydrocarbon-hydrocarbon system has been found to be very accurate. When a binary system contains a non-hydrocarbon, the SRK equation must include at least a
temperature-independent binary interaction parameter (K_{ij} in Equation 30). For a system containing a polar component, temperature-dependent binary parameters are necessary. Evaluation of these parameters is from binary mixture data, and preferably from phase-equilibrium data. According to Graboski and Daubert (1978b), the best criterion for selecting the optimal interaction parameter is a minimization of the bubble point pressure variance, as defined by the equation

$$\sigma^2 = \sum_{k=1}^n \left[\frac{P_e - P_{cal}}{P_e} \right]_k^2 \tag{39}$$

This criterion was used in two optional search procedures to evaluate the binary interaction parameters in the extended SRK equation. In the first procedure, a singlevariable Fibonacci search technique was used to determine a temperature-independent optimal interaction parameter. The experience in this study suggests two ranges of this parameter to begin the search procedure. One is from 0 to 0.25 and the other is from -0.3 to 0. A computer program BFAIN (see Chang 1984) is available to evaluate a temperature-independent binary interaction parameter such as K_{ii} by fixing C_{ii} equal to zero. In the second procedure, a multivariable pattern search was used to determine the optimal $K_{ij}^0, K_{ij}^1, C_{ij}^0$ and C_{ij}^1 . Zero is a good starting value in the estimation of these parameters. However, the search for the first two may take the values reported previously (Chang et al., 1983) as initial estimates. The parameter search may need a small initial step size (0.0001) to prevent the parameters from jumping out of the range in which the equation of state can perform the calculation using that adjusted parameter set. Hence, the pattern search takes a very long computing time (30 to 120 minutes on VAX 11/780, depending on the system and the number of data points). A computer program PTAIN is available for the above purpose (see Chang 1984). Figure 3 gives a schematic diagram outlining the calculations.

Binary P-T-x data were used in the parameter evaluations. The calculated pressure for each data point was evaluated through a bubble point computational routine using the given values of temperature and mole fraction. The criterion for this equilibrium calculation has been shown to be

$$y_i \phi_i^V = x_i \phi_i^L \tag{13}$$

where ϕ_i^V and ϕ_i^L are obtained from Equation 17. Iterations proceed until mole fractions in the vapor phase sum up to one. Double precision and tight tolerances in both the Newton convergence technique, the absolute magnitude of the left hand side of Equation 37 < 10⁻¹⁴) and bubble point pressure calculations ($|\sum y_i - 1| < 10^{-7}$) were used. These tolerances become essential for calculation of liquid phase behavior where compressibility is very small (< 0.03). A schematic diagram for the bubble point



Figure 3. Logic Flow Chart for Binary Interaction constant Evaluation in the Phi Method.

pressure computational technique is given in Figure 4.

In addition to the binary parameters referred to above, the extended SRK equation of state requires critical temperature, critical pressure, acentric factor, and polar correction factor for each of the components of a mixture. Table 4 lists the values of these properties for the components of interest in this study.

Interaction parameters for the binary mixtures formed by methanol, carbon dioxide, hydrogen sulfide, nitrogen, carbonyl sulfide, hydrogen, carbon monoxide, methane, ethane, ethylene, propane, propylene, methyl mercaptan, dimethyl sulfide and water were evaluated from binary equilibrium or solubility data that cover the operating temperature and pressure ranges for an acid gas removal system that uses refrigerated methanol as a solvent. The interaction parameters of gas-gas systems were assumed to be independent of system temperature, but the interactions parameters in methanol-gas systems were assumed to be linearly dependent on temperature.





Component	T _c (K)	P _c (atm)	V _c (ml/mole)	ω	р	
Ha	33.19 ^b	12.98 ^b	65.0	-0.220	0.00	
N_{c}^{2}	126.2	33.5	89.5	0.040	0.00	
co^2	132.9	34.5	93.1	0.049	0.00	
CH,	190.6	45.4	99.0	0.008	0.00	
$C_{0}H_{4}$	282.4	49.7	129.0	0.085	0.00	
$C_{0}^{2}H_{e}^{4}$	305.4	48.2	148.0	0.098	0.00	
$C_{2}^{2}H_{6}^{0}$	365.0	45.6	181.0	0.148	0.00	
C H	369.8	41.9	203.0	0.152	0.00	
co	304.2	72.8	94.0	0.225	0.00	
H _a Ś	373.2	88.2	98.5	0.100	0.00	
cós	378.8°	62.66 ^c	$135.0^{\rm c}$	0.099	0.00	
CH _a SH	470.0	71.4	145.0	0.155	$0.0237^{ m e}$	
C,H ₅ SH	499.0	54.2	207.0	0.190	0.0010^{e}	
CH ₃ SCH ₃	503.0	54.6	201.0	0.190	-0.0012 ^e	
MeŎH	512.6	79.9	118.0	0.559	0.2359^{d}	
H ₂ O	647.3	217.6	56.0	0.344	0.1277 ^d	

TABLE 4PURE COMPONENT PHYSICAL PROPERTIES^a

^a Reid et al. (1977)
 ^b Lin (1980)
 ^c Robinson and Senturk (1979)
 ^d Mathias (1983)

^e Evaluated by program ASAIN

Methanol-Supercritical Gases

Supercritical gases that are present in large amounts in the raw gas from coal gasification include hydrogen, nitrogen, carbon monoxide and methane. The quantities of these gases can sum to 70 to 75 mole% of the total produced gas. These gases are classified in Group I, as shown in Figure 1, because they have low fluid densities and similar molecular properties. The solubilities of these gases in methanol may be sufficiently large to represent a significant economic loss at an extremely low temperature and high pressure. An accurate description of the binary phase equilibria of these gases in methanol is necessary for the development of an extended SRK equation that can be used to describe the phase equilibria of multicomponent systems containing coal gas and methanol.

Several modified versions of the SRK equation of state can be used in phase equilibrium calculations involving supercritical components, especially hydrogen. Hydrogen creates special problems because it is a quantum fluid. Graboski and Daubert (1979) replaced the temperature function α in the SRK equation with an exponential function to be used with the "classical" critical constants $T_c = 41.67$ K, $P_c = 20.75$ atm, and $\omega = 0$. These constants are estimated on the basis of classical mechanics which do not take quantum effects into account. Boston and Mathias (1980) have suggested a generalized extrapolation of α at a supercritical temperature for a supercritical substance. However, Lin (1980) used the original temperature function α , even for hydrogen, with the true critical constants and acentric factor: $T_c = 33.19$ K, $P_c = 12.98$ atm, and $\omega = -0.22$. Lin's approach was used in this work because it is simple and it may be the best way to handle supercritical components. Since the function α proposed by Soave is well behaved, the adoption of other α functions for supercritical components is unnecessary.

The solubility data of hydrogen, carbon monoxide, and methane were read from the chart prepared by Landolt-Bornstein *et al.* (1976) and were converted to Henry's constants (see Chang 1984) at four temperatures. A set of P-T-x data was then generated by using Henry's law calculations for each gas component. Under the absorption operating conditions, the solubilities of these gases follow Henry's law very well. The data from this source cover a broad range of temperatures, and they are believed to be reliable because they match the data from other sources (Krichevskii *et al.*, 1937; Krichevskii and Efremova, 1951; Michels *et al.*, 1953) at room temerature.

The generated data were used to evaluate the binary interaction parameters in the

extended SRK equation of state for the methanol-hydrogen, methanol-carbon monoxide, and methanol-methane systems. The four parameters in the equation for each binary system were determined simultaneously, and the resulting optimal parameter sets are listed in Table 5. The generated data sets cover a temperature range from 223 to 303 K and a pressure range from 1 to 60 atm; each data set has a total of 16 calculated points.

Methanol-Hydrogen System--

Figure 5 shows an excellent fit of the calculated bubble point pressures to the generated data. The root mean square deviation of bubble pressures (RMSD%) is less than 1%. The solubility of hydrogen in methanol increases with increasing temperature. The temperature effect on gas solubility can be qualitatively obtained by analyzing the terms in partial molar entropy or enthalpy change. A detailed discussion has been given by Prausnitz (1969). Generally, the solubility for a sparsely dissolved gas increases with temperature.

Methanol-Carbon Monoxide System--

Figure 6 shows a good fit of the calculated values to the generated data. The root mean square deviation of bubble pressures is less than 3%. The solubility of carbon monoxide increases as the temperature decreases.

Methanol-Methane System--

Figure 7 shows an excellent fit of the calculated results to the generated data. About a 2% deviation was found in the fitting process. The solubility of methane in methanol obviously increases as the temperature drops.

Methanol-Nitrogen System--

The data of Weber and Knapp (1978) were used to evaluate the interaction parameters in this system. The data cover a temperature range from 225 to 300 K and a pressure range from 20.7 to 177 atm. Although a previous paper (Chang *et al.*, 1983) used only the temperature-dependent interaction parameter K_{ij} to fit the data, both temperature-dependent parameters K_{ij} and C_{ij} are included in this work. The results of fitting the data are shown in Table 5 for a total of 21 data points; the root mean square deviation of bubble pressures was 2.24%. Figure 8 shows the excellent fit of the calculated results to the data.

System	κ _a 0	Ka ¹ (10 ⁻³)	к _b 0	κ _b 1 (10 ⁻³)	RMSD ^a %	Eyb	Ra T, K	nges P, atm	No. of data	Ref.
MeOH-H2 MeOH-C0 MeOH-C2H4 MeOH-C2H4 MeOH-C2H6 MeOH-C3H6 MeOH-C3H6 MeOH-C3H8 MeOH-C02 MeOH-H2S MeOH-C43SH MeOH-CH3SCH3 MeOH-CH3SCH3 MeOH-H2O H2O-C02	-1.4849 -0.4455 -0.3537 -0.2650 -0.2655 -0.2318 -0.2349 -0.1140 -0.0740 -0.0502 -0.1418 0.0197 -0.0272 -0.1638 -0.5135	3.3560 0.6615 0.5240 0.7882 0.8885 0.8925 0.8434 0.4066 0.3767 0.3286 0.6720 0.1500 0.2140 0.2090 1.2492	-2.0324 -0.4702 -1.1193 0.0228 0.2765 0.0887 0.0840 -0.2349 0.2332 0.1710 0.0585 -0.1334 -0.1511 -0.0733 0.3694	6.4330 0.8860 4.2590 -0.7030 -1.1000 -0.4030 -0.0510 0.9930 -0.5905 -0.0190 0.1690 1.0770 1.1120 0.3280 0.0673	0.87 2.60 2.24 2.11 2.36 4.79 2.44 8.90 4.61 4.84 6.23 5.55 6.88 2.44 4.40	- - - - - - - - - - - - - - - - - - -	223-303 223-303 225-300 223-303 228-248 248-323 228-303 238-303 238-303 248-273 233-293 263-288 263-288 298-338 273-298	1.0-60.2 $1.0-60.2$ $20.7-177.0$ $1.0-60.2$ $1.0-18.0$ $10.0-60.0$ $1.0-1.2$ $1.0-7.9$ $1.0-79.5$ $2.0-10.0$ $0.38-11.1$ $0.19-1.38$ $0.08-0.45$ $0.04-1.02$ $1.0-36.0$	16 16 16 18 21 9 19 130 22 51 18 24 72 93	C C d C e f,g C,h i-o 1 p q r-u V
<pre>a RMSD % = { $\Sigma [(P_e - P_{cal})/Pe]^2/n$}^{1/2} x 100 % , where n = no. of data points. n 1 b Ey = [$\Sigma y_{1e} - y_{1cal}]/n$. ^C Landolt-Bornstein et al. (1976). 1 d Weber and Knapp (1978). ^e Shenderei et al. (1962). ^f Ma and Kohn (1964). g Ohgaki et al. (1976). ^h Nagahama et al. (1971). ⁱ Krichevskii and Lebedeva (1947). j Bezdel and Teodorovich (1958). ^K Shenderei et al. (1959). Yorizane et al. (1969). Katayama et al. (1975). ⁿ Ohgaki and Katayama (1976). ^o This work. ^p Oscarson (1981). g Jackowski (1980). ^r Butler et al. (1933). ^s Ratcliff and Chao (1969). ^g McGlashan and Williamson (1976). ^u Kooner et al. (1980). ^v Houghton et al. (1957).</pre>										

Table (5.) Correlations of VLE Binary Pairs Containing Methanol or Water.





Figure 6. Methanol-Carbon Monoxide Equilibria.



Figure 7. Methanol-Methane Equilibria.



Binary Parameters K_{ij} and C_{ij} --

Figure 9 shows the plot of K_{ij} vs. temperature for the methanol-hydrogen, methanol-carbon monoxide, methanol-nitrogen, and methanol-methane systems. The K_{ij} 's are all negative values between 0 and -0.8 in the temperature range of interest. A light gas has a tendency to have a large negative K_{ij} value. Figure 10 plots C_{ij} vs. temperature, and shows that except for the methanol-methane system, the value of C_{ij} increases as the temperature increases. The C_{ij} values for these binary systems are between -0.7 to 0.3 in the temperature range of interest.

Methanol-Light Hydrocarbon Gases

The light hydrocarbon gases included in the present study were ethylene, propylene, ethane, and propane. Although these compounds are present only in small amounts in crude coal gas, they have relatively large solubilities in methanol. Accurate calculation of the phase equilibria between these gases and methanol is important to the gas separation and solvent regeneration.

Methanol-Ethylene System--

The data of Shenderei *et al.* (1962) were used to evaluate four binary parameters in the extended SRK equation. The data include a temperature range from 228 to 248 K and a pressure range from 1 to 18 atm. The optimal parameter values are listed in Table 5. Figure 11 shows that the calculated and experimental results agree well up to an ethylene mole fraction of 0.6 in the liquid; however, no experimental data exist at mole fractions of ethylene above 0.6. The bubble pressure deviation was less than 2.4% for a total of 18 data points. This system exhibits liquid-liquid-gas (LLG) equilibria at temperatures above 260 K (Zeck and Knapp, 1983).

Methanol-Ethane System--

The P-T-x data of Ma and Kohn (1964), and Ohgaki et al. (1976) were used in the binary parameter evaluation. These data cover a temperature range from 248 to 323 K and a pressure range from 10 to 60 atm. Table 5 lists the optimal parameters and indicates a 4.8% deviation in bubble pressures for a total of 21 data points. Figure 12 shows a good fit of the calculated results to the experimental data in the liquid phase; it also shows a good prediction of ethane compositions in the vapor phase. Zeck and Knapp (1983) have found that this system exhibits LLG equilibria at temperatures in the range from 240 K to 298.15 K. The calculated results indicate a phase split (dotted line) for



Figure 9. Binary Interaction Parameters for Methanol-Supercritical Gases.



Figure 10. Binary Interaction Parameters for Methanol-Supercritical Gases.





each of the isotherms in Figure 12 at ethane mole fractions of about 0.23 in the methanol-rich phase, although the experimental data show phase separation at ethane mole fraction of 0.4. The portions of calculated equilibrium curves which show local maxima and minima represent metastable phase equilibrium conditions. Figure 12 gives the P-x plot at 323.15 K, a temperature above the critical point of ethane. The vapor (ethane-rich) curve has detached from the pure ethane edge, and it shows a large change in curvature. Detailed phase diagram calculation near the critical region is beyond the scope of this work, but Hong et al. (1983) and Streett (1983) have given good discussions and diagrams for similar systems at high pressure.

Methanol-Propylene System--

The converted P-T-x data from the solubility chart (Landolt-Bornstein *et al.*, 1976) were used to evaluate the binary parameters. These converted data have a temperature range from 228 to 303 K and pressures around 1 atm. Table 5 lists the optimal set of parameters. Because the extended SRK equation can be applied to a wide range of temperatures and pressures, the evaluated parameters are believed sufficient to extend the application of the available data to pressures higher than 1 atm.

Methanol-Propane System--

The data of Nagahama *et al.* (1971) at 293.05 K and the *P*-*T*-*x* data calculated from the solubility chart (Landolt-Bornstein *et al.*, 1976) were used together to obtain binary parameters in the extended SRK equation. The optimal values of the parameters are listed in Table 5. The root mean square deviation of bubble pressures is high, about 8.9%, because the calculated values do not agree with the experimental data at propane mole fractions in the liquid exceeding 0.3. Figure 13 shows the calculated bubble pressures and the experimental data of Nagahama *et al.* (1971). The calculated results, which show local maximum and minimum, may belong to metastable state solutions, and they imply that a LLG equilibrium condition is predicted by the equilibrium calculation from the cubic equation of state. Another justication for this discrepancy between the data and calculated values is that the quadratic mixing rule in the equation may be insufficient for a mixture of methanol and propane at high pressure. The system cannot be correlated by the quadratic mixing rule since a large miscibility gap would be predicted.

Binary Parameters K_{ij} and C_{ij} --

Figure 14 shows the dependence of K_{ij} on temperature for the binary systems methanol-ethylene, methanol-ethane, methanol-propylene, and methanol-propane over the range of temperatures from 220 to 320 K. The values are between -0.07 to 0.05, and





Figure 14. Binary Interaction Parameters for Methanol-Light Hydrocarbon Gases.

they increase with increasing temperature. Figure 15 shows the dependence of C_{ij} on temperature. All values of C_{ij} are between -0.08 and 0.08. Note that the temperature dependence of both parameters for the methanol- C_3H_8 system is quite different than it is for the other three systems. This could simply be the result of a relatively poor fit of the binary data by the equation of state for the methanol- C_3H_8 system at high pressures.

Methanol-Acid Gases

Carbon dioxide, hydrogen sulfide, carbonyl sulfide, and mercaptans are the primary components whose removal is desired in an acid gas removal system. The phase equilibrium behavior of these acid gases in methanol has great importance in the absorption-stripping operations of acid gas removal systems. Optimal operation of the system may be geared to maximize the removal of these acid gases and to separate the sulfur species from carbon dioxide. Conditions leading to optimal operation can be determined by using an appropriate model of the phase equilibrium behavior in the design of the system. The data from the binary systems presented here cover a broad range of temperatures and pressures, including those found in acid gas removal systems using methanol as a physical solvent. The data are used to evaluate all four binary interaction parameters in the extended SRK equation, and thereby develop a model useful for the prediction of multicomponent phase equilibrium behavior.

Methanol-Carbon Dioxide System--

This binary system is the most important system under consideration, since carbon dioxide occupies about 20 to 35 mole% of the product gas from coal gasification, and it has a very large solubility in methanol. The data of Krichevskii and Lebedeva (1947), Bezdel and Teodorovich (1958), Shenderei *et al.* (1959), Yorizane *et al.* (1969), Katayama *et al.* (1975), Ohgaki and Katayama (1976), and the data generated in this laboratory (see experimental) were used to evaluate binary interaction parameters. These data have a temperature range from 223 to 313 K and a pressure range from 1.0 to 79.5 atm. The data of Krichevskii and Lebedeva (1947) at 298.15 K were not used because they have large deviations from model calculations; these deviations are over five times the average error of the data of Katayama *et al.* (1975), and Ohgaki and Katayama (1976) from model calculations.

Table 5 lists the values of the optimal binary interaction parameters. The root mean square deviation of bubble pressures was less than 5% for a total of 130 data points. The pressure-liquid composition diagram of Figure 16 shows the fit of the calculated values to the data. Small discrepancies exist between the literature data at 298



Figure 15. Binary Interaction Parameters for Methanol-Light Hydrocarbon Gases.



Figure 16. Methanol-Carbon Dioxide Equilibria.

and 273 K. As shown in Figure 16, the calculated bubble pressures at 298 K are higher than the literature data when the carbon dioxide mole fraction in the liquid is less than 0.6, while the calculated bubble pressures at 273 K are lower than the literature data. On the other hand, the experimental data from the present work seem to be fit well by the model calculations. Although Figure 16 does not show the predicted vapor-phase compositions, the extended SRK equation of state gives very good agreement with the 21 data points for which vapor compositions were measured; the average deviation of carbon dioxide mole fractions in the vapor phase was 0.0007. The data used for comparison with the SRK equation were taken at 298.15 K by Katayama *et al.* (1975) and Ohgaki and Katayama (1976).

Methanol-Hydrogen Sulfide System--

The data of Yorizane *et al.* (1969) were used exclusively in this study to determine the interaction parameters for this binary system. The data include liquid-phase compositions at temperatures of 248, 258, and 273 K and at pressures from 2 to 10 atm. Table 5 lists the binary parameters in the extended SRK equation that provided the best fit to the equilibrium data. The fit to the data resulted in less than 5% root mean square deviation between bubble pressures of the 22 data points and the equation of state. Figure 17 shows an excellent fit of the calculated values to the data for liquids containing less than a 0.6 to 0.7 mole fraction of hydrogen sulfide.

Figure 17 also shows three dotted curves that correspond to the bubble pressures calculated by setting all the binary interaction parameters in the extended SRK equation to zero. The dotted curves are nearly straight lines between the two pure-component vapor pressures at the system temperatures. Although the extended SRK equation is able to calculate pure-component vapor pressures accurately, computations involving the binary mixture provide results that are close to those obtained from Raoult's law when the quadratic mixing rule is applied without a binary interaction parameter. The four binary interaction parameters correct for deviations from ideal behavior that result from mixing the pure components. However, these corrections seem insufficient for liquids containing a hydrogen sulfide mole fraction larger than 0.6 to 0.7.

Methanol-Carbonyl Sulfide System--

The data of Oscarson (1981) reported to the Design Institute for Physical Property Research were used in the binary interaction parameter evaluation for the methanolcarbonyl sulfide system. The data cover a temperature range from 233 to 293 K and a pressure range from 0.38 to 11.1 atm. The binary interaction parameters determined from the data are listed in Table 5, which also shows a 6.2% root mean square deviation of bubble pressures for a total of 51 data points. Figure 18 shows that the



Figure 17._ Methanol-Hydrogen Sulfide Equilibria.

50



Figure 18. Methanol-Carbonyl Sulfide Equilibria.

calculated results fit the data very well for liquids having a carbonyl sulfide mole fraction of less than a 0.5. Oscarson also reported vapor-phase compositions for this binary system. By comparing these values with the predicted vapor-phase compositions from the bubble point pressure calculations, the average error in mole fraction of the vapor is 0.0011. The calculated equilibrium pressures do not fit the data well for liquids containing a carbonyl sulfide mole fraction of more than 0.5 at temperatures of 273 and 293 K. In addition, the exhibition of local maxima and minima in the equation of state calculations indicates the existence of metastable solutions, and the concomitant formation of two liquid phases. The data, do not show liquid-phase separation.

Methanol-Methyl Mercaptan and Methanol-Dimethyl Sulfide Systems--

The P-T-x data reported by Jackowski (1980) were used to evaluate the interaction parameters for both methanol-methyl mercaptan and methanol-dimethyl sulfide mixtures. The data cover a temperature range from 263 to 288 K. The methanol-methyl mercaptan data have a pressure range from 0.19 to 1.38 atm, and the methanoldimethyl sulfide data range in pressure from 0.08 to 0.45 atm. Table 5 lists the optimal binary interaction parameter sets for both systems. The root mean square deviations in bubble pressures were 5.6% and 6.9% for the fittings of 18 data points from the methanol-methyl mercaptan system and 24 data points from the methanol-dimethyl sulfide system, respectively.

Figures 19 and 20 show the pressure-composition diagrams for the methanol-methyl mercaptan system and the methanol-dimethyl sulfide system, respectively. There was good agreement between calculated and experimental bubble pressures for both systems as long as the methanol mole fraction was at least 0.5. The predicted vapor-phase compositions for methanol-methyl mercaptan mixtures compare favorably up to a vapor-phase methyl mercaptan mole fraction of 0.95 (compared with the results from an activity coefficient correlation of Chapter 5). The predicted vapor-phase compositions for methanol-dimethyl sulfide are good up to a 0.8 mole fraction of dimethyl sulfide in the vapor phase (compared with the results from an activity coefficient correlation of Chapter 5). Both Figure 18 and Figure 19 show local extrema in both vapor- and liquid-phase equilibrium curves. The methanol-dimethyl sulfide data of Jackowski (1980) exhibits an azeotrope at each temperature; however, the cubic equation used with quadratic mixing rule incorrectly predicts phase splitting. A similar result was given by Huron and Vidal (1979) for an acetone-water system.

Binary Parameters K_{ij} and C_{ij} --

Figure 21 shows the values of K_{ij} for methanol-carbon dioxide, methanol-hydrogen sulfide, methanol-carbonyl sulfide, methanol-methyl mercaptan, and methanoldimethyl mercaptan mixtures. These results cover the temperature range from 220 to









Figure 21. Binary Interaction Parameters 6 for Methanol-Acid Gases.

320 K, and the K_{ij} parameters vary between 0 and 0.07. The parameters increase with increasing temperature for all the binary systems. Figure 22 shows the values of C_{ij} , which vary from 0.04 to 0.20 in a temperature range of 220 to 320 K.

Systems Containing Water

Systems containing water provide a good test of any model since they generally exhibit significant nonideality. In the experimental part of this study, a water and methanol mixture was used as a solvent to study the solubilities of carbon dioxide. Therefore, binary systems of methanol-water and carbon dioxide-water are examined here.

The methanol-water vapor-liquid equilibrium data of Butler *et al.* (1933), Ratcliff and Chao (1969), McGlashan and Williamson (1976), and Kooner *et al.* (1980) were used to develop extended SRK correlations. The data cover a temperature range from 298 to 338 K and a pressure range from 0.04 to 1.02 atm. The interaction parameters were obtained for the carbon dioxide-water system by using the data compiled by Houghton *et al.* (1957). The data used in the calculations were in a temperature range from 273 to 298 K and pressure range from 1 to 36 atm. Table 5 lists the optimal binary parameters, and it also shows good agreement between calcuated and measured bubble pressures for both binary systems. Figure 23 demonstrates that the extended SRK can correlate equilibrium data for the methanol-water system. The interaction parameters K_{ij} and C_{ij} increase with increasing temperature for both binary systems, but the effect of temperature on C_{ij} for mixtures of carbon dioxide and water is slight.

<u>Comparison of Results Using a Full Parameter Set to Those</u> <u>Using a Reduced Parameter Set</u>

Binary systems of methanol-carbon dioxide, methanol-water, and carbon dioxidewater are discussed here. Table 6 gives binary parameters obtained when either the complete extended SRK equation (optimal K_{ij} and C_{ij}) or a reduced form of the equation (C_{ij} set to zero) were fit to data on these systems.

Numerical comparisons in Table 6 show that better fits to the methanol-carbon dioxide and carbon dioxide-water equilibrium data were obtained when both K_{ij} and C_{ij} were included in the equation of state. Note that the improvement in the fit when both are used is slight for the methanol-water system; this may be because K_{ij} is more important than C_{ij} in a symmetric mixture such as that formed by methanol and







System	K_0	κ _a 1	_{لا} ل	Кb1	RMSD ^a	Fvb	Ra	inges	No.	Ref.
Jy 3 6 Cm	'`d	(10 ⁻³)	<u>ם</u> יי	(10 ⁻³)	70 	∟у _	Т, К	P, atm	data	
MeOH-CO2	-0.0740	0.3767 0.3551	0.2332	-0.5905	4.61 8.32		223-313	1.0-79.5	130	c-i
MeOH-H ₂ O	-0.1638 -0.1873	0.2090	-0.0733	0.3280	2.44	0.0141	298-338	0.04-1.02	72	j-m
CO2-H2O	-0.5135 -0.4820	1.2492 1.1831	0.3694 0.	0.0673 0.	4.40 12.61	-	273-298	1.0-36.0	93	n
a RMSD % = { $\sum_{n=1}^{n} [(P_e - P_{cal})/P_e]^2/n$ } ^{1/2} x 100 %, where n = no. of data points. b Ey = [$\sum_{n=1}^{n} y_{1e} - y_{1cal}]/n$. C Krichevskii and Lebedeva (1947). d Resided and Teederswick (1950) = C Sherdersei et al. (1950) = f Veries and Lebedeva (1950)										
g Katayam J Butler ^M Kooner	and leddord na et al. (1 et al. (193 et al. (198	1975). 1975). 133). k 130). n	h Ohgaki Ratcliff Houghton	and Katay and Chao et al. (1	ama (19 (1969) 957).	976) _{1 M}	'i This w cGlashan	ork. and William	nson (19	976).

Table 6. Comparison of Correlated Results for VLE Binary Pairs Using a Full Parameter Set to a Reduced Parameter Set.

water. As K_{ij} modifies the parameter in the SRK equation that accounts for intermolecular attractive forces, the hydrogen bonding in the methanol-water system could make K_{ij} even more important. C_{ij} is more significant in the slightly asymmetric methanol-carbon dioxide system (RMSD improved from 8.32% to 4.61%), and of even greater importance in the asymmetric carbon dioxide-water system (RMSD improved from 12.61% to 4.40%).

For a mixture of close boiling components, such as methanol and water, values of α for both components are similar (1.778 for methanol and 1.769 for water at 0°C). An adjustment on the K_{ij} parameter set, which expresses a deviation from a geometric mean of $a_c \alpha$ of the pure components, will be enough to correlate the bubble point pressures of the mixture. However, values of α are 1.088 for carbon dioxide and 1.769 for water at 0°C. The large difference between these values may indicate that adjustment on the K_{ij} parameter set is insufficient to fit the data for mixtures of these compounds. Although a related discussion was given by El-Twaty and Prausnitz (1980) for the extremely asymmetric system of hydrogen and a heavy hydrocarbon, the temperature function α becomes small for hydrogen and causes K_{ij} insensitivity.

Gas-Gas Systems

Graboski and Daubert (1978b) observed that the interaction parameter in the Soave modification of the Redlich-Kwong equation of state did not play a strong role in equilibrium calculations for permanent gas components. Hence, in the present work the parameters in the extended SRK equation were set for gas components (defined in Figure 1) as follows: K_{ij} independent of temperature and C_{ij} equal to zero. Additionally, by setting the polar correction factor equivalent to zero for all the gases described here, the equation was reduced to a Graboski-Daubert (GD) version SRK equation of state.

The interaction parameters for gas-gas pairs were calculated from equilibrium data. Table 7 gives the parameter values for carbon dioxide-hydrogen sulfide, carbon dioxide-nitrogen, carbon dioxide-propane, and nitrogen-hydrogen sulfide systems. These values are slightly different from those determined by Graboski and Daubert (1978b), apparently because different data were used in their evaluation. However, there are no significant differences in the results calculated with the parameters from the present work and those from the work of Graboski and Daubert. The root mean square deviations of bubble point pressures were less than 4% for the carbon dioxide-hydrogen sulfide and carbon dioxide-propane mixtures. For the carbon dioxide-nitrogen and nitrogen-hydrogen sulfide mixtures, the deviations were between 6% and 7%.

	Optimal K _a			Rang	No.				
Binary	Crobacka	This	RMSD oz	тк	D atm	of	Ref		
System	Glaboske		/0	1, K	1,200	<u>((</u> 4) 4			
CO ₂ -H ₂ S	0.102	0.1036	2.00	224.82/313.15	6.8/60.0	76	b,c		
$CO_{2}-N_{2}$	-0.0 22	-0.0295	6.32	218.15/273.15	12.6/137.1	34	d-i		
CO ₂ -C ₂ H ₂	0.1018	0.1358	3.62	244.26/310.95	3.30/37.43	66	j-l		
N ₂ -H ₂ S	0.140	0.1727	7.00	227.98/300.04	3.30/204.14	40	m,n		
				· · · · · · · · · · · · · · · · · · ·	·				

 TABLE 7

 CORRELATIONS OF FOUR BINARY GAS-GAS SYSTEMS

where

RMSD % =
$$\left[\sum_{1}^{n} [(P_e - P_{cal})/P_e]^2\right]^{1/2} x 100\%$$

and n equals the number of data points.

b. Bierlein and Kay (1953). c. Sobocinski and Kurata (1959).

d. Aral et al. (1971). e. Krichevskii and Lebedeva (1962).

f. Kaminishi and Toriumi (1963). g. Muirbrook and Prausnitz (1965).

h. Yorizane et al. (1970). i. Zenner and Dana (1963).

j. Hamam and Lu (1976). k. Nagahama et al. (1974).

I. Reamer et al. (1951). m. Besserer and Robinson (1975).

n. Kalra et al. (1976).

Figure 24 gives isothermal pressure composition diagrams for carbon dioxidehydrogen sulfide mixtures. Excellent agreement is noted over the range of compositions and temperatures studied. Similar agreement was noted for carbon dioxide-propane mixtures.

Figure 25 shows good agreement between experimental and model predictions of bubble point pressures and vapor compositions for carbon dioxide-nitrogen mixtures, except for those close to the critical regions. Similar results were obtained for mixtures of hydrogen sulfide and nitrogen.

Table 8 summarizes the evaluated binary parameters K_{ij} for all gas-gas systems, including those from the present work as well as values from the literature. Values from the literature are the result of either using the original SRK equation or a GD version of the SRK equation (which has a slightly different set of constants in the *m* function).






Figure 25. Carbon Dioxide-Nitrogen Equilibria.

Parameters from these sources may be used directly or they may simply be assumed equal to zero in a vapor-liquid equilibrium calculation without introducing serious errors. For a mixed gas-methanol system the gas-gas interactions in the liquid are small. Lin's approach (see Section on Methanol-Supercritical Gases) was used for hydrogen-containing systems in this work, and some results are shown in Table 8.

PHASE EQUILIBRIA IN MULTICOMPONENT SYSTEMS

A program EQNBP for calculation of bubble point pressure in multicomponent systems has been developed and is presented by Chang, 1984. This program was used to calculate the binary phase equilibrium diagrams described in the previous sections. In this section, two methanol-containing ternary mixtures are used to demonstrate the bubble point pressure calculations. These multicomponent phase equilibrium calculations use only the pure and binary parameters determined earlier. The bubble point pressure calculation procedure for a multicomponent system is the same as for a binary system (see Figure 4). The subroutine DVLFGM2 was replaced by DVLFGMN for the dimensional expansion.

Methanol-Hydrogen-Nitrogen System

The data reported by Krichevskii and Efremova (1951) at 25° C were used in the evaluation. Liquid-phase composition and temperature were used in the model to calculate bubble point pressure and vapor-phase composition for each data point. Table 9 lists the results for the 11 data points. The average error in the predicted bubble point pressures is about 6%. The absolute average errors in the hydrogen and nitrogen vapor phase compositions are 2.8% and 3.1%, respectively.

Binary		K
-		a
COH_S	0.1036^{a}	0.102 ^b
$CO_{2}-N_{2}$	-0.0295^{a}	-0.022 ^b
CO_{0}^{2} -CH	$0.0973^{\mathbf{b}}$	
$CO_{0}^{2}-H_{0}^{4}$	-0.0883^{a}	0.134 ^c
$CO_0^2 - CO$	-0.0372^{a}	-0.064 ^b
CO _o -C _o H _o	$0.1346^{\rm b}$	
$CO_{0}^{2}-C_{2}^{2}H_{0}^{0}$	0.1358^{a}	$0.1018^{b}, 0.134^{d}$
$CO_{0}^{2}-C_{0}^{3}H_{1}^{3}$	0.0562^{a}	
$CO_{2}^{2}-C_{2}^{2}H_{e}^{4}$	$0.0914^{\mathbf{b}}$	
H _o S-H _o	-0.3002^{a}	
H ₂ S-CO	0.0688^{a}	
H ₂ S-N ₂	0.1727^{a}	0.140^{b}
H ₂ S-CH ₄	$0.0850^{\mathrm{b}}_{\cdot}$	0.0850 ^d
H ₂ S-C ₂ H ₆	0.0829 ^b	
$H_2^{I}S-C_3^{I}H_8$	0.0831^{b}	
N ₂ -CH ₄	0.0319 ^b	
$N_2 - H_2$	0.1016 ^a	
N_2^-CO	0.0460^{b}	
N ₂ -C ₂ H ₆	0.0388 ^b	0.039 ^d
$N_{2}^{-}C_{3}^{-}H_{8}^{-}$	0.0807 ^D	
CH_4-H_2	0.0050 ^c	
CH ₄ -CO	0.0300	
$CH_4-C_3H_8$	0.0110 ^d	
CH_4 - C_2H_4	0.0440°	
н ₂ -со	0.0904	· · · · · · · · · · · · · · · · · · ·
$H_{2}-C_{2}H_{6}$	0.0980	
$H_2-C_3H_8$		
$^{\rm CO-C_2H_6}$	0.0000 ⁰	
CO-C ₂ H ₂	0.0200 ⁰	

TABLE 8 RECOMMENDED BINARY INTERACTION PARAMETER IN THE SRK EQUATION OF STATE FOR GAS-GAS SYSTEMS

a Evaluated by program BFAIN.

b Graboski and Daubert (1978b).

c Lin (1980).

d Paunovic et al. (1981).

Methanol-Hydrogen-Carbon Monoxide System

Table 10 lists the experimental data of Krichevskii *et al.* (1937) and the predicted results from the model at 30° C. For a total of 12 data points, the average error in the predicted bubble point pressures was 4.4%. The absolute average errors in the hydrogen and carbon monoxide vapor-phase compositions were 6.4% and 6.7%, respectively.

Methanol-Hydrogen-Hydrogen Sulfide System

The predicted results for the methanol-hydrogen-hydrogen sulfide system do not compare satisfactorily with the data of Yorizane *et al.* (1969). This is believed to be caused by the fact that the solubility of hydrogen in methanol reported by Yorizane *et al.* (1969) is almost double that shown by the chart of Landolt-Bornstein *et al.* (1976). A different binary parameter set is required for the methanol-hydrogen system in order to have a satisfactory comparison of this hydrogen-containing ternary data set. Similar difficulties with nitrogen solubilites are encountered by taking the data on an apparatus similar to the one used by Yorizane *et al.* This problem will be discussed in the experimental section.

GAS SOLUBILITY CALCULATIONS USING AN EQUATION OF STATE

A gas solubility calculation, which is useful in the analysis of absorption-stripping processes, neglects the presence of solvent in the vapor phase, and it calculates the solute mole fraction in the liquid phase from the temperature, pressure, and composition of the vapor phase. The fundamental relationship used in such calculations is

$$f_i^V = f_i^L \tag{1}$$

A solubility calculation uses the equilibrium relationship in Equation 1 for each gas component. Moreover, using an equation of state that accurately describes the influence of temperature, pressure, and composition on the fugacities in both the vapor and liquid phases accounts for all the nonidealities in the mixture.

A solubility calculation program SOLMAN (see Chang 1984) has been developed by using the extended SRK equation of state with the binary parameters evaluated as described earlier. Figure 26 shows the logic flow diagram for this calculation. Since the

	x(Exp.)		Ρ.	atm	y(MeOH)	y(H2)	у(N2)
МеОН	`H ₂	N ₂	Exp.	Cal.	Čal. (Exp.	Cal.	Exp.	Cal.
0.9782	0.0143	0.0075	135.	125.68	0.0035	0.750	0.7474	0.250	0.2490
0.9757	0.0142	0.0101	129.	136.73	0.0036	0.672	0.6847	0.328	0.3116
0.9725	0.0047	0.0228	135.	130.82	0.0048	0.217	0.2353	0.783	0.7599
0.9750	0.0167	0.0083	142.	145.69	0.0034	0.750	0.7577	0.250	0.2389
0.9720	0.0186	0.0094	163.	164.46	0.0035	0.750	0.7520	0.250	0.2446
0.9696	0.0179	0.0125	166.	174.49	0.0036	0.672	0.6845	0.328	0.3119
0.9640	0.0062	0.0298	166.	178.99	0.0052	0.217	0.2296	0.783	0.7652
0.9588	0.0072	0.0340	188.	210.74	0.0056	0.217	0.2284	0.783	0.7660
0.9639	0.0210	0.0151	203.	210.21	0.0038	0.668	0.6741	0.332	0.3222
0.9625	0.0254	0.0121	224.	227.09	0.0036	0.750	0.7579	0.250	0.2385
0.943/	0.0103	0.0460	268.	313.13	0.0073	0.217	0.2261	0.783	0.7666
		Avg. e	rror P ^b	= 6.03%	Avg.	error y ^c	= 2.82%		3.09%
	^a Kriche	evskii and	Efremov	a (1951)	1997 - ander der rennen die de 1997 - Annekeren de	· · · · · · · · · · · · · · · · · · ·			
	^b Avg. e	error P =[11 Σ (Pe	- P _{cal})/F	Pe]/11 x 10	0%			
			.L 11						
		$\frac{1}{2}$		- V - 1 /		∩ ∩∕			
	Avy. e	itor y -L	4 (Уе	- yca)/y	,611/11 X TO	JU/6			

Table 9. Predicted and Experimental^a VLE Results for Methanol-H₂-N₂ System at 25^oC.

	x(Exp.)		P.	atm	v(MeOH)	y(H2)	y (CO)	
МеОН	H2	CO	Exp.	Cal.	Čal. (Exp.	Cal.	Exp.	Cal.	
 0.9865	0.0022	0.0139	50.	48.87	0.0077	0.270	0.2559	0.730	0.7363	
0.9682	0.0048	0.0270	100.	99.67	0.0062	0.270	0.2715	0.730	0.7223	
0.9533	0.0078	0.0389	150.	148.29	0.0063	0.270	0.2872	0.730	0.7064	
0.9389	0.0108	0.0503	200.	195.01	0.0070	0.270	0.2947	0.730	0.6983	
0.9248	0.0138	0.0614	250.	240.07	0.0078	0.270	0.2978	0.730	0.6944	
0.9104	0.0171	0.0724	300.	286.10	0.0088	0.270	0.3026	0.730	0.6886	
0.9865	0.0055	0.0080	50.	54.86	0.0065	0.638	0.6028	0.362	0.3907	
0.9744	0.0113	0.0144	100.	107.88	0.0050	0.638	0.6258	0.362	0.3692	
0.9639	0.0170	0.0191	150.	156.87	0.0048	0.638	0.6493	0.362	0.3459	
0.9539	0.0231	0.0230	200.	206.57	0.0049	0.638	0.6694	0.362	0.3257	
0.9432	0.0301	0.0267	250.	262.85	0.0051	0.638	0.6899	0.362	0.3049	
0.9323	0.0374	0.0302	300.	321.59	0.0055	0.638	0.7050	0.362	0.2895	
		Avg. e	rror P ^b	= 4.39%	Avg.	error y ^C	= 6.37%		6.69%	

Table 10. Predicted and Experimental^a VLE Results for Methanol-H₂-CO System at 30^oC.

^a Krichevskii et al. (1937). ^b Avg. error P = $\begin{bmatrix} \Sigma & |(P_e - P_{cal})/P_e|]/12 \times 100\%$ ^c Avg. error y = $\begin{bmatrix} \Sigma & |(y_e - y_{cal})/y_e|]/12 \times 100\%$ ¹



Figure 26. Logic Flow Chart for Gas Solubility Calculation

liquid-phase fugacity is a strong function of temperature and pressure, but not the liquid phase compositions, a direct-substitution method can be used to achieve convergence easily. The gas solubility calculation program has the ability to calculate mixedgas solubilities in pure and mixed solvents. For a mixed solvent, the ratio of solvent mole fractions must be specified.

The data from the methanol-hydrogen-nitrogen system at 25°C reported by Krichevskii and Efrenova (1951) were used to test these calculations. Figure 27 compares the calculated hydrogen and nitrogen solubilities in methanol to measured values. The average deviations of these values were 7.4% and 3.7% for hydrogen and nitrogen, respectively.

For the methanol-hydrogen-carbon monoxide system, the data of Krichevskii *et al.* (1937) at 30° C were examined. The average error for hydrogen solubilities was 5.8%, while that for carbon monoxide solubilities was 9.2%. Figure 28 shows a good match of calculated and measured values.

The solubility calculations for a methanol-carbon dioxide-nitrogen system and methanol-water-carbon dioxide system are reported in the experimental section of this report.



Figure 27. Calculated and Measured Solubilities of Nitrogen and Hydrogen in Methanol at 298.15 K.



Figure 28. Calculated and Measured Solubilities of Carbon Monoxide and Hydrogen in Methanol at 303.15 K.

MODELING PHASE EQUILIBRIA WITH ACTIVITY COEFFICIENT EQUATIONS

Activity coefficients have been used successfully to describe systems that exhibit high liquid-phase nonideality. This method works well for systems at low to moderate pressure and at low reduced temperature. As described in the preceding section, cubic equations of state also have been used for such systems, but they do not describe easily the liquid-phase nonidealities for polar systems. Although density-dependent mixing rules (Won, 1983; Mathias and Copeman, 1983) have promise of being able to treat all systems, they need further testing. Hence, in the near future, the activity coefficient method probably will continue to be used to describe systems containing polar compounds.

The basic relationship used in the activity coefficient method is obtained by combining Equation 1, Equation 16, and Equation 17, to give

$$\phi_i y_i P = \gamma_i x_i f_i^{\,o} \tag{40}$$

In this expression, the fugacity coefficient ϕ_i , activity coefficient γ_i , and reference fugacity f_i^o must be calculated in terms of temperature, pressure, and/or composition. The symmetric convention for the normalization of activity coefficients (defined with reference to Raoult's law) is adopted in this study. The methods used to obtain the quantities in Equation 40 are described in the following sections.

VAPOR PHASE FUGACITY COEFFICIENTS

The fugacity coefficient ϕ_i which represents the deviation of the vapor-phase from an ideal vapor phase for component i can be calculated from Equation 14 using a pressure-explicit equation of state. The equation of state used for this purpose need not be very complex because the vapor phase will not deviate greatly from the ideal gas at low and moderate pressures. The most frequently used equations are the Redlich-Kwong and virial equations of state. The nonideality of the vapor-phase becomes large when the system pressure is high, and under these conditions the accuracy of the vapor-phase fugacity coefficient may have a significant effect on the vapor-liquid equilibrium calculation. According to Tarakad *et al.* (1979), the most appropriate equation of state depends upon the mixture. The Redlich-Kwong equation and its modifications are found equally reliable.

The SRK equation of state was chosen to evaluate vapor-phase fugacity coefficients in the present study because of the large number of binary parameters that have been evaluated as described earlier. (At high pressure, these binary interaction parameters improve the predicted vapor-phase fugacity coefficients (Lin and Daubert, 1980)). The SRK equation and the method for calculating fugacity coefficients were present in an earlier section. Table 11 lists the binary parameters for systems containing methanol; as these parameters have little impact at low and moderate pressures, they were set to zero for the systems on which there were no data.

TABLE 11BINARY INTERACTION PARAMETERS IN THE SRK EQUATION

OF STATE FOR SYSTEMS CONTAINING METHANOL Binary K_{ij}^0 K_{ij}^1 MeOH-H₂ -1.7951 4.2830E-03 MeOH-N₂ -0.5406 1.1160E-03 MeOH-CO -0.6532 1.3445E-03 MeOH-CH₄ -0.3400 1.0002E-03 MeOH-C₂H₄ -0.2805 0.8895E-03 MeOH-C₂H₄ -0.2558 0.9005E-03

$MeOH-N_{2}$	-0.5406	1.1160E-03	
${ m MeOH} ext{-}{ m C} ilde{ m O}$	-0.6532	1.3445E-03	
$MeOH-CH_4$	-0.3400	1.0002 E-03	
$MeOH-C_2\dot{H_4}$	-0. 2805	0.8895 E-03	
$MeOH-C_2H_6$	-0.2558	0.9005 E-03	
MeOH-C ₃ H ₆	-0.2420	$0.8534\mathrm{E}$ - 03	
MeOH-C ₃ H ₈	-0.2235	0.7901E-03	
MeOH-CO2	-0.09 72	0.4741E-03	
$MeOH-H_9S$	-0.1074	0.5556E-03	
MeOH-COS	-0.1436	0.7020E-03	

The polar correction factor of methanol at zero.

ACTIVITY COEFFICIENTS

Activity coefficients cannot in general be predicted on an a priori basis. Rather,

binary equilibrium data usually are used to evaluate parameters in a liquid solution model that can be extended to multicomponent systems. Although a variety of equations has been used for to express activity coefficients as functions of temperature and liquid composition, the four-suffix Margules, Wilson, and UNIQUAC equations are used in the present study. They are believed to be better than others in vapor-liquid equilibrium calculations on mixtures involving polar compounds and highly nonideal solutions. In addition, the Wilson and UNIQUAC equations can be directly extended to multicomponent systems without simplifying assumptions.

Four-Suffix Margules Equation

This is a special case of the Wohl expansion model which was recommended by Adler *et al.* (1968). The original Wohl polynomial is truncated so as to include terms through the fourth order, and equal molar volumes of system constituents are assumed. For a binary system, the activity coefficients can be expressed as a function including three adjustable parameters:

$$\ln \gamma_1 = x_2^2 \left[A_{12} + 2(A_{21} - A_{12} - D_{12}) x_1 + 3 D_{12} x_1^2 \right]$$
(41a)

$$\ln \gamma_2 = x_1^2 \left[A_{21} + 2(A_{12} - A_{21} - D_{12}) x_2 + 3 D_{12} x_2^2 \right]$$
(41b)

The parameters A_{12} , A_{21} , and D_{12} are inversely proportional to temperature for a regular solution. These relationships have been used successfully by Adler *et al.* (1966) for many binary mixtures of subcritical components.

In an N-component system, the activity coefficient of component i is given by

$$\ln \gamma_i = 4 \sum_{j=1}^{N} \sum_{k=1}^{N} \sum_{l=1}^{N} x_j x_k x_l \beta_{ijkl}$$
(42)

$$-3\sum_{i=1}^{N}\sum_{j=1}^{N}\sum_{k=1}^{N}\sum_{l=1}^{N}\sum_{l=1}^{N}x_{i}x_{j}x_{k}x_{l}\beta_{ijkl}$$

where the values of β_{ijkl} depend upon the binary parameters as given in Table 12.

Adler *et al.* (1966) studied the effect of C_{ijk}^{*} , a parameter evaluated from ternary equilibrium data, on the deviation of predicted vapor composition from estimated

values for a number of ternary systems. They found C_{ijk}^* to be very near zero in all cases. Based on this conclusion and the general lack of ternary data, C_{ijk}^* was assumed to be zero in this study.

TABLE 12 RELATIONSHIPS OF MULTICOMPONENT MARGULES PARAMETERS TO BINARY AND TERNARY PARAMETERS

Combination	β_{ijkl}
i—j—k—l	0
i=j=k≠l	$A_{li}/4$
i —j≠k —l	$(A_{ik} + A_{ki} - D_{ik})/6$
i ≕j ≠k≠l	$[(A_{ki} + A_{li} + A_{ikl}) - C_{ijk}^{*}]/12$
i≠j≠k≠l	$(A_{ijk} + A_{ikl} + A_{jkl})/24$

where

$$2A_{ikl} = A_{ik} + A_{ki} + A_{il} + A_{li} + A_{kl} + A_{ll}$$

and

 $C_{ijk}^{*} = ternary \ parameter$

The Wilson Equation

The equation developed by Wilson (1964) was the first solution model based on the local composition theory. Because it has only two adjustable parameters and it is mathematically simple, the Wilson equation is widely used, especially for solutions containing alcohols. However, it is not applicable to mixtures that exhibit liquid-liquid miscibility gaps. The activity coefficients for a binary system are given by the Wilson equation as

$$\ln \gamma_1 = -\ln \left(x_1 + \Lambda_{12} x_2 \right) + \frac{\Lambda_{12} x_2}{x_1 + \Lambda_{12} x_2} - \frac{\Lambda_{21} x_2}{x_2 + \Lambda_{21} x_1}$$
(43a)

$$\ln \gamma_2 = -\ln \left(x_2 + \Lambda_{21} x_{21} \right) + \frac{\Lambda_{21} x_1}{x_2 + \Lambda_{21} x_1} - \frac{\Lambda_{12} x_1}{x_1 + \Lambda_{12} x_2}$$
(43b)

where

$$\Lambda_{12} = \frac{v_2^L}{v_1^L} \exp\left[\frac{-\Delta\lambda_{12}}{RT}\right]$$
$$\Lambda_{21} = \frac{v_1^L}{v_2^L} \exp\left[\frac{-\Delta\lambda_{21}}{RT}\right]$$

The liquid molar volumes, v_1^L and v_2^L , used here are functions of temperature. They are calculated at a pressure of 1 atmosphere using the Chueh-Prausnitz method, which will be described in a later section. This method cannot be used when the reduced temperature is above 0.99. Additionally, the calculated liquid molar volumes for gas components at reduced temperatures between 0.9 and 0.99 are usually high, as shown be the comparison with the data listed in Table 13. Therefore, in the present study the liquid molar volume at a reduced temperature of 0.9 is used whenever the reduced temperature is larger than 0.9. The liquid molar volumes calculated from the Chueh-Prausnitz method at the reduced temperature of 0.9 for various gases are listed in Table 13. This Table also lists the liquid molar volumes at 25° C given by Prausnitz and Shair (1961); Yen and McKetta (1962); Lee, Erbar, and Edmister (1973).

The energy parameters $\Delta \lambda_{12}$ and $\Delta \lambda_{21}$ can be adjusted to fit equilibrium data over a wide range of temperatures. However, Λ_{12} and Λ_{21} are often used as the two adjustable parameters to fit isothermal data.

For a system containing N components, the activity coefficient of component i is expressed by

$$\ln \gamma_i = -\ln \sum_j^N x_j \Lambda_{ij} + 1 - \sum_k^N \frac{x_k \Lambda_{ki}}{\sum_j^N x_j \Lambda_{kj}}$$
(44)

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Note that this expression requires only the parameters obtained by fitting binary data.

		Liquid Molar	Volume v ^L , m	l/mole	
Gas	Chueh & T _r	z Prausnitz = 0.9	Prausniz & Shair	Yen & McKetta	Lee, Erbar &
	<u>1 atm</u>	10 atm			Edmister
H ₂	33.34	31.03	31.0	37.3	40.0
N_{2}	46.81	45.52	32.4	40.0	44.0
0,	38.47	37.71	33.0	49.6	·
CÔ	48.67	47.36	32.1	40.2	-
CH_{4}	51.90	50.78	52.0	50.7	64.0
C ₂ H	67.35	66.13	65.0	50.0	-
$C_{2}H_{6}^{4}$	77.16	75.71	70.0	70.0	73.0
C_H	105.14	103.04	-	-	86.0
്റ്റ്	48.15	47.62	55.0	62.0	57.0
H ₉ Ś	51.40	50.85	-	-	74.0

TABLE 13LIQUID MOLAR VOLUMES OF GASES FROM VARIOUS SOURCES

UNIQUAC Equation

The UNIQUAC equation was introduced by Abrams and Prausnitz (1975), and slightly modified later by Anderson and Prausnitz (1978). This activity coefficient equation also has only two adjustable parameters. Although it is mathematically complex, it has a better theoretical basis than the Margules and Wilson equations. The UNIQUAC equation is applicable to both vapor-liquid and liquid-liquid equilibria of small and large molecules, and it is readily extended to multicomponent systems. For a binary mixture, the activity coefficients γ_1 and γ_2 are given by

$$\ln \gamma_{1} = \ln \frac{\Phi_{1}}{x_{1}} + \frac{zq_{1}}{2} \ln \left(\frac{\Theta_{1}}{\Phi_{1}}\right) + \Phi_{2} \left[l_{1} - \frac{l_{2}r_{1}}{r_{2}}\right]$$

$$+ q_{1}' \left[-ln \left(\Theta_{1}' + \Theta_{2}'\tau_{21}\right) + \frac{\Theta_{2}'\tau_{21}}{\Theta_{1}' + \Theta_{2}'\tau_{21}} - \frac{\Theta_{2}'\tau_{12}}{\Theta_{2}' + \Theta_{1}'\tau_{12}}\right]$$

$$\ln \gamma_{2} = \ln \frac{\Phi_{2}}{x_{2}} + \frac{zq_{2}}{2} \ln \left(\frac{\Theta_{2}}{\Phi_{2}}\right) + \Phi_{1} \left[l_{2} - \frac{l_{1}r_{2}}{r_{1}}\right]$$

$$+ q_{2}' \left[-ln \left(\Theta_{2}' + \Theta_{1}'\tau_{12}\right) + \frac{\Theta_{1}'\tau_{12}}{\Theta_{2}' + \Theta_{1}'\tau_{12}} - \frac{\Theta_{1}'\tau_{21}}{\Theta_{1}' + \Theta_{2}'\tau_{21}}\right]$$

$$(45b)$$

where

$$l_1 = \frac{z(r_1 - q_1)}{2} - (r_1 - 1)$$

$$l_2 = \frac{z(r_2 - q_2)}{2} - (r_2 - 1)$$

$$\Phi_1 = \frac{x_1 r_1}{x_1 r_1 + x_2 r_2}$$

$$\Phi_2 = \frac{x_2 r_2}{x_1 r_1 + x_2 r_2}$$

$$\Theta_1 = \frac{x_1 q_1}{x_1 q_1 + x_2 q_2}$$

$$\Theta_{2} = \frac{x_{2}q_{2}}{x_{1}q_{1} + x_{2}q_{2}}$$
$$\Theta_{1}' = \frac{x_{1}q_{1}'}{x_{1}q_{1}' + x_{2}q_{2}'}$$
$$\Theta_{2}' = \frac{x_{2}q_{2}'}{x_{1}q_{1}' + x_{2}q_{2}'}$$
$$\tau_{12} = \exp\left[\frac{-\Delta u_{12}}{RT}\right]$$
$$\tau_{21} = \exp\left[\frac{-\Delta u_{21}}{RT}\right]$$

and

z = Coordination number = 10

 $r_1, r_2 =$ Structural size parameters

 $q_1, q_2 =$ Structural area parameters

 $q_1', q_2' =$ Modified structural area parameters

The structure size parameter, r, and structure area parameters, q and q' are purecomponent physical properties. Prausnitz *et al.* (1980) have listed these parameters for a large number of condensable components. Breivi (1982) has calculated these parameters for some simple polar and nonpolar components directly from their molecular structure. Two methods can be used to estimate quantities that do not appear in the above sources. Breivi (1982) has correlated the structure parameters as functions of critical volume and radius of gyration. The r parameters are found proportional to van der Waals volumes as suggested by Bondi (1968). The ratio (q/r) is a measure of the shape of the molecule, and as r becomes very large, q/r approachs 2/3 for a linear chain molecule (Donohue and Prausnitz, 1975). Hence, Prausnitz (1983) has suggested a simple scaling of these parameters with critical volume:

$$\frac{r_i}{r_j} = \frac{v_{ci}}{v_{cj}} \tag{46}$$

$$\frac{q_i}{q_j} = \left[\frac{v_{ci}}{v_{cj}}\right]^{2/3} \tag{47}$$

Here the reference substance j is selected based on having a molecular structure that is similar to component i. Table 14 lists the structure parameters of the components of interest in this study.

Substance	r	q	q^{\prime}	Source	
H ₂	0.42	0.570	a	с	
$\tilde{N_2}$	0.94	0.99	a	с	
O_2	0.91	0.98	a	с	
CÕ	1.06	1.07	а	с	
CH_4	1.54	1.38	a	с	
$C_2 \dot{H_4}$	1.57	1.49	а	b	
C_2H_6	1.80	1.70	a	b	
$C_{3}H_{6}$	2.25	2.02	a	b	
C ₃ H [~] 8	2.48	2.24	a	Ъ	
CŎ,	1.32	1.28	а	b	
$H_2\bar{S}$	1.0	1.0	а	b	
CÕS	1.90	1.63	a	d	
$CH_{3}SH$	1.76	1.64	а	d	
C ₂ H ₅ SH	2.62	2.27	a	d	
С́H ₃ ŠCH ₃	2.62	2.27	a	d	
MeŎH	1.43	1.43	0.96	Ъ	
H ₂ O	0.92	1.40	1.0	b .	

TABLE 14UNIQUAC STRUCTURE PARAMETERS

where

a q' = q
b Prausnitz et al. (1980).
c Breivi (1982).
d Estimated from the scaling hypothesis suggested
by Prausnitz (1983). Reference substances:
COS-CO₂, CH₃SH-CH₃OH, C₂H₅SH-C₂H₅OH.

 Δu_{12} and Δu_{21} are adjustable binary parameters that must be evaluated from experimental data, which may cover a range of temperatures. Alternatively, isothermal data could be fit by choosing τ_{12} and τ_{21} as adjustable parameters.

In an N-component system, the activity coefficient of component i for the UNI-QUAC equation is given by

$$\ln \gamma_{i} = \ln \frac{\Phi_{i}}{x_{i}} + \frac{z}{2} q_{i} \ln \frac{\Theta_{i}}{\Phi_{i}} + l_{i} - \frac{\Phi_{i}}{x_{i}} \sum_{j}^{N} x_{j} l_{j} - q_{i}' \ln \left[\sum_{j}^{N} \Theta_{j}' \tau_{ji}\right]$$

$$+ q_{i}' - q_{i}' \sum_{j}^{N} \left[\frac{\Theta_{j}' \tau_{ij}}{\sum_{k}^{N} \Theta_{k}' \tau_{kj}}\right]$$

$$(48)$$

where

$$\Phi_{i} = \frac{r_{i} x_{i}}{\sum_{k}^{N} r_{k} x_{k}}$$
$$\Theta_{i} = \frac{q_{i} x_{i}}{\sum_{k}^{N} q_{k} x_{k}}$$
$$\Theta_{i}' = \frac{q_{i}' x_{i}}{\sum_{k}^{N} q_{k}' x_{k}}$$

LIQUID REFERENCE STATE FUGACITIES

The reference state for the corresponding activity coefficient is defined here as the pure component at the system temperature and pressure. The reference state fugacity then is the pure component liquid fugacity f_i^{o} which can be calculated by Equation 18 for a subcritical component, or by a generalized correlation for a supercritical or near-critical component.

Subcritical Components

Equation 18 was used for methanol, water, carbonyl sulfide, and propane. The vapor pressures were estimated from the following expression which applies to a wide temperature range:

$$\log p^*(mmHg) = A + B/T(K) + C \log(T) + DT + ET^2$$
(49)

Constants A through E are listed in Table 15.

<u></u>						<u> </u>
Compound	Α	В	С	D	E	Source
MeOH	-42.629	-1186.2	23.279	-35.082E-3	17.578E-6	a
H ₂ O	16.373	-2818.6	-1.6908	-5.7546E-3	4.0073E-6	a
cốs	10.222	-1255.8	0.00	-10.193E-3	11.376E-6	ь
$C_{3}H_{8}$	36.007	-1737.2	-11.666	8.5187E-3	0.00	a

TABLE 15VAPOR PRESSURE CONSTANTS FOR EQUATION 49

a Yaws (1977).

b Robinson and Senturk (1979).

For other subcritical components, e.g. methyl mercaptan and dimethyl sulfide, the vapor pressures can be estimated from the Antoine equation:

$$\ln p^* (mmHg) = A_t - B_t / (T - C_t)$$
(50)

Reid et al. (1977) have listed the Antoine constants A_t , B_t , and C_t for a large number of compounds.

The fugacity coefficient of component i, ϕ_i^* , at the saturated vapor pressure in Equation 18 was calculated by the SRK equation of state. The liquid molar volume used in Equation 18 was calculated from the following corresponding state correlation of Chueh and Prausnitz, which is described in detail by Reid *et al.* (1977).

$$v^{L} = \frac{1}{\rho_{s}} \left[1 + \frac{9z_{c}N_{v}(P - p^{*})}{\rho_{c}} \right]^{-1/9}$$
(51)

where

$$N_{v} = (1.0 - 0.89\omega) \left[\exp \left(6.9547 - 76.2853 T_{r} + 191.3060 T_{r}^{2} \right) - 203.5472 T_{r}^{3} + 82.7631 T_{r}^{4} \right]$$

$$\rho_{s} = \frac{\rho_{c}}{\left[V_{r}^{(0)} + \omega V_{r}^{(1)} + \omega^{2} V_{r}^{(2)} \right]}$$
(51b)

$$V_r^{(j)} = a_j + b_j T_r + c_j T_r^2 + d_j T_r^3 + e_j / T_r + f_j \ln(1 - T_r)$$
(51c)

The coefficients for Equations 51 are given in Table 16.

f, j ^b; ď; aj °j е_ј 0 0.11917 0.0095130.21091-0.069220.07480-0.0844760.98465 1.82484-0.61432 -1.60378-0.345460.087037 1 2 -0.55314-0.15793-1.016010.340950.46795-0.239938

TABLE 16COEFFICIENTS FOR EQUATION 51c

Using the above correlations for the liquid molar volume and evaluating the integral in Equation 18, the following expression is obtained for the reference fugacity of a subcritical component

$$f^{o} = p^{*} \phi^{*} \exp \left[\frac{P_{c}}{8RT\rho_{s} z_{c} N_{V}} \left\{ \left(1 + \frac{9z_{c} N_{v} (P - p^{*})}{\rho_{c}} \right)^{8/9} - 1 \right\}$$
(52)

Supercritical and Near-Critical Components

The pure-component liquid fugacity coefficients of carbon dioxide, hydrogen sulfide, nitrogen, methane, and hydrogen at system temperature and pressure can be estimated by a generalized correlation developed by Lee, Erbar, and Edmister (1973). This correlation, which can also be applied to all the hydrocarbons, is

$$\ln \phi^{L} = A_{1} + A_{2}T_{r}^{-1} + A_{3}\ln(T_{r}) + A_{4}T_{r} + A_{5}T_{r}^{2} + A_{6}T_{r}^{7}$$
(53)
+ $\left(A_{7} + A_{8}T_{r}^{-1} + A_{9}\ln(T_{r}) + A_{10}T_{r}^{2} + A_{11}T_{r}^{7}\right)P_{r} + A_{12}T_{r}^{3}P_{r}^{2}$
+ $\omega \left((1 - T_{r})(A_{13} + A_{14}T_{r}^{-1} + A_{15}T_{r}) + A_{16}P_{r}T_{r}^{-1} + A_{17}T_{r}P_{r}^{2}\right)$
- $\ln P_{r}$

The constants A_1 through A_{17} in Equation 53 are listed in Table 17 for eight different cases defined by Lee *et al.* (1973). Because of the molecular similarity of nitrogen and carbon monoxide, the constants in Table 17 for nitrogen may be used for carbon monoxide. With Equation 53 and the associated parameters, reference state fugacities can be calculated from the relationship

$$f^{o} = \phi^{L} P \tag{54}$$

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	Constant	All hydro	carbons					Has	Но
	τοποταπτ	included) $T_{r} \leq 1.0$	excluded) $T_r > 1.0$	Methane T _r > 0.93	Nitro 1.0 <t<u>r<2.2</t<u>	gen T _r > 2.2	For all temp.	For all temp.	For all temp.
-	A1 A2 A3 A4 A5 A6 A7 A8 A10 A11 A12 A13 A14 A15 A16 A17	6.2741 -7.3401 -4.2751 -0.22647 0.93842 -0.23825 0.03798 -0.00344 -0.21974 0.10862 0.0298 -0.00188 10.2920 -11.6780 -1.6470 -0.03885 -0.00101	9.52326 -9.88046 -6.00351 -0.41660 0.18150 0.0 -0.02010 0.10390 -0.06538 0.08916 0.0 -0.00188 -1.027 -0.59264 0.0 -0.03885 -0.00101	9.55412 -8.31211 -3.23962 -2.26419 0.46272 0.0 -0.09953 0.2516 0.2727 0.01198 0.0 -0.00188 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0	9.26614 -10.538 -7.98618 0.76209 0.21677 0.0 -0.05624 0.18917 0.12474 -0.00023 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.	6.82287 -8.9725 -9.78514 2.67084 0.0 0.90970 -1.01342 -0.40848 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.	28.9284 -20.01 -10.3989 -12.5 3.52631 0.0 -12.7 12.9708 15.4946 -0.94143 0.0 -0.22382 0.0 0.0 0.0 0.0 0.0 2.32463	$13.94 \\ -1.75213 \\ 14.0164 \\ -12.5 \\ -0.00024 \\ 0.0 \\ 2.84127 \\ -4.94796 \\ -8.0 \\ 1.5889 \\ 0.0 \\ 0.48453 \\ 0.0 \\ 0.0 \\ 0.0 \\ 0.0 \\ 0.0 \\ -0.00101 \\ 0.0 \\ $	0.43571 5.34346 -0.46 -0.1043 0.04794 0.0 0.35304 -0.68039 -0.10673 -0.00023 0.0 0.0 0.0 0.0 0.0 0.0 0.0

Table 17. Constants in Equation 53.

EVALUATION OF BINARY PARAMETERS IN ACTIVITY COEFFICIENT EQUATIONS

The four-suffix Margules, Wilson, and UNIQUAC equations were used to describe the dependence of activity coefficients on liquid composition and temperature. The parameters in these activity coefficient equations must be evaluated through the reduction of vapor-liquid equilibrium data on binary mixtures. With these parameters, the equations can be used to calculate binary vapor-liquid equilibrium conditions at temperatures and pressures other than those covered by experiment. In addition, the binary parameters can be used directly to predict the vapor-liquid equilibrium behavior of a multicomponent system. Methods used to evaluate the binary parameters from equilibrium data are described in the following sections.

Evaluation Method and Procedure

The method used in the present study to evaluate model parameters from binary equilibrium data is based on the principle developed by Barker (1953). A bubble point pressure calculation procedure is included in the parameter search routine, which evaluates total pressure as a function of the estimated parameters, the measured temperature, and the measured liquid-phase composition. This procedure does not require measurement of vapor-phase composition, which many binary VLE experimental data sets do not have, but the mole fractions of each component in the vapor phase is calculated in the course of the parameter search routine. Ideal gas behavior is not assumed. The objective function used in the present study is

$$OF = \sum_{k=1}^{n} \left[\frac{P_e - P_{cal}}{P_e} \right]_k^2$$
(55)

and it was minimized by a Gauss-Marquardt nonlinear regression procedure. It is important in the use of the Gauss-Marquardt technique to derive the analytical formulas of the derivatives of the objective function with respect to each model parameter. Careful manipulation is necessary to handle the nonlinear activity coefficient equations involved. The manipulation of the necessary derivatives for the three activity coefficient equations is listed by Chang 1984.

The input information for the parameter search program includes the purecomponent physical properties, the binary P-T-x data, the parameters that control the algorithm, and the initial estimates of the model parameters. An initial guess of total pressure for each data point is assigned to start the bubble point calculation. The best choice of initial pressure is the measured total pressure. The iterations will proceed until the equilibrium criterion of Equation 40 is satisified; in addition, convergence requires the mole fractions in the vapor phase to sum to one and that the calculated total pressure does not change in subsequent iterations. After each data point has been used to determine P_{cal} , the objective function and its derivatives are calculated. New estimates of the model parameters are evaluated by the Gauss-Marquardt technique, and the whole process is repeated until the objective function is minimized. The outline of this parameter-search procedure is given in Figure 29. Note that the procedure is similar to the evaluation of the binary interaction parameters in the extended SRK equation of state. Figure 30 shows the procedure for performing the bubble point pressure calculations. A computer program GMACC (see Chang 1984) has been developed to evaluate the binary parameters in the Margules, Wilson, and UNIQUAC equations.

The application of other objective functions and the use of the maximum likelihood principle were also tested. In minimizing pressure deviation, Barker's method did a better job. The maximum likelihood principle is attractive but requires much longer computational time for results that are no better than were obtained with the objective function in Equation 55.

It is desirable that a phase equilibrium model has an ability to estimate equilibrium behavior over a range of conditions. In this study, two options were adopted in the evaluation of model parameters which could then be used over a wide range of temperatures. In the first option, the temperature-independent model parameters were evaluated from all available data on the binary systems methanol-carbon dioxide. methanol-carbonyl sulfide, methanol-hydrogen sulfide, methanol-water, methanolpropane, methanol-methyl mercaptan, methanol-dimethyl sulfide, and carbon dioxidehydrogen sulfide. Note that both components in each binary system are condensable. For systems containing a supercritical component, such as methanol-nitrogen, carbon dioxide-nitrogen, and hydrogen sulfide-nitrogen, the above option did not work, so the second option was used. In this procedure the temperature-dependent model parameters were evaluated at each available set of isothermal data. Selected parameter sets were fit by an empirical temperature function (a / T + b). The selection of parameter sets to be fit was based on the standard error associated with their estimation. However, parameter sets with large standard errors were often in good agreement with the empirical parameter function reduced from the parameter sets with small standard errors.

Binary Correlation Results

Table 18 lists the binary systems examined in this study accompanied by their sources, conditions, and number of data points used. The optimal parameters in the four-suffix Margules, Wilson, and UNIQUAC equations, with the deviations resulting







Figure 30. Logic Flow Chart for Bubble Point Pressure Calculation in the Gamma Method.

Binary	No. of		Ranges	References
system	data	Τ, Κ	P, atm	
MeOH-CO ₂	101	223/313	1.0/79.53	Bezdel & Teodorovich (1958); Katayama et al. (1975); Krichevskii & Lebedeva (1947); Ohgaki & Katayama (1976); Shenderer et al. (1959); Yorizane et al. (1969).
MeOH-COS MeOH-H2S MeOH-CH2SH	51 22 18	233/293 248/273 263/288	0.38/11.11 2.0/10.0 0.1908/1.3809	Oscarson (1981). Yorizane et al. (1969). Jackowski (1980).
MeOH-CH3SC MeOH-C3H8	H ₃ 24 11	263/288 293.05 209 (229	0.0834/0.4533 2.67/7.94	Jackowski (1980). Nagahama et al. (1971).
M604-450	12	290/330	0.0331/0.9389	Ratcliff & Chao (1969). Kooner et al. (1980). Butler et al. (1933).
CO2-H2S	76	225/313	6.8/60.0	Bierlein & Kay (1953); Sobocinski & Kurata (1959).
MeOH-N2 CO2-N2	21 56	225/300 218/301	20.7/177.0 12.6/115.8	Weber & Knapp (1978). Aral et al. (1971); Krichevskii & Lebedeva (1962); Kaminishi & Toriumi (1966);
N2-H2S	41	228/300	3.30/204.34	Muirbrook & Prausnitz (1965); Yorizane et al. (1970); Zenner & Dana (1963). Besserer & Robinson (1975);
-				Kalra et al. (1976).

Table 18. Binary VLE Data Used in Evaluation of Parameters in Activity Coefficient Equations.

from the fitting procedures, are listed in Tables 19, 20, and 21, respectively. Generally, the three activity coefficient correlations fit the data equally well; the root mean square deviations of bubble point pressures vary considerably from one system to another, but all are under or near 10%.

The Wilson and UNIQUAC equations are superior to the Margules equation for the methanol-carbonyl sulfide system. Figure 31 shows how well the Wilson equation fits the data of Oscarson (1981). The four-suffix Margules equation incorrectly predicts liquid-phase separation as indicated by local extrema in the P-x diagram of Figure 31.

The UNIQUAC and Margules equations are slightly better than the Wilson equation for the methanol-carbon dioxide binary. However, in the correlations of the methanolcarbon dioxide data, the Margules equation resulted in more systematic errors than the Wilson and UNIQUAC equations. Figure 32 shows that the pressure deviations resulting from the Margules equation are positive at temperatures above 273 K and negative below 273 K. That is, use of the Margules equation resulted in higher bubble pressures in the low-temperature isotherms and lower bubble pressures in the high-temperature isotherms, when the calculations are compared to data. Deviations between the UNI-QUAC equation and the methanol-carbon dioxide data are more random than systematic, as is illustrated by Figure 32.

Figure 33 shows a good fit of the UNIQUAC equation to the data of Nagahama *et al.* (1971) for the methanol-propane system. The Wilson equation did as well as the UNIQUAC equation, but the four-suffix Margules equation incorrectly predicted liquid-phase separation for this system.

Figure 34 shows the pressure-composition diagram for the methanol-methyl mercaptan system. It indicates that the UNIQUAC equation fits the P-T-x data of Jackowski (1980) excellently, and it also gives the vapor-phase compositions predicted from a bubble point pressure calculation. Figure 35 shows the pressure-composition diagram for the methanol-dimethyl sulfide system. The three activity coefficient equations gave good agreement with the P-T-x data of Jackowski (1980), although the Margules equation was slightly better than the Wilson and UNIQUAC equations. All equations also predict an azeotrope at each isotherm. Figure 36 plots the calculated vaporphase composition vs. the liquid composition at 288.15 K for the methanol-dimethyl sulfide system; an azeotrope is shown at the dimethyl sulfide mole fraction of 0.86.

Severe difficulty has been encountered in the evaluation of binary parameters for systems containing a supercritical component. The workable parameters for these systems are bound to a very small region; if an initial parameter estimate is not in that region, the optimization procedure that is part of the parameter evaluation process cannot be executed. Nevertheless, the binary parameters for three nitrogen-containing systems have been evaluated in this study using the method as described.

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Binary A ₁₂ A ₂₁ D ₁₂ RMSD% ^a EP ^b Ey ^c system atm						
	Binary A ₁₂ system	A ₂₁	D ₁₂	RMSD% ^a	EP ^b atm	Ey ^C
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	$\begin{array}{llllllllllllllllllllllllllllllllllll$	214.57/T 454.89/T 130.13/T 442.69/T 534.50/T 673.69/T 140.36/T -136.18/T 3.8692 1153.9/T-2.8897 -32089/T+83_371	115.76/T 425.27/T -160.26/T 344.38/T 451.29/T 336.36/T -72.590/T -723.25/T -4.1996 8061.4/T-33.663 -37934 /T+95.060	8.76 9.07 4.45 1.18 0.87 5.62 3.07 5.22 6.59 7.49	1.71 0.278 0.18 0.0073 0.0015 0.15 0.0045 1.09 4.54 3.32 5.33	0.0014 - - - 0.0075 0.0408 0.0898 0.0514

Table 19. Recommended Margules Parameters in the Activity Coefficient Correlations.

^a RMSD % = { $\sum_{1}^{n} [(P_e - P_{cal})/P_e]^2/n$ $^{1/2} \times 100$ %, where n = no. of data points.

^b EP =
$$\begin{bmatrix} \Sigma \\ 1 \end{bmatrix} |P_e - P_{cal}|]/n$$
, ^c Ey = $\begin{bmatrix} \Sigma \\ 2 \end{bmatrix} |y_{le} - y_{lcal}|]/n$.

Binary system	Δλ12	Δλ21	RMSD% ^a	EP ^b atm	Ey ^C
MeOH(1)-CO ₂ (2	?) 48.604	-0.62504	11.00	1.52	
$MeOH(1)-CO\overline{S}(2)$	2) 110.35	7.9072	1.84	0.049	0.0011
MeOH(1)-H ₂ S(2	2) 15.645	3.5334	4.88	0.20	-
MeOH(1)-CH3SH	(2) 61./96	8.2665	1.45	0.0061	-
$MeOH(1) - CH_3SC$	H3(2) 61.299	/.8623	1.64	0.0026	-
	2) 124.89	13.919	5.8/	0.22	
$MEUH(1) - H_2U(2)$		25.150	3.31	0.0043	0.00/9
	[^] 12	Λ ₂₁			
MeOH(1)-N2(2)	-1.0151	0.15410	6.61	4.64	
CO2(1)-N2(2)	-111.23/T+0.35348	3 -314.71/T+1.7771	6.22	2.31	0.0927
Na/1\ 4a5/0\	150.74/T-0.19793	-1265.0/T+3.4689	9.86	5.48	0.0484

Table 20. Recommended Wilson Parameters in the Activity Coefficient Correlations.

				atm	
MeOH(1)-CO ₂ (2)	-5.7734	88.471	8.13	1.10	· _
MeOH(1)-COŠ(2)	-0.50644	1672.3	1.65	0.049	0.0010
MeOH(1)-H ₂ S(2)	3.5301	18.081	4.89	0.21	-
MeOH(1)-CH ₃ SH(2)	-0.25523	70.519	1.45	0.0066	-
$MeOH(1)-CH_3SCH_3(2)$	-2.7289	70.140	1.85	0.0030	
MeOH(1)-CzHg(2)	2.3676	116.35	5.73	0.18	· _
MeOH(1)-H2O(2)	-10.652	15.107	2.70	0.0033	0.0066
CO2(1)-H25(2)	5.0145	1.8468	6.60	1.42	0.0450
<u>n</u>			/2	⊥ • ¬C	

Table 21.	Recommended	UNIQUAC	Parameters	in	the	Activity	Coefficient
		Co	orrelations.	•			

^a RMSD % = { $\Sigma [(P_e - P_{cal})/Pe]^2/n$ }^{1/2} x 100 1 where n = no. of data points. ^b EP = [$\Sigma |P_e - P_{cal}|]/n$. ^c Ey = [$\Sigma |y_{1e} - y_{1cal}|]/n$.



Figure 31. Comparison of the Correlated Results by Wilson and Margules Equations for Methanol-COS Equilibria.



Figure 32. Residual Ratios (Pe - Pcal)/Pe of Fitting Margules and UNIQUAC Equations for Methanol-CO2 VLE.


Figure 33. Methanol-Propane Equilibria with Predictions calculated by UNIQUAC Equation.



Figure 34. Methanol-Methyl Mercaptan Equilibria with Predictions calculated by UNIQUAC Equation.



Figure 35. Methanol-Dimethyl Sulfide Equilibria with Predictions calculated by Margules Equation.



Figure 36. x-y Diagram of Methanol-Dimethyl Sulfide Equilibria at 288.15 K.

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Effects of Reference Fugacity

Three binary systems -- methanol-carbon dioxide, methanol-hydrogen sulfide, and carbon dioxide-hydrogen sulfide -- were studied using the Robinson-Chao (1971) reduced state correlation for calculating the reference fugacities of carbon dioxide and hydrogen sulfide. Table 22 lists the correlated results. The optimal model parameters for the three activity coefficient equations are quite different from those using the Lee-Erbar-Edmister (1973) reference fugacity model. The Robinson-Chao model gave better results for the carbon dioxide-hydrogen sulfide system for all three activity coefficient correlations (see Table 22). For the methanol-carbon dioxide and methanol-hydrogen sulfide systems, the use of the Robinson-Chao model improved the correlations slightly for the Wilson and UNIQUAC equations, even though the model parameters could not be properly optimized in the parameter evaluation process. However, the Robinson-Chao model did a poorer job for the Margules equation than did the Lee-Erbar-Edmister model. An interesting comparison of the two methods of calculating reference state fugacities is provided by the results obtained using the Margules equation to fit data on the methanol-carbon dioxide. These results are presented in Figure 37 and show local maxima and minima in bubble pressures when the correlation is developed using the Robinson-Chao model. Maxima and minima indicate that liquid-phase separation was predicted by the model calculation, even though the data do not support such predictions. The differences between carbon dioxide vapor pressures calculated from the Robinson-Chao and Lee-Erbar-Edmister models, and between experimentally determined vapor pressures and those calculated from the two models should also be noted.

MULTICOMPONENT VLE CALCULATIONS

As described earier, there are four types of VLE calculations: bubble point pressure (BUBLP), bubble point temperature (BUBLT), dew point pressure (DEWP) and dew point temperature (DEWT). In principle, such calculations for a multicomponent system are not different from those for a binary system. The BUBLP block diagram shown in Figure 30 can be applied to the multicomponent bubble point pressure calculation by substituting an arbitrary pressure as an initial guess.

The bubble point pressure calculation requires specifications of liquid composition and system temperature, and it results in an estimation of the equilibrium vapor composition and system pressure. A computer program VLEBP (see Chang 1984) has been developed to accomplish the above calculation, and it has been used in the previous section to describe the behavior of binary systems. Success of this program should be expected in calculations involving a multicomponent system comprised of subcritical

Margules	A ₁₂	A ₂₁	D ₂₁	RMSD% ^a	EP ^b atm	Ey ^C
MeOH(1)-CO ₂ (2) MeOH(1)-H ₂ S(2) CO ₂ (1)-H ₂ S(2)	796.56/T 617.54/T 357.54/T	319.47/T 284.67/T 388.96/T	384.63/T 442.12/T 403.19/T	15.15 4.79 1.87	2.31 0.21 0.45	- 0.0149
Wilson	Δλ12	∆ړ∠	1 RMS	D% ^a EF at	,b Հա	Ey ^C
MeOH(1)-CO ₂ (2) MeOH(1)-H ₂ S(2) CO ₂ (1)-H ₂ S(2)	5794.9 208.25 11.370	6.12 -1.45 15.2	72 8. 64 3. 39 3.	51 1.1 73 0.1 48 0.8	L7 L1 B7	0.0180
UNIQUAC	Δu12	۵u2	1		<u></u>	
MeOH(1)-CO ₂ (2) MeOH(1)-H ₂ S(2) CO ₂ (1)-H ₂ S(2)	1.2419 -0.4486 16.457	1159 1 1502 7.91	.3 10. .4 3. 26 3.	36 1.5 64 0.1 41 0.8	54 12 36	 0.0178
a RMSD % = $\begin{cases} & \\ & \\ & \\ & \\ & \\ & \\ & \\ & \\ & \\ & $	n [∑ [(P _e - 1] = no. of da P _e - P _{cal}]	P _{cal})/Pe] ² ta points.]/n.	/n} ^{1/2} x 1	00 %,		
^C Ey = $\begin{bmatrix} \Sigma \\ 1 \end{bmatrix}$	yle − ylca	ן]/n.				

Table 22. Activity Coefficient Correlations with Robinson-Chao Reference Fugacity Model for CO₂ and H₂S.





compounds (excluding components in Group I). However, there are no appropriate data on systems containing methanol that can be used to test the accuracy of the multicomponent calcualations. Satisfactory results should not be expected when the program is used to perform VLE calculations on a multicomponent system that contains a supercritical component. This is partly due to the difficulty of obtaining temperatureindependent parameter sets on binary mixtures involving supercritical components. It is also due partly to inaccuracies in the measurement of the liquid mole fraction of the supercritical component, which has an enormous effect on the pressure calculation.

EXPERIMENTAL

QUALITY ASSURANCE AND EXPERIMENTAL PROCEDURE

The research work reported on here included both the development of thermodynamic models to predict vapor-liquid equilibria, and experimental data to use with the models. The main emphasis of the quality assurance program for this portion of the research was focused on the quality of the experimental data. As with other parts of the overall research program, the responsibility for quality assurance was shared among all personel responsible for the project. All costs associated with quality assurance were included in the project budget. Details of the experimental equipment and procedures are described below.

Vapor-Liquid Equilibrium Apparatus

The experimental apparatus, shown in Figure 38, included an equilibrium cell, a constant-temperature bath, temperature control devices, a pressure gauge, and a pump for recirculating the gas. The stainless steel equilibrium cell had a volume of 1084 ml and internal baffles. The entire cell was immersed in a 50% ethylene glycol-50% water bath housed in an industrial freezer. The bath temperature was maintained within 0.1° C of the set-point temperature by a 300 watt immersion heater with an electronic temperature controller and a precision mercury thermoregulator. A copper-constantan thermocouple and a calibrated digital temperature indicator were used to measure bath temperature. A calibrated 16-inch Heise gauge was used to measure pressure in the equilibrium cell. The gas phase in the cell was bubbled through the liquid phase using a microflo diaphragm metering pump with a pumping capacity of 810 ml/hr.



Figure 38.) Vapor-Liquid Equilibrium Apparatus.

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Sampling Procedure

An experiment was started by evacuating the equilibrium cell and drawing about 400 ml of solvent into the cell. Further evacuation was applied overnight for degassing the solvent. When the bath temperature reached the desired value, the gas was introduced to the cell. The diaphragm metering pump was started to bubble gas through the liquid and assist in bringing the system to equilibrium. After 2 to 3 hours, the pressure in the cell became constant; recirculation of the gas phase was continued for another 3 hours and then the solution was allowed to sit unagitated overnight. Approximately 0.5 ml of liquid was purged through a sampling line and collected in a glass graduated cylinder, so that the flow rate of liquid sample was estimated before sampling. A 500-ml tefion-coated steel bomb, wrapped with heating tape, was used to sample the equilibrated liquid. A 0.5 to 3-ml liquid sample, obtained by timing the sampling period, was allowed to expand through capillary tubing and a low dead-volume needle valve into the evacuated sample bomb. The sample size was small enough that it could be completely vaporized, and yet it was large enough to insure accurate analysis by a gas chromatograph. The sample was heated to 140°C for 3 hours and was pressurized with helium to approximately 60 psig. The stainless steel tubing from the sampling bomb to the gas chromatograph and the gas exit were also heated to 140°C by heating tape to prevent methanol condensation during the sample analysis process.

The sampling device for the gas phase was similar to that for liquid phase. Gas sampling was done quickly, within 10 seconds, and the pressure in the equilibrium cell was not upset by more than 10 psig. The gas sampling bomb was then heated and pressurized with helium, as was done with the liquid sampling bomb.

Sample Analysis

The sample was analyzed by a Tracor 550 gas chromatograph using a 10-in x 1/8-in Porapak QS packed column and a thermal conductivity detector. The flow rate of the carrier gas (helium) was 25 ml/min, and the column temperature was set at 110° C. Each sample analysis was repeated five times at 5 psig. The component peaks were integrated by a digital integrator and recorded on a strip chart recorder. Calibration curves were prepared for the carbon dioxide-methanol, nitrogen-methanol, and water-methanol mixtures by plotting peak ratio vs. mole ratio. They are shown in Figures 39, 40, and 41. The thermal response factors (the slopes of the plots) were 1.075, 0.935, and 0.709 for carbon dioxide-to-methanol, nitrogen-to-methanol, and water-to-methanol, respectively. These calibration curves were made by analyzing samples with known compositions in a sampling bomb with a septum. The calibrated samples of carbon dioxide in methanol were prepared by first filling the 500 ml bomb with carbon dioxide.

The pressure of the carbon dioxide was adjusted by a vacuum pump and measured by a mercury manometer. Then a fixed amount of methanol between 0.5 and 2.0 ml was injected by a syringe into the bomb. The bomb was heated and pressurized with helium as usual. The calibration of nitrogen in methanol was similar to that of carbon dioxide. The thermal response factor for nitrogen-to-carbon dioxide was obtained by dividing the factor for nitrogen-to-methanol by the factor for carbon dioxide-to-methanol. The factor of 0.870 was used in this work, which is very close to 0.875 reported by Dietz (1967).











Figure 41. GC Calibration Curve for Methanol-Water System.

<u>Chemicals</u>

Carbon dioxide with a purity of 99.99% and nitrogen with a purity of 99.999% were used in the experiment. These gases were supplied by the Airco Company. Certified A.C.S. grade methanol with a purity of 99.9% was obtained from the Fisher Scientific Company. Distilled water was obtained from the laboratory.

EXPERIMENTAL RESULTS AND DISCUSSION

Vapor-liquid equilibrium data for the methanol-carbon dioxide, methanol-carbon dioxide-nitrogen, and methanol-carbon dioxide-water systems obtained in this work are presented in Tables 23, 24, and 25, respectively. The comparison of these data to the literature data and/or the calculated results from the extended SRK equation of state are discussed in the following sections.

243.	15 K	258	.15 K	273	.15 K	298	$15~{ m K}$
P atm	×2	P atm	x_2	P atm	x_2	P atm	×2
	<u></u>						
2.03	0.0588	2.19	0.0398	1.91	0.0228	2.57	0.0180
4.75	0.1500	5.50	0.1056	5.15	0.0643	5.50	0.0391
7.11	0.2307	10.32	0.2070	1 0.7 4	0.1368	1 0.29	0.0733
9.91	0.3505	15.85	0.3475	20.62	0.2834	17.38	0.1300
12.40	0.5339	19.13	0.4845	28.14	0.4451	29.79	0.2296
13.28	0.7154	21.28	0.7179	31.92	0.6462	39.85	0.3334
						47.64	0.4354
						53.82	0.5683

TABLE 23EXPERIMENTAL VAPOR-LIQUID EQUILIBRUM P - T - x DATA FORTHE METHANOL(1)-CO₀(2) SYSTEM

Methanol-Carbon Dioxide Binary System

The experimental apparatus and procedure described in the preceding section were tested by comparing the experimental equilibrium data on the methanol-carbon dioxide system with literature data. The gas-phase compositions were not determined because the concentrations of methanol were too small to be measured.

TABLE 24 EXPERIMENTAL VAPOR-LIQUID EQUILIBRIUM P - T - x DATA FOR THE METHANOL(1)-CO₂(2)-N₂(3) SYSTEM

P atm	x ₁	^x 2	x ₃	У2	y ₃
		T = 24	43.15 K		
$10.25 \\ 20.16 \\ 30.15 \\ 40.13$	0.9322 0.7379 0.7386 0.7355	$\begin{array}{c} 0.0649 \\ 0.2565 \\ 0.2517 \\ 0.2508 \end{array}$	$\begin{array}{c} 0.0029 \\ 0.0057 \\ 0.0098 \\ 0.0137 \end{array}$	$0.1881 \\ 0.4365 \\ 0.3195 \\ 0.2590$	$\begin{array}{c} 0.8119 \\ 0.5635 \\ 0.6805 \\ 0.7410 \end{array}$
		T = 27	$73.15~{ m K}$		
39.79 30.40 20.40 10.54	0.7823 0.8133 0.8413 0.8817	$0.2074 \\ 0.1804 \\ 0.1551 \\ 0.1173$	0.0103 0.0063 0.0036 0.0010	$0.4501 \\ 0.5112 \\ 0.6269 \\ 0.8343$	$\begin{array}{c} 0.5499 \\ 0.4888 \\ 0.3731 \\ 0.1657 \end{array}$

As shown in Figure 16, the experimental data are in good agreement with the calculated results from the extended SRK equation of state at all four temperatures of 243, 258, 273, and 298 K. The root mean square deviation of bubble pressures from calculated values is 4.18% for a total of 26 data points. The root mean square deviation of bubble pressures is 4.68% for the data of Katayama *et al.* (1975), and Ohgaki and Katayama (1976) at 298 K, while the deviation is 1.24% for the data of this work at that temperature. This comparison indicates a favorable correspondence of the experimental data of this work and the two sets of literature data.

Methanol-Carbon Dioxide-Water System

The vapor-liquid equilibrium P-T-x data of this ternary system were taken at temperatures of 243, 258, 273, and 298 K. These data show that carbon dioxide is less soluble in the methanol-water mixture than in pure methanol at low pressures, and the equilibrium pressures level off near the carbon dioxide vapor pressure.

The use of the fitted binary parameter sets listed in Table 6 to predict ternary methanol-carbon dioxide-water bubble point pressures by the extended SRK equation of state gave results that compared favorably with experimental data. The use of both the K_{ij} and C_{ij} parameter sets gave better results than use of K_{ij} only; this is reflected by root mean square deviations between calculated and measured bubble pressures of 8.46% for use of a full parameter set and 12.45% for use of a reduced parameter set.

Calculated results at the water-to-methanol mole ratio of 0.2 are also plotted with experimental data in Figure 42. Although a local maximum was noted in each calculated isotherm, none was found in the experimental data. It should be recognized that calculation of equilibrium conditions for the ternary mixture requires use of binary parameters evaluated from data on mixtures of methanol-carbon dioxide and of watercarbon dioxide. Parameters for water-carbon dioxide mixtures were evaluated from data in a Henry's law region, while parameters for methanol-carbon dioxide were evaluated from data covering the entire composition range. The simple quadratic mixing rules used in the SRK calculations may be inappropriate for these systems, and give the metastable state solutions of local maxima and minima, which imply existance of LLG equilibria. At the temperature of 298 K, which is near the critical temperature of carbon dioxide, the equation failed to calculate bubble pressures of the ternary system having carbon dioxide mole fractions over 0.39.

Figure 43 presents a plot of bubble point pressure vs. carbon dioxide mole fraction in the liquid from r = 0 to $r = \infty$ at 273.15 K, as calculated by the extended SRK equation. Similar calculations can be performed at other temperatures, and the calculated results are believed to have good reliability as the results fit the experimantal data well at r = 0.2.

The carbon dioxide solubilities in a methanol-water mixture at a molar ratio of 0.2 were calculated by the extended SRK equation of state from system temperature, pressure, and assuming that the vapor-phase contained only carbon dioxide (see the section Gas Solubility Calculation Using an Equation of State). The calculated and measured carbon dioxide solubilities are listed in Table 26. For a total of 35 data points, the average error for the carbon dioxide solubilities was 12.73%. The average error could be reduced to 8.71% if the comparison between calculated and experimental values was restricted to the 29 data points having a mole fraction of carbon dioxide in the liquid of 0.4. Additionally, the solubility calculations became inaccurate as the system pressure



Figure 42. Methanol-Carbon Dioxide-Water Equilibria at r = 0.2.



Figure 43. Methanol-Carbon Dioxide-Water Equilibria at 273.15 K.

approached an asymtote near the vapor pressure of carbon dioxide at the system temperature.

TABLE 25EXPERIMENTAL VAPOR-LIQUID EQULIBRIUM P - T - x DATA FORTHE METHANOL(1)-CO(2)-HO(3) SYSTEM AT r = 0.2

P atm	× ₁	x ₂	x ₃
	-		
	T=2	$43.15~\mathrm{K}$	
1.61	0.8062	0.0323	0.1615
3.31	0.7777	0.0686	0.1537
5.53	0.7306	0.1160	0.1534
7.02	0.7092	0.1548	0.1360
9.31	0.6469	0.2198	0.1333
12.17	0.5604	0.3308	0.1088
13.61	0.4085	0.5092	0.0823
	T = 2	$58.15~{ m K}$	
2.35	0.8108	0.0292	0.1600
5.10	0.7782	0.0660	0.1558
11.15	0.7099	0.1476	0.1425
18.46	0.5752	0.3153	0.1095
21.67	0.3600	0.5743	0.0657
21.85	0.2972	0.6458	0.0570
	T=2	$73.15~{ m K}$	
2.44	0.8218	0.0193	0.1589
5.73	0.7971	0.0474	0.1555
8.99	0.7742	0.0766	0.1492
13.58	0.7376	0.1197	0.1427
18.79	0.6869	0.1802	0.1329
24.87	0.6318	0.2504	0.1178
29.97	0.5444	0.3522	0.1034
33.04	0.3570	0.5730	0.0700
33.14	0.3003	0.6403	0.0594

 $=\frac{x_3}{x_1}$

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TABLE 25 (CONTINUED)EXPERIMENTAL VAPOR-LIQUID EQULIBRIUM P - T - x DATA FORTHE METHANOL(1)-CO2(2)-H2O(3) SYSTEM AT r = 0.2

P atm	x ₁	x ₂	x ₃
	$\mathrm{T}=2$	98.15 K	
2.91	0.8219	0.0145	0.1636
5.14	0.8051	0.0279	0.1670
8.20	0.7949	0.0469	0.1582
12.57	0.7846	0.0670	0.1484
16.20	0.7700	0.0830	0.1470
20.49	0.7487	0.1070	0.1443
25.70	0.7205	0.1427	0.1368
30.79	0.6879	0.1775	0.1346
35.11	0.6659	0.2073	0.1268
40.22	0.6351	0.2432	0.1217
45.01	0.5991	0.2914	0.1095
49 .9 1	0.5569	0.3397	0.1034
54.04	0.5124	0.3928	0.0948

$$r=\frac{x_3}{x_1}$$

Methanol-Carbon Dioxide-Nitrogen System

Vapor-liquid equilibrium data were taken for methanol-carbon dioxide-nitrogen mixtures at 243.15 and 273.15 K. These eight data points are given in Table 24. The mole fractions in the vapor were determined for carbon dioxide and nitrogen; the methanol content of the vapor phase was neglected.

The solubility calculation with the extended SRK equation of state was used to predict the solubility of the nitrogen-carbon dioxide mixture in methanol. Table 27 lists the calculated and measured solubilities. Figure 44 shows excellent agreement between calculated carbon dioxide solubilities and experimental data; the average error is 8.25%. However, the calculated nitrogen solubilities are lower than the measured values; the average error is 39.5% for the eight data points.



Figure 44. Calculated and Measured Solubilities of Carbon Dioxide and Nitrogen in Methanol.

TABLE 26 CALCULATED AND EXPERIMENTAL CARBON DIOXIDE SOLUBILITIES, $x(CO_2)$, IN THE MIXTURE OF METHANOL AND WATER AT r = 0.2

ТК	P atm	Experimental	Calculated
243.15	1.61	0.0323	0.0368
	3.31	0.0686	0.0755
	5.53	0.1160	0.1267
	7.02	0.1548	0.1624
	9.31	0.2198	0.2212
	12.17	0.3308	0.3098
	13.61	0.5092	0.3716
258.15	2.35	0.0292	0.0338
	5.10	0.0660	0.0733
	11.15	0.1476	0.1627
	18.46	0.3153	0.2906
	21.6	0.5743	0.3719
	21.85	0.6458	0.3778
273.15	2.44	0.0193	0.0238
	5.73	0.0474	0.0557
	8.99	0.0766	0.0874
	13.58	0.1197	0.1328
	18.79	0.1802	0.1865
	24.87	0.2504	0.2553
	29.97	0.3522	0.3246
	33.04	0.5730	0.3795
	33.14	0.6403	0.3816
298.15	2.91	0.0145	0.0169
	5.14	0.0279	0.0298
	8.20	0.0469	0.0475
	12.57	0.0670	0.0727
	16.20	0.0830	0.0936
	20.49	0.1070	0.1185
	25.70	0.1427	0.1490
	30.79	0.1775	0.1792
	35.11	0.2073	0.2055
	40.22	0.2432	0.2375
1	45.01	0.2914	0.2688
	49.91	0.3397	0.3026
	54.04	0.3928	0.3332

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Avg Error =
$$\left(\sum_{1}^{35} (x_e - x_{cal})/x_e\right) \left(\frac{100}{35}\right) = 12.73\%$$

 $r = \frac{x_{H_2O}}{x_{MeOH}}$

TABLE 27CALCULATED AND EXPERIMENTAL SOLUBILITY RESULTS FOR
METHANOL(1)-CO2-(2)-N2 (3) SYSTEM

P atm	y(Exp.)		x(CO ₂)		x(N ₂)	
	CO_2	N ₂	Exp	Cal	Exp	Cal
		Т	= 243.15 K	-		· · ·
10.25	0.1881	0.8119	0.0649	0.0493	0.0029	0.0021
20.16	0.4365	0.5635	0.2565	0.2352	0.0057	0.0032
30.15	0.3195	0.6805	0.2517	0.2366	0.0098	0.0056
40.13	0.2590	0.7410	0.2508	0.2340	0.0137	0.0080
		Т	= 273.15 K	-		
00 70		0 5 100	0.0074	0.1000	0.0100	0.0004
39.79	0.4501	0.5499	0.2074	0.1929	0.0103	0.0064
30.40	0.5112	0.4888	0.1804	0.1754	0.0063	0.0043
20.40	0.6269	0.3731	0.1551	0.1511	0.0036	0.0022
10.54	0.8343	0.1657	0.1173	0.1071	0.0010	0.0005
Avg Error				8.25%		39.47%

Avg Error =
$$\left(\sum_{1}^{8} (x_e - x_{cal})/x_e\right) \left(\frac{100\%}{8}\right)$$

The discrepancies between experimental and calculated nitrogen mole fractions may be due to experimental errors. Specifically, nitrogen may migrate faster than methanol in transferring a sample through the capillary tube to the sampling bomb and/or from the sample bomb (where all of the sample has been vaporized) to the gas chromatograph sampling loop. Such occurrences would result in high measured nitrogen solubility. Additionally, the relative insensitivity of the thermal conductivity detector to a low concentration of nitrogen, which exists in a liquid phase sample, may contribute some deviations to the experimental data. The binary data on hydrogen solubilities in methanol reported by Yorizane *et al.* (1969), which were obtained using a technique and apparatus similar to the present work, were found higher than the values shown by Landolt-Bornstein *et al.* (1976). Zeck and Knapp (1983) have used an apparatus similar to that used here to measure gas solubilities in methanol in a range of 0.1 to 1.0 mole fraction of gas in liquid; they, however, used another type of apparatus (volume measurement) to measure gas solubilities in a mole fraction range of 0.0002 to 0.04. These data indicate that the sampling and analytical methods used in the experiments of the present work may not be suitable for a sparsely soluble gas. However, they appear to be very reliable in obtaining data on a very soluble gas such as carbon dioxide.

SUMMARY OF CONCLUSIONS

The objective of the research reported here was to develop a thermodynamic framework that could be used to describe the equilibrium behavior of methanol with compounds found in the gas produced from coal. The approach that was taken divided the constituents into three groups: Group I consisted of supercritical components, Group II consisted of compounds that are normally gases at the conditions of interest, and Group III contained compounds that are liquids at the conditions of interest. This division was used to select either an equation of state or an activity coefficient formulation of the equilibrium criteria. Once this selection was made, appropriate parameters in the formulation were evaluated from binary data obtained from the literature and experiments that were part of this study. With the parameters evaluated in this way, it is possible to predict the behavior of systems containing any number of the components from Group I, Group II, and/or Group III. A more specific discussion of the accomplishments of the work described in this report follows.

A vapor-liquid equilibrium apparatus was developed along with a sampling technique and analytical method to obtain equilibrium data on systems having high gas solubilities. Good data were obtained from this apparatus for carbon dioxide solubilities in methanol with and without an inert gas (nitrogen), and in mixtures of methanol and water. However, low solubilities of nitrogen in methanol cannot be measured accurately.

Bubble point pressure variance provided a useful objective function in the parameter search procedure for both equation-of-state and activity coefficient methods. This search procedure, which includes a bubble point pressure calculation, does not require measurement of vapor-phase composition.

Mathias' polar correction factor improved the calculation of vapor pressures with the SRK equation of state for polar compounds of methanol and water, but this factor may not necessary for ethyl mercaptan and dimethyl sulfide.

Temperature-dependent binary interaction parameters in the extended SRK equation of state have greatly improved the accuracy of correlations of methanol-containing binary VLE systems comprised of constituents from coal gasification. Temperatureindependent binary interaction parameters are satisfactory for gas-gas mixtures. These parameters are applicable in a broad range of temperatures.

Phase equilibrium calculations using the extended SRK equation of state were satisfactory for mixtures of methanol-gas systems as long as the gas component had a mole fraction in the liquid less than 0.6. They did not provide satisfactory predictions for those systems at high gas concentrations in the liquid phase. However, absorptionstripping processes that condition synthetic gas mixtures operate at liquid circulation rates that maintain the levels of dissolved gases below those at which the equation of state loses its accuracy.

The extended SRK equation of state tends to predict false LLG three-phase equilibria in methanol-light hydrocarbon and methanol-acid gas systems. This is believed to be caused by the quadratic mixing rules for interaction parameters.

The use of the optimized parameter sets enables the equation of state to predict the behavior of a methanol-containing multicomponent system; comparisons between experimental data and bubble point pressure calculations for methanol- H_2-N_2 , methanol- $CO-N_2$, and methanol- CO_2-H_2O systems mixtures were good.

A simple gas solubility calculation using the extended SRK equation of state was effective in calculating mixed-gas solubilities in a pure solvent and pure gas solubilities in a mixed solvent.

The activity coefficient models using the four-suffix Margules, Wilson, and UNI-QUAC equation are excellent for binary systems that contain condensable components (those from Groups II and III). They are especially useful in describing the vapor-liquid equilibrium behavior of systems containing volatile liquids, such as methanol, mercaptans and sulfides. The determined parameters in these models may be used to describe the multicomponent system without further adjustment, but there is no guarantee for describing the behavior of a system containing a supercritical component.

The Wilson and UNIQUAC equations are superior to the four-suffix Margules equation for most of the systems studied. The former two equations have a good built-in temperature-dependent relationship and do not predict false phase separations for methanol-acid gas and methanol-light hydrocarbon systems.

Recently developed equations of state--which include density dependent mixing rules (Mathias and Copeman, 1983; Won, 1983) based on the two-fluid, local composition theories--should be useful in future applications describing the vapor-liquid equilibrium behavior of systems having components covering a broad range of densities or with polar or hydrogen-bonding components. Coal-produced gas that is conditioned with a physical solvent is an example of such a system. The use of the bubble point pressure criterion for evaluation of the binary parameters in an equation of state should be maintained. However, a phase envelope calculation or a VLE flash calculation summarized by Van Ness and Abbott (1982) may be appropriate to describe the phase behavior of a system at fixed temperature and pressure.

A direct sampling and analysis method for high pressure liquid sample needs to be developed to simplify the currently-used method and to obtain reliable data for gases of low solubility. The design and construction of an apparatus to be able to measure multicomponent solubilities at constant temperature and pressure are essential in future work.

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LIST OF SYMBOLS

a - energy constant in extended SRK equation $A - aP/R^2T^2$

 A_{ij}, A_{ji}, D_{ij} - binary Margules parameters

 A_t, B_t, C_t - Antoine equation constants

b - volume constant in extended SRK equation

B = bP/RT

 C_{ii} - interaction parameter of b in extended SRK equation

 f_i - fugacity of i

 f_i^o – fugacity of i at reference state

 $g^E =$ excess Gibbs free energy

 $H_{i,j}$ – Henry's law constant for solute i in solvent j

 K_{ii} - interaction parameter of a in extended SRK equation

m – parameter used to correlate α in the SRK equation

n - number of data points

 n_i – moles of i in mixture

N - number of components in mixture

 p^{s} - saturated vapor pressure

 p^* - vapor pressure

p – Mathias' polar correction factor

P - pressure

 P_c – critical pressure

 P_{cal} - calculated pressure

 P_e – experimental pressure

 P_{ref} - reference pressure

q - structure area parameter in UNIQUAC equation

q' - modified structure area parameter in UNIQUAC equation

r -structure size parameter in UNIQUAC equation

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r – water to methanol mole ratio

R - gas constant

T – temperature

 T_c - critical temperature

 T_r - reduced temperature, T/T_c

$\Delta u_{12}, \Delta u_{21}$ – temperature-independent binary UNIQUAC parameters

v - specific volume

 v_i^L – liquid molar volume of i

 $\overline{v_i}^{\infty}$ — partial molar volume of solute i at infinite dilution

V - volume

 V_c – critical molar volume

 x_i – mole fraction i

 x_i — mole fraction i in liquid phase of two-phase mixture

 y_i — mole fraction i in vapor phase of two-phase mixture

z - compressibility factor = Pv/RT

 z_c – critical compressibility factor

<u>Greek</u>

 α_i - temperature-dependent function in extended SRK equation

 β_{iikl} – constant in Margules equation

 γ_i - activity coefficient of i

 δ_i – solubility parameter of i

 $\Delta \lambda_{12}, \Delta \lambda_{21}$ – temperature-independent binary Wilson parameters

 $\Lambda_{ij}, \Lambda_{ki}, \Lambda_{kj}$ - temperature-dependent binary Wilson parameters

 ρ_c – critical liquid molar density

 σ^2 – bubble point pressure variance

 $\tau_{ij}, \tau_{ji}, \tau_{kj}$ – temperature-dependent binary UNIQUAC parameters

 ϕ_i – fugacity coefficient of i

 ϕ_i^* - fugacity coefficient of saturated i

 ϕ^L – fugacity coefficient of liquid

 ω_i – Pitzer acentric factor