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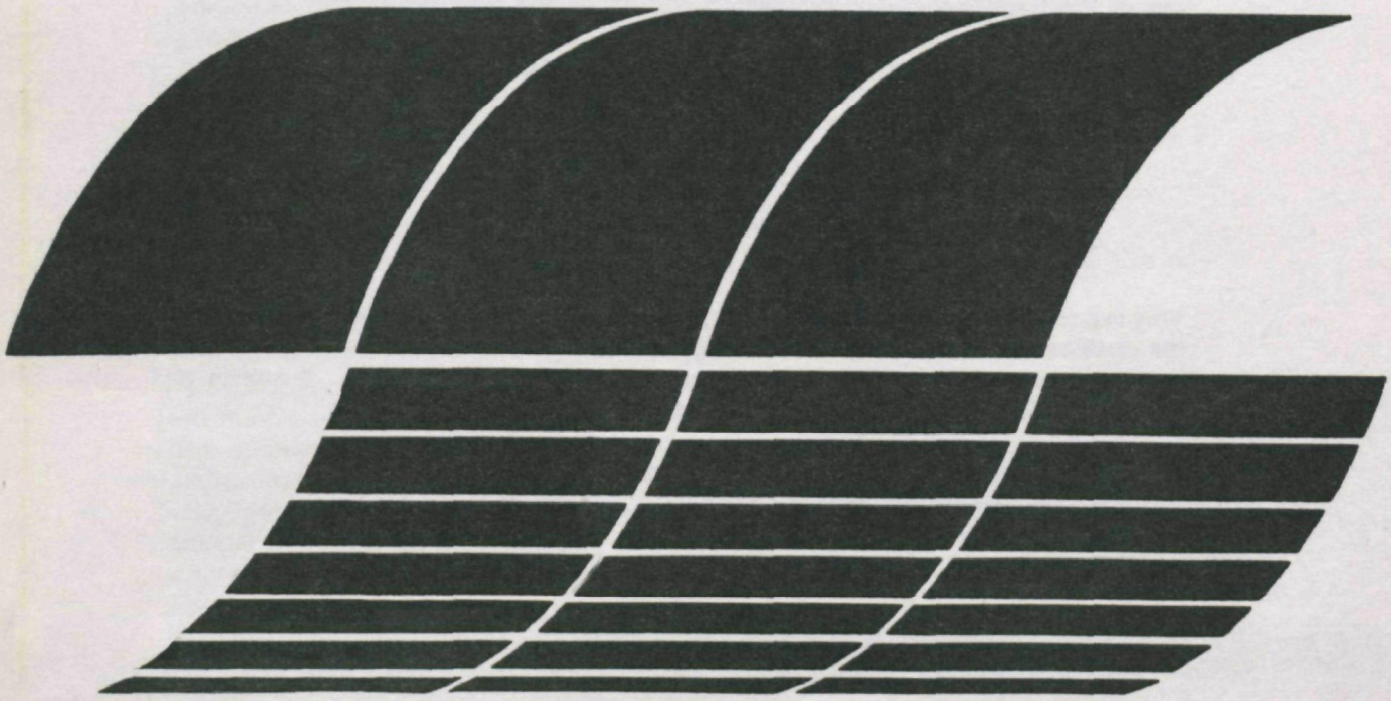
Solubilities of Acid Gases and Nitrogen in Methanol

Interagency Energy/Environment R&D Program Report



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Solubilities of Acid Gases and Nitrogen in Methanol

by

J.K. Ferrell, R.W. Rousseau,
and J.N. Matange

North Carolina State University
Department of Chemical Engineering
Raleigh, North Carolina 27607

Grant No. R804811
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EPA Project Officer: Robert A. McAllister

Industrial Environmental Research Laboratory
Office of Environmental Engineering and Technology
Research Triangle Park, NC 27711

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INTRODUCTION

Considerable attention has been given recently to coal gasification in the hope that a substitute for natural gas and crude oil can be developed, thereby easing the prevailing energy shortage. For coal gasification to be part of a solution to the energy shortage, preparation must be made to gasify literally millions of tons of coal.

Perhaps the most consistent feature of coal is its inconsistency. Its molecular structure is undefined; its composition and characteristics can vary widely depending upon the geographic area, the coal seam, and even the location within the same seam, from which it is mined. Thus when coal is gasified, the gas formed has a very complex composition. Along with the desired products, H_2, CO, hydrocarbons, etc., there is a significant quantity of undesirables such as H_2S, CO_2, COS, benzene, phenol, etc. In this environmentally conscious era, coal gasification would be acceptable only if the environmental impact of coal gasification can be accurately assessed and then properly handled.

Recognizing this situation, the Environmental Protection Agency in 1977 contracted for the design and construction of a coal gasification-gas cleaning test facility at North Carolina State University, to be operated by faculty and staff of the Department of Chemical Engineering. Construction was begun in January 1978 and the plant was completed and turned over to the University in the summer of 1978.

The principal components of the pilot plant are a continuous fluidized bed gasifier, a cyclone separator and venturi scrubber for

removing particulates, condensables, and water-soluble species from the raw synthesis gas, and absorption and stripping towers and a flash tank for acid gas removal and solvent regeneration. The gasifier operates at pressures up to 100 psig (791 kPa), has a capacity of 50 lbs coal/hr (23 kg/hr), and runs with either steam-air or steam-O_2 feed mixtures. The acid gas removal system is modular in design, so that alternative absorption processes may be evaluated. Associated with the plant are facilities for direct digital control of all process systems and for on-line data acquisition, logging, and graphical display. Facilities for sampling and exhaustive chemical analysis of all solid, liquid, and gaseous feed and effluent streams are also available.

The overall objectives of the project are to characterize completely the gaseous and condensed phase emissions from the gasification-gas cleaning process and to determine how emission rates of various pollutants and methanation catalyst poisons depend on adjustable process parameters.

The task of this study was to concentrate on the gas cleaning portion of the project. Broadly speaking, gas cleanup systems can be divided into three groups based on the absorbents used: amine based systems, hot carbonate systems, and physical solvent systems.

In amine based systems the most common solvents are monoethanolamine (MEA) and diethanolamine (DEA). Acid gases, H_2S and CO_2, react with the amine solution to form chemical complexes; the reactions may be reversed by applying heat to the solution and stripping off the H_2S and CO_2 in a regeneration tower. Amine systems are falling into disfavor as they are both non-selective and suffer high vaporization

losses. In addition, MEA forms stable compounds with COS and CS_2 which cannot be regenerated by heat. Diglycolamine is increasingly being employed in gas cleanup systems due to its lower volatility. Another amine that is finding use is diisopropanol amine.

In hot carbonate processes, acid gases are absorbed in a countercurrent contactor by a carbonate solution. The gases are recovered from the rich solution by flashing and steam-stripping in a low pressure regenerator. Modern carbonate systems--such as the Benfield Process, the Catacarb Process, and the Giemmarco-Vetrocoke Process--have found many applications in today's gas, chemical and refinery industries. These systems employ a 20 to 30 percent water solution of potassium carbonate, operate at between 220° and 300°F, and utilize various additives to increase the rate of gas absorption as well as to catalyze the reactions.

The third general method for removing acid-gas from a raw-gas stream is by physical absorption in an organic solvent without chemical reaction. The solvent can be regenerated by heat, pressure reduction, or gas stripping, producing a concentrated stream of the absorbed gas. H_2S and CO_2 as well as minor components in the gas stream--including COS, CS_2 and mercaptans--are more soluble in many organic solvents than fuel-gas species, especially at elevated pressure. In addition, some of the physical solvents are highly selective for H_2S over CO_2. This aspect is important in applications where a H_2S rich stream has to be generated to be sent to a Claus Plant for sulfur recovery.

Refrigerated methanol is the solvent being used currently in the NCSU facility. Methanol is also the solvent used in Lurgi's proprie-

tary Rectisol process. After a careful search of the literature, it was concluded that the data and correlations available to the technical public are not sufficient to analyze this system properly. Thus the objective of this study was to generate part of the data and correlations necessary for analysis of methanol-based acid gas removal systems. The particular emphasis of this study was the multicomponent vapor-liquid equilibrium behavior of selected constituents of crude coal gas.

STATEMENT OF OBJECTIVES

The purpose of this study was to develop a thermodynamic model for the system methanol-carbon dioxide-nitrogen-hydrogen sulfide. To check the validity of the model predictions it was necessary to have experimental vapor-liquid equilibrium data for the four component system. As these data could not be found in the literature, another objective of this research was to develop an experimental apparatus to obtain multicomponent vapor-liquid equilibrium data for mixtures of these components. The objective of the experimental program was to obtain the multicomponent vapor-liquid equilibrium data with the system pressure in the range of five to forty atmospheres and system temperature in the range of 0°C to -20°C.

DEVELOPMENT OF THE THERMODYNAMIC MODEL

FUNDAMENTALS

The main objective of this research was development of a thermodynamic model for prediction of vapor-liquid equilibria for a multicomponent system containing the principal components in an acid gas removal system. The multicomponent system chosen for study consisted of mixtures of methanol, carbon dioxide, nitrogen and hydrogen sulfide. The structure of the thermodynamic model was made flexible to facilitate future inclusion of additional components into the model.

This work was a continuation of that by Bass (1978). In the interest of continuity, the next few paragraphs trace the thermodynamic model development from its inception to its current status.

Development of any phase equilibrium model begins with a consideration of the fundamentals of phase equilibria. Since phase equilibria is a vast subject, the intent here will be to discuss that segment which applies to the thermodynamic model. Since the model was based on one liquid phase in equilibrium with a vapor phase, the phase equilibria discussion also focuses on this situation.

For liquid and vapor phases to be in equilibrium with each other it is necessary that the system be in a state of equilibrium with respect to the three processes of heat transfer, boundary displacement, and mass transfer. Equality of temperature and of pressure between the two phases assures equilibrium for heat transfer and boundary displace-

ment processes. Unfortunately, the conditions necessary for establishing mass transfer equilibrium cannot be expressed in a similar straightforward fashion. At a strictly mathematical level, Gibbs provided a guide by defining the chemical potential function, μ; for mass transfer equilibrium, the chemical potential of each component must be invariant from phase to phase. Thus for a system comprised of N components, equilibrium with respect to the processes mentioned earlier is indicated by the following equalities:

$$T^{Vap} = T^{Liq} \tag{1}$$

$$p^{Vap} = p^{Liq} \tag{2}$$

$$\mu_i^{Vap} = \mu_i^{Liq} \qquad (i = 1 \text{ to } N) \tag{3}$$

To establish equilibrium between the two phases it is clear that temperature and pressure of the two phases must be equal. However what is necessary to obtain the equality of chemical potentials is not clear. What is needed is an expression relating chemical potential (an abstract quantity), to composition, temperature and pressure (measurable quantities).

G. N. Lewis obtained the following expression for a pure ideal gas at constant temperature:

$$\mu - \mu^o = RT \ln \frac{P}{P^o} \tag{4}$$

where

μ = chemical potential of the ideal gas at system temperature T

μ^o = chemical potential of the ideal gas at arbitrary reference conditions

R = gas constant

T = temperature of the ideal gas

P = pressure of the ideal gas at system temperature, T

P^o = pressure of the ideal gas at the arbitrary reference conditions at which μ^o is evaluated

Equation 4 represents an important simplification in it the abstract chemical potential function is expressed in terms of a measurable quantity, pressure. However, this is possible only under pure ideal gas conditions. To remove this constraint, Lewis introduced the function fugacity through the definition

$$\mu_i - \mu_i^o = RT \ln \frac{f_i}{f_i^o} \qquad (5)$$

where

μ_i = chemical potential of component i at system temperature and pressure

μ_i^o = chemical potential of component i at arbitrary reference conditions

f_i = fugacity of component i at system temperature T and pressure

f_i^o = fugacity of component i at the arbitrary reference condition at which μ_i^o is evaluated

The concept of fugacity is akin to that of pressure; under ideal gas conditions, fugacity and pressure are the same. Prausnitz (1969), for example, refers to fugacity as a "corrected pressure." It should

be noted that Equation 5 does not refer to a particular phase and, therefore, applies to gases, liquids and solids.

It can be shown that equality of fugacity of each component in every phase is equivalent to the corresponding equality of chemical potentials. Thus the condition for mass transfer equilibrium can now be written as

$$f_i^{Vap} = f_i^{Liq} \tag{6}$$

where

f_i^{Vap} = fugacity of component i in the vapor phase

f_i^{Liq} = fugacity of component i in the liquid phase

Equation 6 is a significant improvement on Equation 3 as the abstract chemical potential term is replaced by fugacity, a term similar to pressure. Equation 6 is the fundamental thermodynamic relationship to be used for phase equilibria. It now remains to develop expressions relating fugacity to composition, temperature and pressure.

There are two basic methods for calculating the fugacities. The first utilizes the exact relationship

$$\ln f_i = \frac{1}{RT} \int_V^\infty \left[\left(\frac{\partial P}{\partial n_i}\right)_{T,V,n_j} - \frac{RT}{V}\right] dV - \ln \frac{V}{n_i RT} \tag{7}$$

where

R = gas constant

T = temperature

P = total pressure

V = total volume

n_i = moles of component i

f_i = fugacity of component i

A single equation of state is used for both the vapor and the liquid phase. This equation of state is used to solve the partial derivative in Equation 7.

The use of Equation 7 to evaluate f_i requires utilization of a pressure explicit equation of state that describes P-V-T properties of the system over the limits of integration. While such calculations are indeed possible for many single-component substances and for a limited number of mixtures, it is not expected that the components encountered in acid gas removal systems could be handled in this manner.

In the second method, liquid and vapor phases are treated independently. To obtain fugacities in the vapor phase the following expression is used:

$$f_i^{Vap} = \phi_i y_i P \tag{8}$$

where

ϕ_i = fugacity coefficient of component i

y_i = vapor phase mole fraction of component i

P = total pressure

The fugacity coefficient, ϕ_i, is the measure of the deviation from

ideal behavior of component i in the vapor phase.

Either of the following two equations can be used to calculate the fugacity coefficient of component i, ϕ_i:

$$\ln \phi_i = \frac{1}{RT} \int_V^\infty \left[\left(\frac{\partial P}{\partial n_i}\right)_{T,V,n_j} - \frac{RT}{V}\right] dV - \ln z \qquad (9)$$

$$\ln \phi_i = \frac{1}{RT} \int_0^P \left[\left(\frac{\partial V}{\partial n_i}\right)_{T,P,n_j} - \frac{RT}{P}\right] dP \qquad (10)$$

$z \equiv pv/RT$ = compressibility factor

To obtain the fugacity coefficient from Equation 9 a pressure explicit equation of state is necessary, while Equation 10 requires a volume explicit equation of state. Since most equations of state are in the pressure explicit form, Equation 9 is used more easily than Equation 10.

Liquid fugacities are obtained from the definition

$$f_i^{Liq} = \gamma_i x_i f_i^{Ref} \qquad (11)$$

where

γ_i = activity coefficient of component i

x_i = liquid mole-fraction of component i

f_i^{Ref} = reference state fugacity for component i

Although the choice of the reference state is arbitrary, the activity

coefficient, which is a measure of deviation from ideal solution behavior, depends on the composition temperature and the choice of the reference state. There are two choices for the reference fugacity: one leading to an ideal solution in the sense of the Raoult's law and the other to an ideal solution in the sense of the Henry's law.

For an ideal solution at constant temperature and pressure, the fugacity of each component is proportional to its liquid mole fraction. Thus for component i in an ideal solution,

$$f_i^{Liq} = C_i x_i \qquad (12)$$

where C_i is a proportionality constant dependent on temperature and pressure but independent of the mole fraction of component i.

If Equation 12 holds over the entire range of composition, from $x_i = 0$ to $x_i = 1$, then the solution is ideal in the Raoult's law sense. In this case, it is evident from the boundary condition at $x_i = 1$ that the proportionality constant, C_i, is equal to the fugacity of pure liquid i at the temperature and pressure of the solution.

If on the other hand, Equation 12 holds over a small range of x_i, with x_i being close to zero, then the solution is ideal in the Henry's law sense. In this case, the constant C_i is not equated to the fugacity of pure liquid i, but to the fugacity of i in an infinitely dilute solution.

A comparison of Equations 11 and 12 shows that activity coefficients of all the components are equal to unity in an ideal solution. In nonideal solutions, the term normalization of a component is often

used. Normalization of a component refers to the conditions which will lead to ideal behavior for that component. When the reference state of component i is chosen in the Raoult's law sense, normalization for component i implies

$$\gamma_i \rightarrow 1.0 \qquad \text{as} \qquad x_i \rightarrow 1.0$$

On the other hand, if the reference state for component i is chosen in the Henry's law sense, normalization for component i is

$$\gamma_i \rightarrow 1.0 \qquad \text{as} \qquad x_i \rightarrow 0.0$$

If all components of a solution are normalized in the same way, either in Raoult's law sense or in the Henry's law sense, normalization is said to follow the symmetric convention. If some components are normalized in the Raoult's law sense and others in the Henry's law sense, the normalization follows the unsymmetric convention.

Using Equations 6, 8 and 11 to express equilibrium conditions results in the relationship

$$f_i^{Vap} = \phi_i y_i P = \gamma_i x_i f_i^{Ref} = f_i^{Liq} \tag{13}$$

As mentioned in the beginning of this section, the multicomponent system being modelled consists of methanol-carbon dioxide-nitrogen-hydrogen sulfide. Since methanol is a polar compound, and methanol and carbon dioxide are known to associate in the vapor phase (Hemma-

plardh and King, 1972), the thermodynamic model developed in this study was based on the second method of calculating the fugacities; i.e. Equation 13. The temperature and pressure range for which the thermodynamic model was developed suggested the symmetric convention for normalization. Furthermore, as pointed out by O'Connell (1977), severe difficulties exist in using Henry's law for the reference state basis when the solvent consists of more than one component. Since it was believed that more flexibility would result from defining reference liquid state conditions by the Raoult's law convention, particularly in regard to adding components to the system model, this approach was chosen.

THERMODYNAMIC CORRELATIONS

A foundation for the thermodynamic model was found in the final form of the fundamental relationship of phase equilibria (Equation 13). The next step was development of a structure for using the model. The building blocks for this structure were thermodynamic correlations to calculate fugacity coefficients, activity coefficients and reference state fugacities for each component in the multicomponent system methanol-carbon dioxide-nitrogen-hydrogen sulfide.

Vapor Fugacity Coefficients

To obtain the correlation for the fugacity coefficient, it was decided to use Equation 9 with a pressure explicit equation of state.

$$\ln \phi_i = \frac{1}{RT} \int_V^\infty \left[\left(\frac{\partial P}{\partial n_i}\right)_{T,V,n_j} - \frac{RT}{V}\right] dV - \ln z \qquad (9)$$

There are many equations of state, including Redlich-Kwong, the Soave modification of the Redlich-Kwong , Benedict-Webb-Rubin and virial.

The Redlich-Kwong equation is commonly considered one of the best two parameter equations of state and was the first equation of state used in the present thermodynamic model. Subsequently, it was determined that the Soave modification of the Redlich-Kwong equation of state provided a significant improvement in accuracy; it was used in the remainder of this work. The Soave modification of the Redlich-Kwong equation of state is given by

$$P = \frac{RT}{(v-b)} - \frac{\alpha a}{v(v+b)} \qquad (14)$$

where

- v = vapor molar volume
- a,b = constants in the Soave modification of the Redlich-Kwong equation of state
- α = function of temperature and acentric factor, ω

For any pure component, constants a, b and α are obtained from

$$a = 0.42747\ R^2\ T_c^2\ /\ P_c \qquad (14a)$$

$$b = 0.08664\ R\ T_c\ /\ P_c \tag{14b}$$

$$\alpha = [1 + \{0.48508 + 1.55171\omega - 0.15613\omega^2\}\ \{1 - (\frac{T}{T_c})\}]^2 \tag{14c}$$

where

T_c = critical temperature

P_c = critical pressure

ω = Pitzer acentric factor

For a mixture, constants a and b are obtained by the mixing rules

$$b = \sum_{i=1}^{N} y_i b_i \tag{14d}$$

$$\alpha a = \sum_{i=1}^{N} \sum_{j=1}^{N} y_i y_j \alpha_{ij} a_{ij} \tag{14e}$$

where

$$\alpha_{ij} a_{ij} = (\alpha_i \alpha_j a_i a_j)^{1/2}\ (1 - K_{ij}) \tag{14f}$$

N = number of components in the mixture

y_i = mole fraction in the vapor phase of component i

K_{ij} = binary interaction constant considered to be independent of temperature, pressure, and composition

Equation 14 can also be expressed as

$$Pv^3 - RTv^2 + (a - RTb - Pb^2)v - ab = 0 \qquad (15)$$

The largest root of Equation 15 is the vapor phase molar volume.

Substitution of Equation 14 into Equation 9 yields the following equation for fugacity coefficient of component i

$$\ln \phi_i = \frac{b_i}{b}(z-1) - \ln(z-B)$$

$$- \frac{A}{B}\left[\frac{2\sum_{j=1}^{N} y_j \alpha_{ij} a_{ij}}{\alpha a} - \frac{b_i}{b}\right] \ln\left(1 + \frac{B}{z}\right) \qquad (16)$$

where

$$A = \frac{\alpha a P}{R^2 T^2} \qquad (16a)$$

$$B = \frac{bP}{RT} \qquad (16b)$$

Fugacity coefficients were calculated for the component of interest from Equation 16. Binary interaction constants, K_{ij}, are presented in Table 1. Of the six binary interaction constants required by the model, three were found in the literature, while the other three were calculated using experimental binary x-P-T data. The criterion used to obtain these constants was the minimization of the bubble point pressure variance. Generally the binary interaction constants are small and on the order of 0.00 to 0.25 (Graboski and Daubert, 1978). The sum of

the squares of the deviations between pressure predicted by the model and experimental pressure was calculated for several values of K_{ij} in the range 0.00 to 0.25. Using quadratic interpolation the optimum value of K_{ij} was taken as that minimizing the sum of the square of the deviations for each of the three binaries for which literature values were unavailable. Critical constants and Pitzer acentric factors used in the model are given in Table 2.

TABLE 1

Binary Interaction Constants for Soave Modification of Redlich-Kwong Equation of State.

System	K_{ij}	Source
Methanol - CO_2	0.0628	a
Methanol - N_2	0.080	b
Methanol - H_2S	-4.000	c
CO_2 - N_2	-0.022	Graboski and Daubert (1978)
CO_2 - H_2S	0.102	Graboski and Daubert (1978)
N_2 - H_2S	0.140	Graboski and Daubert (1978)

[a]Calculated from x-P-T data found in literature (Yorizane et al., 1969; Katayama et al., 1975).

[b]Calculated from x-P-T data found by Weber and Knapp (unpublished data, Dechnische Universitat, Berlin, Fachdereich 10, Berfahrenseechink, Institut für Thermodynamik and Anlagentechnik, 1978).

[c]Calculated from x-P-T data found in literature (Yorizane et al., 1969).

TABLE 2

Critical Constants and Pitzer Acentric Factors (Reid et al., 1977).

Component	T_c (°K)	P_c (atm)	V_c (cc/mole)	ω
Methanol	512.6	79.9	118.0	0.559
CO_2	304.2	72.8	94.0	0.225
N_2	126.2	33.5	87.5	0.040
H_2S	373.2	88.2	98.5	0.100

Activity Coefficients

A number of correlations are available for activity coefficients. Prominent among them are the Wohl equation, the Wilson equation, and the UNIQUAC equation. Adler et al (1966) have recommended a special case of the Wohl equation, the four-suffix Margules equation, as the best choice for calculating activity coefficients in systems of the type under study here. Based on this recommendation, the four-suffix Margules equation was selected to calculate activity coefficients in the model. It should also be mentioned that the Wilson equation was examined, but convergence problems associated with estimation of model parameters reinforced the decision to use the Margules equation.

Truncating the original Wohl polynomial (1953) to include only the terms up to the fourth power and assuming equal molal volumes for the components, the following expression for the activity coef-

ficient of component i in a multicomponent solution can be obtained:

$$\log \gamma_i = 4 \sum_{j=1}^{N} \sum_{k=1}^{N} \sum_{\ell=1}^{N} x_j x_k x_\ell \beta_{ijk\ell}$$

$$- 3 \sum_{i=1}^{N} \sum_{j=1}^{N} \sum_{k=1}^{N} \sum_{\ell=1}^{N} x_i x_j x_k x_\ell \beta_{ijk\ell} \qquad (17)$$

where $\beta_{ijk\ell}$ are related to binary Wohl constants, A_{ij}, A_{ji} and D_{ij}, and a ternary constant C* (to be discussed in subsequent paragraphs).

Depending on the values of the integers i, j, k, and ℓ, $\beta_{ijk\ell}$ is determined by the following rules:

If $i = j = k = \ell$,

$$\beta_{ijk\ell} = \beta_{iiii} = 0. \qquad (17a)$$

If $i = j = k \neq \ell$,

$$\beta_{ijk\ell} = \beta_{iii\ell} = \beta_{ii\ell i} = \beta_{i\ell ii} = \beta_{\ell iii} = \frac{A_{\ell i}}{4} \qquad (17b)$$

If $i = j \neq k = \ell$,

$$\beta_{ijk\ell} = \beta_{iikk} = \beta_{ikik} = \ldots = 1/6(A_{ik} + A_{ki} - D_{ik}) \qquad (17c)$$

If $i = j \neq k \neq \ell$,

$$\beta_{ijk\ell} = \beta_{iik\ell} = \beta_{ik\ell i} = \ldots \qquad (17d)$$

$$= 1/12\ [(A_{ki} + A_{\ell i} + A_{ik\ell}) - C^*_{i\text{-}ik\ell}] \qquad \text{(17d cont'd)}$$

If $i \neq j \neq k \neq \ell$,

$$\beta_{ijk\ell} = 1/24\ (A_{ijk} + A_{ik\ell} + A_{jk\ell}) \qquad (17e)$$

where

$$2A_{ik\ell} = A_{ik} + A_{ki} + A_{i\ell} + A_{\ell i} + A_{k\ell} + A_{\ell k}, \qquad (17f)$$

$C^*_{i\text{-}ik\ell}$ = ternary constant for component i in the ik ternary mixture.

Adler et al. (1966) studied the effect of C* on the deviation of the predicted vapor composition from the experimental vapor composition for a number of ternary systems. Their study indicated that for all systems the value of C* can be expected to be very near zero. This implies that the term in the series expansion of the excess free energy owing to clusters of three molecules, all different, is not exceptionally important. In fact, the expected population of such clusters seems to be about equal to the average of the populations expected for triple clusters from the binary data. Based on this the value of C* was taken as zero in the model.

To calculate values for $\beta_{ijk\ell}$, it is necessary to know the constants A_{ij}, A_{ji} and D_{ij} for all binary mixtures that can be formed by the system components. Unfortunately, solution theory is not at a point where these constants can be calculated <u>a priori</u> from pure

component properties; they must be estimated from binary experimental vapor-liquid equilibrium data.

A total of six binaries result from the combinations of the components of the multicomponent system, methanol-carbon dioxide-nitrogen-hydrogen sulfide. They are methanol-carbon dioxide, methanol-nitrogen, methanol-hydrogen sulfide, carbon dioxide-nitrogen, carbon dioxide-hydrogen sulfide, and nitrogen-hydrogen sulfide. For each of these binaries, extensive equilibrium data were collected from the literature.

For a binary system, the four-suffix Margules equation simplifies to

$$\log \gamma_i = x_j^2 [A_{ij} + 2(A_{ji} - A_{ij} - D_{ij})x_i + 3D_{ij}x_i^2] \qquad (18)$$

The binary constants A_{ij}, A_{ji} and D_{ij} were evaluated from the binary experimental x-P-T data using a number of techniques. The constants which were finally used in the model were evaluated by the technique which resulted in the smallest deviation between the predicted pressure and the experimental pressure. The details of this technique will be discussed in the section dealing with parameter evaluation.

It should be noted that the binary constants, A_{ij}, A_{ji} and D_{ij}, are evaluated for a fixed temperature and pressure. The effect of pressure on the liquid phase is usually small and the pressure dependence of the constants was neglected. For the temperature dependence, a simple inverse relationship with respect to temperature has been suggested (Adler et al., 1966). Assumptions of A_{ij}, A_{ji} and D_{ij} to be

inversely proportional to absolute temperature were used in the parameter evaluation techniques. For the binary mixtures involving nitrogen, use of the inverse temperature dependence for the constants was found to give unsatisfactory results. A number of alternatives were tested to obtain the constants for these binaries. The one which was most successful involved the interpolation of experimental binary x-P-T data. System pressure P was evaluated for a number of values of the liquid mole fraction x at the temperatures of interest using linear interpolation of the experimental system pressure with respect to the temperature. These interpolated x-P-T data then were used to obtain the binary constants at the temperatures of interest.

Reference Fugacities

Reference states for all the components were chosen as the pure liquid at the temperature and pressure of the system.

Methanol. The reference state fugacity for methanol was obtained from the following exact thermodynamic relationship:

$$f_i^{Ref} = P_i^*(T)\phi_i^*(T,P)\exp \int_{P_i}^{P} \frac{v_i^{Liq}(T,P)dP}{RT} , \qquad (19)$$

where

P_i^* = vapor pressure of component i

ϕ_i^* = vapor phase fugacity coefficient of saturated i

v_i^{Liq} = liquid molar volume

The vapor pressure for methanol was calculated from the Antoine equation:

$$\log_{10} P^*(\text{mmHg}) = 7.87862 - \frac{1473.11}{T(K)-43.247} \tag{20}$$

Antoine constants were determined from experimental vapor pressure data of Eubank (1970) for temperatures from -40°C to +30°C. Molar volumes of methanol were calculated from a corresponding states correlation of Chueh and Prausnitz (Reid et al, 1977)

$$1/v_i^{Liq} = \rho = \rho_s\left[1 + \frac{9 z_c N_v (P-P^*)}{P_c}\right]^{1/9} \tag{21}$$

$$N_v = (1.0 - 0.89\omega)\,[\exp(6.9547 - 76.2853\, T_r + 191.3060\, T_r^2 - 203.5472\, T_r^3 + 82.7631\, T_r^4)] \tag{21a}$$

$$\rho_s = \rho_c/(V_r^{(o)} + \omega V_r^{(1)} + \omega^2 V_r^{(2)}) \tag{21b}$$

$$\rho_c = 1/V_c \tag{21c}$$

$$V_r^{(j)} = a_j + b_j T_r + c_j T_r^2 + d_j T_r^3 + e_j/T_r + f_j \ln(1-T_r) \tag{21d}$$

where

z_c = critical compressibility factor

ω = Pitzer acentric factor

T_r = reduced temperature = T/T_c

V_c = critical volume

Constants for Equation 21d are given in Table 3. Using the above correlation for the liquid molar volume and evaluating the integral in Equation 19, the following expression is obtained for the reference fugacity of methanol:

$$f_i^o = P_i^* \Phi_i^* \exp\left\{\frac{P_{c_i}}{8RT\,\rho_{s_i}\,z_{c_i}}\left[\left(1 + \frac{9z_{c_i}N(P-P_i^*)}{P_{c_i}}\right)^{8/9} - 1\right]\right\} \qquad (22)$$

TABLE 3

Constants Used in Equation 21d for Calculating Methanol Liquid Molar Volume

j	a_j	b_j	c_j	d_j	e_j	f_j
0	0.11917	0.009513	0.21091	-0.06922	0.07480	-0.084476
1	0.98465	-1.60378	1.82484	-0.61432	-0.34546	0.087037
2	-0.55314	-0.15793	-1.01601	0.34095	0.46795	-0.239938

Carbon Dioxide and Hydrogen Sulfide. Fugacities for pure carbon dioxide and hydrogen sulfide were determined from a three-parameter reduced states correlation (Robinson and Chao, 1979).

$$\log \frac{f_i^o}{P} = \log \nu^{(0)} + \omega \log \nu^{(1)} \tag{23}$$

$$\log \nu^{(0)} = B_0 + B_1 P_r + B_2 P_r^2 - \log P_r \tag{23a}$$

$$B_0 = -20.651608 + 84.517272\ T_r - 15.376424\ T_r^2$$

$$+ 152.65216\ T_r^3 - 84.899391\ T_r^4 + 24.84688\ T_r^5$$

$$- 2.9786581\ T_r^6 \tag{23b}$$

$$\text{If } 0.8 > T_r \geq 0.3 \qquad B_1 = \left(\frac{0.293}{2.303\ T_r}\right)^{[1+(1-T_r)^{0.286}]} \tag{23c}$$

$$\text{If } 0.9 > T_r \geq 0.8 \qquad B_1 = 0.321895\ T_r - 0.184316 \tag{23d}$$

$$\text{If } 1.8 \geq T_r \geq 0.9 \qquad B_1 = 58.16962 - 326.54444\ T_r$$

$$+ 775.11716\ T_r^2 - 1006.8122\ T_r^3$$

$$+ 773.32667\ T_r^4 - 351.56938\ T_r^5$$

$$+ 87.677429\ T_r^6 - 9.2617986\ T_r^7 \tag{23e}$$

If $0.8 > T_r \geq 0.3$ $\quad B_2 = 0$ (23f)

If $0.9 > T_r \geq 0.8$ $\quad B_2 = 0.0549369\ (0.8 - T_r)$ (23g)

If $1.0 > T_r \geq 0.9$ $\quad B_2 = 0.673344 \times 10^{-3} - 0.685226 \times 10^{-2}\ T_r$ (23h)

If $T_r \geq 1.0$ $\quad B_2 = 0.72203901 - 2.7182597\ T_r$

$$+ 3.984423\ T_r^2 - 2.8712448\ T_r^3$$

$$+ 1.0202739\ T_r^4 - 0.14314712\ T_r^5 \qquad (23i)$$

$$\log \nu^{(1)} = \log \nu_{0.6}^{(1)} + (P_r - 0.6)\left(\frac{\partial \log \nu^{(1)}}{\partial P_r}\right) \qquad (23j)$$

$$\log \nu_{0.6}^{(1)} = -660.08698 + 7766.7774\ T_r$$

$$-40007.379\ T_r^2 + 116582.6\ T_r^3$$

$$-209756.24\ T_r^4 + 238673.14\ T_r^5$$

$$-167856.45\ T_r^6 + 66762.602\ T_r^7$$

$$-11504.984\ T_r^8 \qquad (23k)$$

$$\frac{\partial \log \nu^{(1)}}{\partial P_r} = -0.28997623 + 0.96418856\ T_r$$

$$-1.3344703\ T_r^2 + 0.82575807\ T_r^3$$

$$-0.18939410\ T_r^4 \qquad (23L)$$

Nitrogen. The Chao-Seader equation with adjusted parameters was used to obtain the reference fugacity of nitrogen.

$$\log \frac{f_i^o}{P} = 2.7365534 - 1.9818310/T_r - 0.51487289\ T_r + 0.042470988\ T_r^2 - 0.002814385\ T_r^3 + (-0.029474696 + 0.021495843\ T_r)\ P_r - \log P_r + \omega_i \qquad (24)$$

STRUCTURE OF THERMODYNAMIC MODEL

Starting from the fundamental thermodynamic relationship of phase equilibria (Equation 13), two routes are available for phase equilibria calculations. One is the bubble point calculational procedure and the other is the dew point calculational procedure.

Input data for the bubble point calculations are the pure component constants, T_c, P_c, V_c, and ω, the Margules constants for all the binaries in the system and the liquid mole fractions of all the components in the system. One more piece of information is necessary and that could be either the system temperature or the system pressure. Thus within the bubble point calculational procedure itself there are two options. In the first, the system temperature is chosen as the last input variable. In this case the output of the calculational procedure is the system pressure and the vapor mole fraction of the system components. In the second, it is the system pressure

that is the last input variable and the output variables are the system temperature and the vapor mole fractions of the system components.

Also, for the dew point calculational procedure either the system temperature or the system pressure can be made an input variable. The other data necessary for this procedure are the pure component constants, the Margules constants for all the binaries in the system, and the vapor mole fractions for all the components in the system. The output from this procedure includes the liquid mole fractions and either the system pressure (if temperature was the input variable) or the system temperature (if the pressure was the input variable).

Of the four calculational procedures the isothermal bubble point calculational procedure (temperature is an input variable) is the simplest and models based on this procedure require the least amount of computer time to yield a solution. With this in mind the thermodynamic model developed was based on the isothermal bubble point calculational procedure and was called BUBLT. Figure 1 shows the flow chart for model BUBLT. Later, another model was developed to perform the isothermal dewpoint calculations and was called DEWT. The flow chart for model DEWT is shown in Figure 2. Complete listings of programs for BUBLT and DEWT are given by Matange (1980).

Model BUBLT

The flow chart for model BUBLT is shown in Figure 1. The program starts by reading critical constants and Pitzer acentric factors (T_c, P_c, V_c, and ω) for all system components. Margules constants (A_{ij}, A_{ji}, and D_{ij}) for all binary combinations are read next, followed by an input of system temperature and liquid mole fractions for

all components. In the first iteration an initial guess of the system pressure is made. Convergence is not significantly affected by the initial value of the pressure, but an initial guess of zero or some very high pressure (supercritical) is unacceptable. Arbitrarily, two atmospheres was chosen as the initial guess.

Since the system temperature and liquid mole fractions are known, the activity coefficients, γ_i, of all system components are calculated next using the Margules equation in subroutine WOHL. The iterative procedure begins with the next step.

Subroutine REFSTS is called to calculate reference fugacities, f_i^{Ref}, of all components using expressions developed in the previous section. The vapor mole fraction of each component is then calculated using the relationship

$$y_i = \frac{\gamma_i x_i f_i^{Ref}}{\phi_i P} \tag{25}$$

SUMY is set equal to the sum of all y_i and system pressure is obtained from the expression

$$P = \sum_i \frac{\gamma_i x_i f_i^{Ref}}{\phi_i} \tag{26}$$

The pressure calculated by Equation 26 is compared to the previous value, which on the first iteration is 2.0 atmospheres. If the difference between these two values is greater than 0.01 atmosphere, values of vapor mole fractions, y_i, are normalized and vapor fugacity

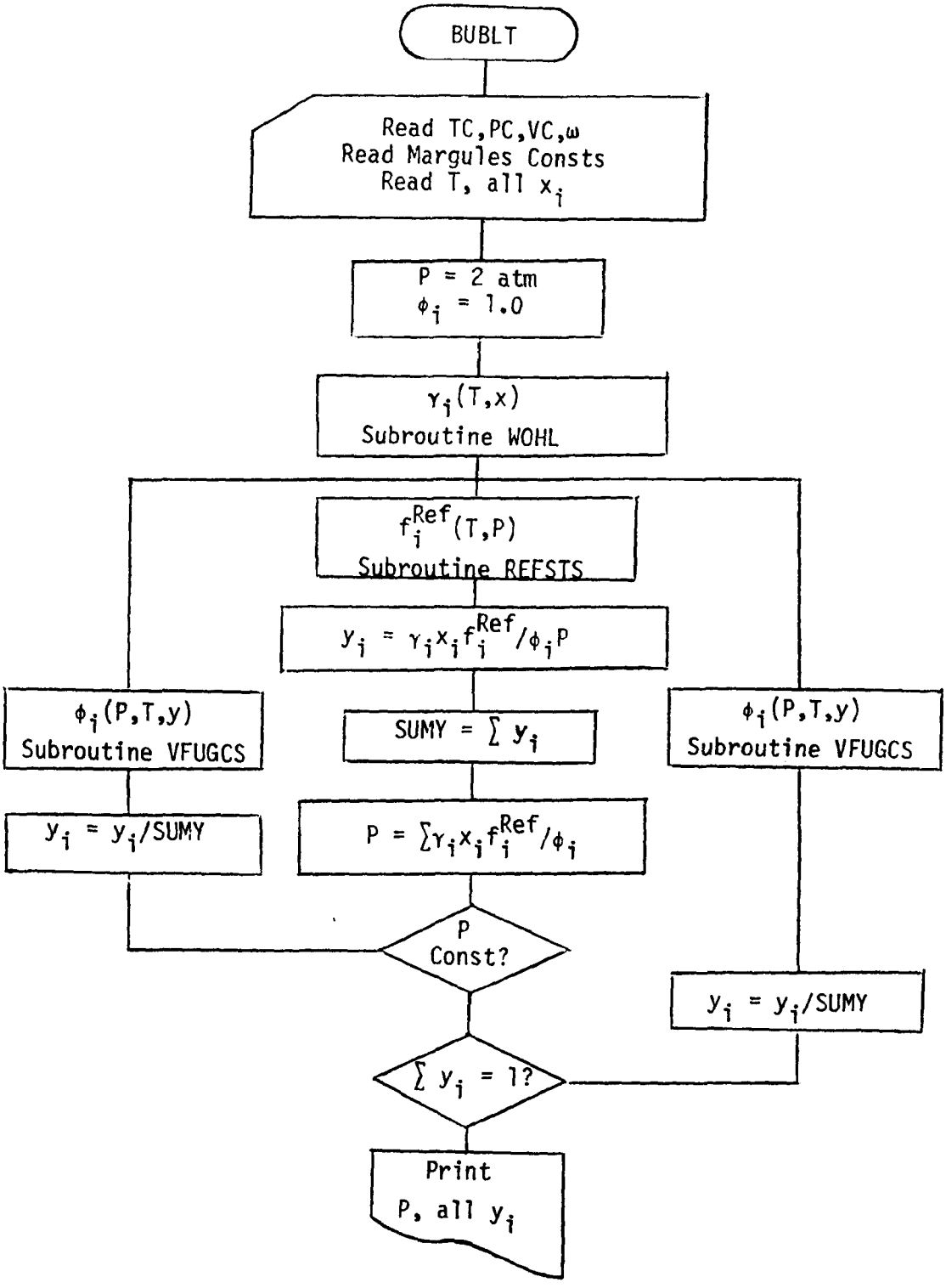

Figure 1 Flow Chart for BUBLT

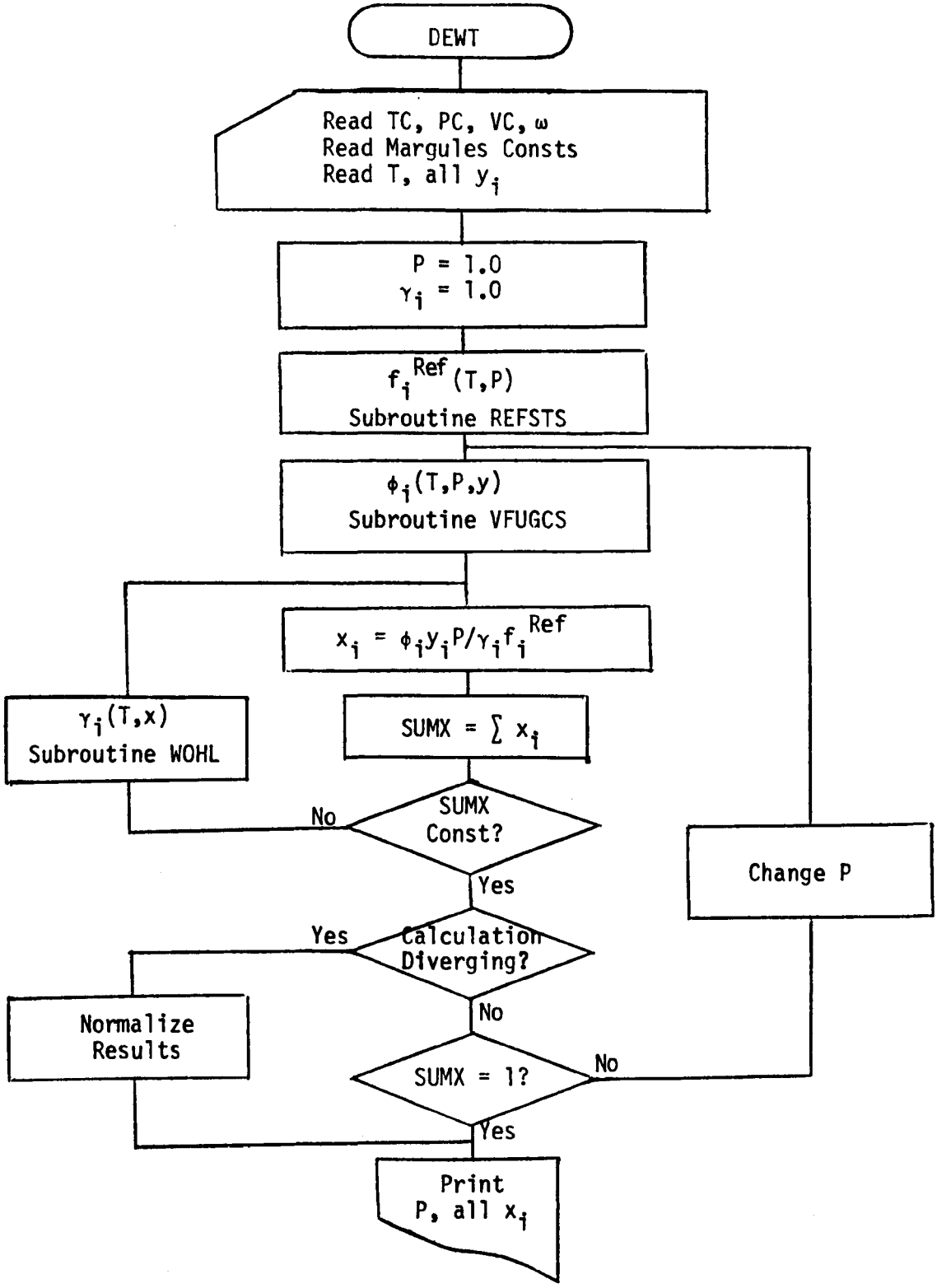

Figure 2 Flow Chart for DEWT

coefficients, ϕ_i, are calculated by calling subroutine VFUGCS. The reference state fugacity is recalculated in the next iteration using the pressure calculated from Equation 26 and the next iteration is begun.

When an unchanging value of pressure is achieved (tolerance being 0.01 atmosphere) the stoichiometric check SUMY = 1.0 is made (tolerance being 0.0001). If SUMY is not equal to unity, vapor composition is normalized, the vapor fugacity coefficients are recalculated and the program loops back to the step where the reference fugacities were calculated.

If SUMY is equal to unity convergence has been achieved and system pressure and vapor composition are printed.

Model DEWT

Figure 2 shows the information flow chart for the computer model DEWT. As mentioned earlier, this model performs the isothermal dew point calculation.

Model DEWT begins by reading in critical constants and Pitzer acentric factors for all system components. This is followed by reading in Margules constants, A_{ij}, A_{ji}, and D_{ij}, for all binaries in the system, system temperature and vapor compositions.

Calculations begin by initializing the system pressure and the activity coefficients to unity. Next the reference fugacities, f_i^{Ref}, and the vapor fugacity coefficients, ϕ_i, are calculated. The liquid mole fractions, x_i, are calculated and SUMX is set equal to the sum of all x_i.

If SUMX is not constant (tolerance 0.0001), the program loops back. Subroutine WOHL is called and the activity coefficients are recalculated and the control is transferred back to the point where x_i is calculated. When SUMX is a constant, the program moves ahead.

In the next step, a check is made to see if the calculations are diverging. This is necessary because it is possible to specify a vapor composition and a temperature for which no equilibrium solution exists and which would give rise to diverging behavior. If diverging behavior is encountered, the best results obtained so far are normalized and output; otherwise, normal calculations continue. Next, a check is made to verify is SUMX is equal to unity (tolerance being 0.0001). If not, system pressure is adjusted using a Newtonian interpolation method, working from successive values of SUMX. If SUMX is equal to unity, convergence has been achieved and the system pressure and the liquid composition are output.

EVALUATION OF MARGULES PARAMETERS

Earlier work with the thermodynamic model made it quite clear that the success of the model hinges heavily on the accuracy of the Margules constants. This has been the impetus to investigate thoroughly the process of obtaining these constants.

As mentioned earlier, the four-suffix Margules equation was used to calculate activity coefficients for binary mixtures. Three Margules constants, A_{ij}, A_{ji}, and D_{ij}, are required for each binary mixture. The four components of interest are methanol, carbon dioxide, nitrogen, and hydrogen sulfide. They can be combined to give a total

of six binary systems: methanol-carbon dioxide, methanol-nitrogen, methanol-hydrogen sulfide, carbon dioxide-nitrogen, carbon dioxide-hydrogen sulfide and nitrogen-hydrogen sulfide. Thus, a total of eighteen Margules constants had to be evaluated.

A number of parameter estimation techniques were investigated. With few exceptions, the basis of these techniques was a program called GMAR, which is a nonlinear parameter search program written by G. W. Westley of the Computing Technology Center of Union Carbide Corporation in Oak Ridge, Tennessee. This program was modified by Dr. R. M. Felder of the Chemical Engineering Department, North Carolina State University. Typically, input data to program GMAR consist of m data points for any given function $f(x_1, x_2, \ldots, x_m; b_1, b_2, \ldots, b_p) = f(\underline{x}, \underline{b})$, where $x_1, \ldots, x_m$ are the variables and $b_1, \ldots, b_p$ are the parameters. Program GMAR calculates the values of the parameters $b_1, \ldots, b_p$ which minimize the weighted sum of squares of the residual, where

$$\text{Residual} = \sum_{i=1}^{m} (WE)_i[\text{data point} - f(\underline{\tilde{x}}_i, \underline{b})]^2, \tag{27}$$

where $(WE)_i$ is a weighting factor assigned to the i^{th} data point. Also necessary to run program GMAR are the derivatives of the function $f(\underline{x},\underline{b})$ with respect to the parameter $b_1, \ldots, b_p$. These derivatives were provided to GMAR by writing a subroutine called FUNC. Listings of program GMAR and all necessary subroutines are given by Matange, (1980).

The original approach to evaluation of Margules parameters used the Margules expression for activity coefficients as the function $f(\underline{x},\underline{b})$ in the program GMAR. Experimental values of the activity coefficients were obtained using binary x-y-P-T data and the following equation:

$$\gamma_i = \frac{\phi_i y_i P}{x_i f_i^{Ref}} \tag{28}$$

The fugacity coefficient, ϕ_i, was obtained from subroutine VFUGCS and the reference fugacity, f_i^{Ref}, from subroutine REFSTS. The Margules parameters were thus obtained for all six binaries. The Margules parameters of each binary were then used in the model BUBLT to predict the pressure and the vapor composition for that binary. It was found that the predicted variables compared well with the experimental data for all the binaries.

The Margules expression for the activity coefficients was not the only available choice for the function $f(\underline{x},\underline{b})$ used in program GMAR. The expression for $\log(\gamma_i/\gamma_j^2)$ was also tried and was found to improve the accuracy of the Margules constants. Even further improvement was achieved when the Margules constants were obtained using a Fletcher Powell search procedure in the program FPOW which minimizes the residual given by

$$\text{Residual} = \sum_{i=1}^{m} [(\gamma_{1C}-\gamma_{1D})^2 + (\gamma_{2C}-\gamma_{2D})^2] \tag{29}$$

where

γ_{1C}, γ_{2C} = calculated values of γ_1 and γ_2, from Equation 18,

γ_{1D}, γ_{2D} = values of γ_1 and γ_2 obtained from experimental data

Although these efforts were rewarded by improvement in the fit to experimental data, there is a scarcity of reliable data in the x-y-P-T form. However, several sets of data were found of the form x-P-T; i.e. vapor compositions were not measured in the reported experimental programs. Data in this form were found for all six of the binary combinations.

A program for evaluating Margules parameters from x-P-T equilibrium data was developed. This program, called GMAIN, used bubble point calculation procedures in conjunction with GMAR to calculate the Margules constants. Values of Margules parameters are adjusted until the difference between the system pressure calculated by the model and the experimental pressure was minimized.

Another advantage of the above technique was the flexibility it allowed in using data at different temperatures. For the methanol-carbon dioxide, the methanol-hydrogen sulfide and the carbon dioxide-hydrogen sulfide systems, it was found that assuming the Margules parameters to be inversely proportional to the absolute temperature was quite satisfactory. For these binaries, a simple modification of program GMAR made it possible to obtain the optimum Margules parameters using data at all temperatures. This significantly improved the accuracy of the constants. For binary mixtures involving nitrogen, the inverse temperature relationship for the Margules parameters

was unacceptable. For these systems Margules parameters at each temperature of interest were obtained.

Methanol-CO_2. The optimum values of the Margules parameters for the methanol-carbon dioxide system were obtained by using data by Katayama et al. (1975) at 298.15 K and data by Yorizane et al. (1969) at 258.15 K and 243.15 K. Margules parameters were evaluated using the three data sets and assuming the parameters to be inversely proportional to temperature. Table 4 compares model predictions to experimental data for methanol-carbon dioxide mixtures. Since vapor compositions were available for the data at 298.15 K, both system pressures and vapor compositions have been compared in Table 4 for this data set. Vapor composition data were not available at 258.15 K and 243.15 K and hence only the system pressures are compared at these temperatures. Figure 3 compares the predicted pressures with the experimental pressures at 298.15 K, 258.15 K and 243.15 K. Excellent agreement was obtained between predicted and experimental values of the vapor mole fractions of carbon dioxide at 298.15 K. Good agreement was obtained between the predicted and experimental system pressures for all three temperatures.

Methanol-N_2. Data provided by Knapp and Weber[1] were used to evaluate Margules parameters for methanol-nitrogen mixtures. As indicated

[1]H. Knapp and W. Weber. Unpublished data. Dechnische Universitat, Berlin. Fachdereich 10. Berfahrenseechink. Institut für Thermodynamik and Anlagentechnik (1978).

Table 4

Comparisons of Experimental Vapor-Liquid Equilibrium Data with Model Correlations for Methanol (1)-Carbon Dioxide (2)-Mixtures

298.15 K

x_2	P_{exp} (atm)	P_{calc} (atm)	DP (atm)	$y_{2_{exp}}$	$y_{2_{calc}}$	Dy
0.015	2.16	2.17	0.01	0.9202	0.9221	0.0019
0.041	5.58	5.46	-0.12	0.9685	0.9679	-0.0006
0.070	9.39	8.90	-0.49	0.9797	0.9796	-0.0001
0.131	17.08	15.66	-1.42	0.9878	0.9875	-0.0003
0.256	29.62	28.66	-0.96	0.9917	0.9920	0.0003
0.361	40.80	39.12	-1.68	0.9928	0.9931	0.0003
0.450	46.97	46.94	-0.03	0.9930	0.9934	0.0004
0.610	53.88	54.60	0.72	0.9929	0.9931	0.0002
0.662	55.77	54.79	-0.98	0.9922	0.9931	0.0009

$DP = P_{calc} - P_{exptl}$; $DY = y_{2,calc} - y_{2,exptl}$

Average percent deviation for pressure = 3.0
Average percent deviation for y_2 = 0.06

Experimental data by Katayama et al. (1975)

258.15 K

x_2	P_{exp} (atm)	P_{calc} (atm)	DP (atm)
0.072	4.0	4.95	0.95
0.145	8.0	8.96	0.96
0.219	12.0	12.49	0.49
0.333	16.0	17.11	1.11
0.471	20.0	20.81	0.81

$DP = P_{calc} - P_{exptl}$

Average percent deviation for pressure = 10.2

Experimental data by Yorizane et al. (1969)

(continued)

Table 4
(continued)

243.15°K

x_2	P_{exp} (atm)	P_{calc} (atm)	DP (atm)
0.048	2.0	2.54	0.54
0.107	4.0	5.05	1.05
0.172	6.0	7.35	1.35
0.240	8.0	9.41	1.41
0.327	10.0	11.60	1.60
0.426	12.0	13.35	1.35
0.550	13.0	14.21	1.21
0.789	13.7	12.86	-0.84

$DP = P_{calc} - P_{exptl}$

Average percent deviation for pressure = 17.0

Experimental data by Yorizane et al. (1969)

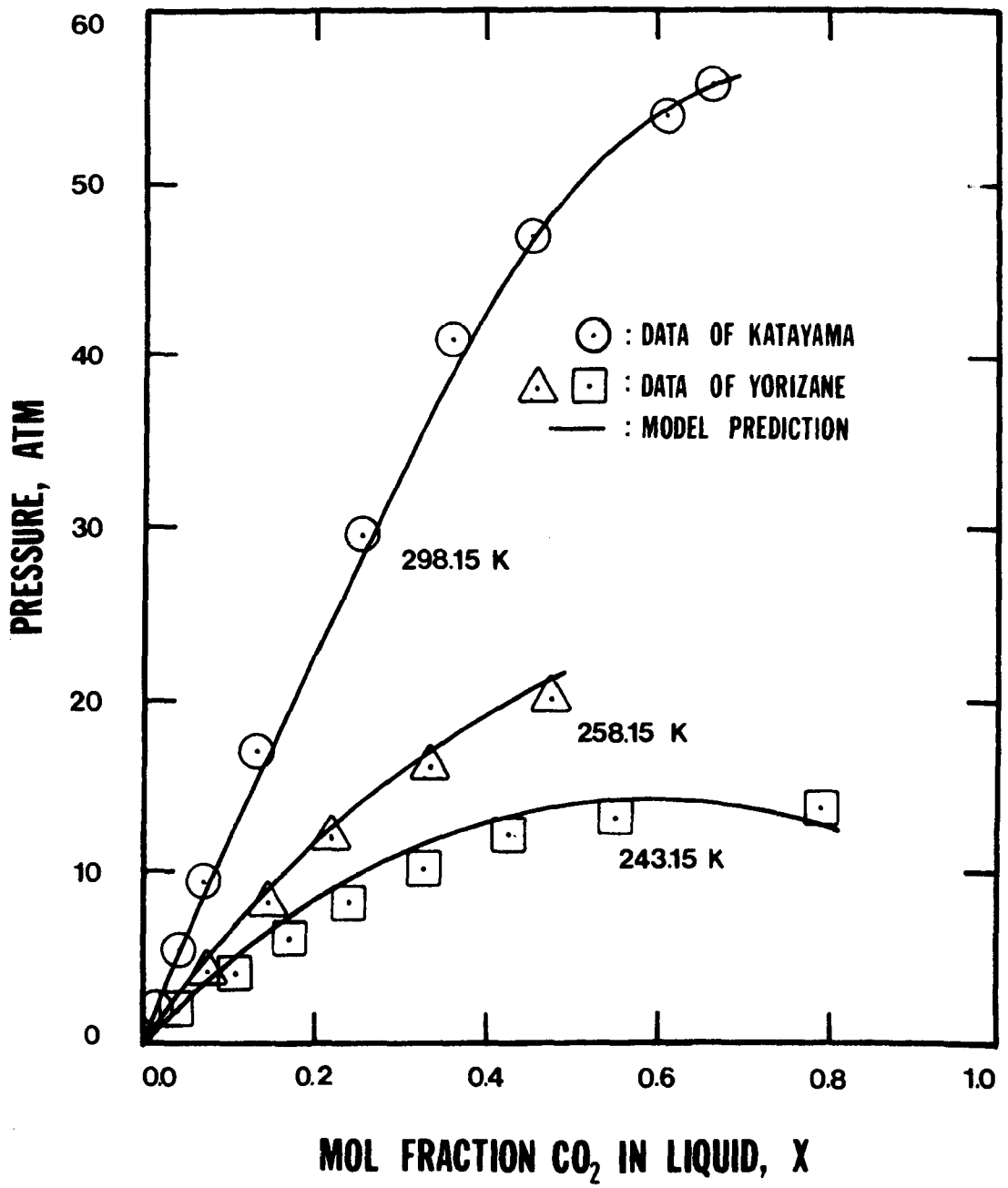

Figure 3. Comparison of Equilibrium Experimental Predicted Pressures for Methanol - Carbon Dioxide Mixtures.

earlier the inverse temperature relationship for the Margules parameters does not work and values were obtained at each temperature. Since the multicomponent model was to be tested at 273.15 K and 258.15 K equilibrium pressure and liquid compositions for methanol-nitrogen mixtures at 273.15 K and 258.15 K were obtained by linear interpolation of experimental pressure with respect to temperature at a number of values of the liquid mole fraction. Data at each temperature (273.15 K and 258.15 K were used separately in GMAR to obtain optimum values of the Margules parameters at specific temperatures. Table 5 and Figure 4 compare the system pressure predicted by the model and the experimental pressure for the methanol-nitrogen system. Excellent agreement between the predicted and experiment pressure was obtained.

Methanol-H_2S. Optimal Margules parameters for the methanol-hydrogen sulfide system were obtained using data by Yorizane et al. (1969) at 273.15 K, 258.15 K and 248.15 K. The Margules parameters for this system were found to be inversely proportional to temperature so that the optimal parameters were based on data at all three temperatures. As shown in Table 6 and Figure 5, good agreement was found between the system pressure predicted by the model and the experimental pressure.

CO_2-N_2. The carbon dioxide-nitrogen system followed the pattern set by the methanol-nitrogen system: Margules parameters were not inversely proportional to temperature. Data of Zenner and Dana (1969) and Kaminishi et al. (1966) were interpolated to obtain x-P values at

Table 5 Comparisons of Interpolated Experimental Vapor-Liquid Equilibrium Data with Model Correlations for Methanol (1) - Nitrogen (2) Mixtures

273.15 K

x_2	P_{exptl} (atm)	P_{calc} (atm)	DP (atm)
0.0000	0.00	0.04	0.04
0.0025	10.00	9.91	-0.09
0.0050	20.00	20.25	0.25
0.0058	24.20	23.66	-0.54
0.0118	50.30	50.90	0.60
0.0165	74.00	74.47	0.47

$DP = P_{calc} - P_{exptl}$

Average percent deviation for pressure = 1.2

Experimental data obtained by interpolation of data by Knapp and Weber[a]

258.15 K

x_2	P_{exptl} (atm)	P_{calc} (atm)	DP (atm)
0.0000	0.00	0.01	0.01
0.0025	10.00	10.09	0.09
0.0050	20.00	20.49	0.49
0.0075	31.30	31.25	-0.05
0.0100	42.50	42.38	-0.12
0.0125	53.00	53.93	0.93
0.0150	66.20	65.92	-0.28
0.0175	78.00	78.39	0.39

$DP = P_{calc} - P_{exptl}$

Average percent deviation for pressure = 0.9

Experimental data obtained by interpolation of data by Knapp and Weber[a]

[a]Knapp and Weber. Unpublished data. Dechnische Universitat, Berlin. Fachdereich 10. Berfahrenseechink. Institut für Thermodynamik and Anlagentechnik (1978).

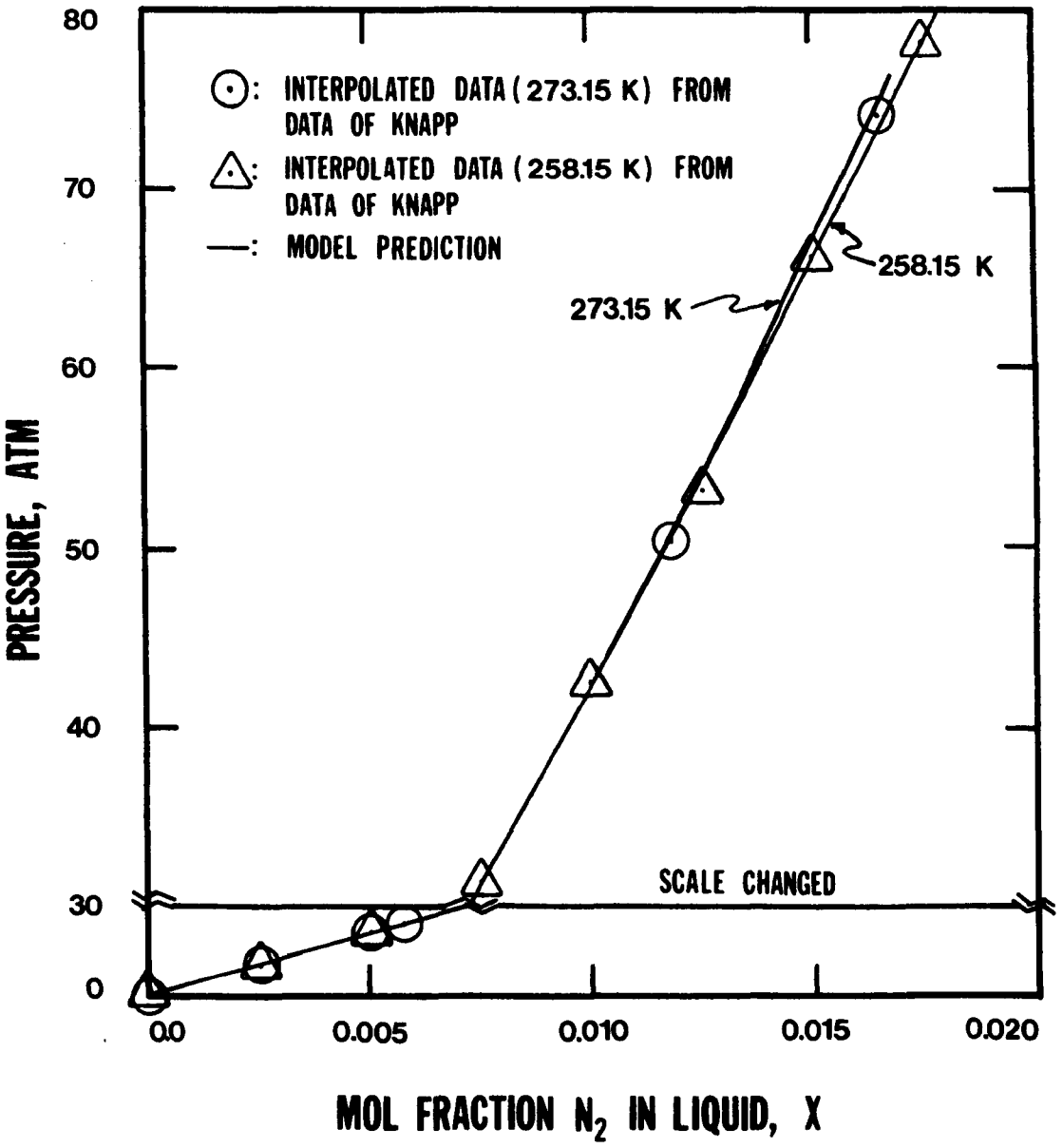

Figure 4. Comparison of Equilibrium Experimental and Predicted Pressures for Methanol-Nitrogen Mixtures.

Table 6 Comparisons of Experimental Vapor-Liquid Equilibrium Data with Model Correlations for Methanol (1) - Hydrogen Sulfide (2) Mixtures.

273.15 K

x_2	P_{exptl} (atm)	P_{calc} (atm)	DP (atm)
0.092	2.0	2.16	0.16
0.199	4.0	3.83	-0.17
0.329	6.0	5.72	-0.28
0.453	7.5	7.45	-0.05
0.484	8.0	7.83	-0.17
0.608	9.1	8.98	-0.12
0.743	9.8	9.44	-0.36
0.840	10.0	9.48	-0.52

$DP = P_{calc} - P_{exptl}$

Average percent deviation for pressure = 3.7

Experimental data by Yorizane et al. (1969)

258.15 K

x_2	P_{exptl} (atm)	P_{calc} (atm)	DP (atm)
0.165	2.0	2.26	0.26
0.231	3.0	2.90	-0.10
0.298	3.4	3.54	0.14
0.367	4.2	4.19	-0.01
0.403	4.4	4.52	0.12
0.490	5.0	5.23	0.23
0.585	5.4	5.79	0.39
0.662	5.8	6.04	0.23

$DP = P_{calc} - P_{exptl}$

Average percent deviation for pressure = 4.9

Experimental data by Yorizane et al. (1969)

(continued)

Table 6 (continued)

248.15 K			
x_2	P_{exptl} (atm)	P_{calc} (atm)	DP (atm)
0.203	2.0	1.96	-0.04
0.290	2.5	2.57	0.07
0.327	3.0	2.82	-0.18
0.465	3.4	3.71	0.31
0.582	4.0	4.22	0.22
0.733	4.3	4.43	0.13

$DP = P_{calc} - P_{exptl}$

Average percent deviation for pressure = 4.7

Experimental data by Yorizane et al. (1969)

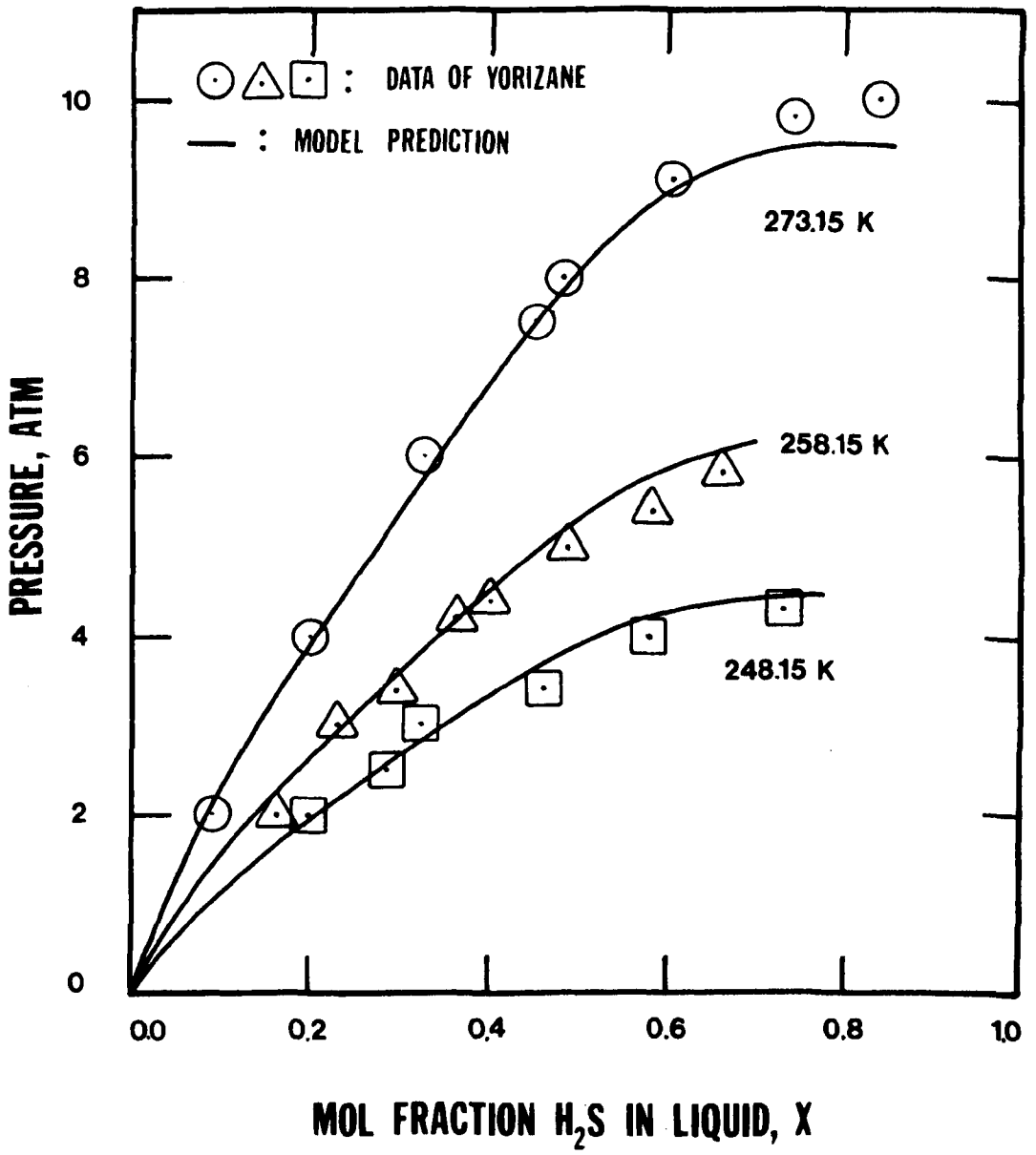

Figure 5. Comparison of Equilibrium Experimental and Predicted Pressures for the Methanol-Hydrogen Sulfide Mixtures.

273.15 K and 258.15 K. Optimal values of the Margules parameter were obtained for the two temperatures using the interpolated data in GMAR. Model predictions based on optimal Margules parameters are compared to experimental values in Table 7 and Figure 6. The comparison between predicted pressure and experimental pressure is excellent.

CO_2 - H_2S. Sobocinski and Kurata (1969) have reported data for carbon dioxide-hydrogen sulfide mixtures at 288.71 K, 266.48 K and 244.26 K. Since the inverse temperature relationship was found to be acceptable for this system, optimal values of Margules constants were obtained using data at all three temperatures. Table 8 compares system pressure and vapor composition with the corresponding experimental data for carbon dioxide-hydrogen sulfide mixtures. Comparisons between predicted pressure and experimental pressure for this system is shown graphically in Figure 7.

N_2-H_2S. Data of Robinson and Besserer (1972) were interpolated as described earlier to obtain equilibrium x-P values at 273.15 K and 258.15 K. Interpolated data were used to evaluate optimal Margules parameters at 273.15 K and 258.15 K using GMAR. Comparisons between experimental and model-predicted equilibrium pressures are shown in Table 9 and Figure 8; Agreement is excellent.

Table 7 Comparisons of Interpolated Experimental Vapor-Liquid Equilibrium Data with Model Correlations for Carbon Dioxide (1) - Nitrogen (2) Mixtures

273.15 K

x_2	P_{exptl} (atm)	P_{calc} (atm)	DP (atm)
0.000	34.20	31.19	-3.01
0.025	47.20	46.79	-0.41
0.050	60.00	59.20	-0.80
0.075	71.40	70.07	-1.33
0.100	82.40	80.53	-1.87

$DP = P_{calc} - P_{exptl}$

Average percent deviation for pressure = 3.0

Experimental data obtained by interpolation of data by Zenner and Dana (1963) and Kaminishi et al. (1966).

258.15 K

x_2	P_{exptl} (atm)	P_{calc} (atm)	DP (atm)
0.000	21.50	20.69	-0.81
0.025	35.80	35.33	-0.47
0.050	49.00	48.72	-0.28
0.075	62.00	61.25	-0.75
0.100	74.60	73.26	-1.34

$DP = P_{calc} - P_{exptl}$

Average percent deviation for pressure = 1.7

Experimental data obtained by interpolation of data by Zenner and Dana (1963) and Kaminishi et al. (1966).

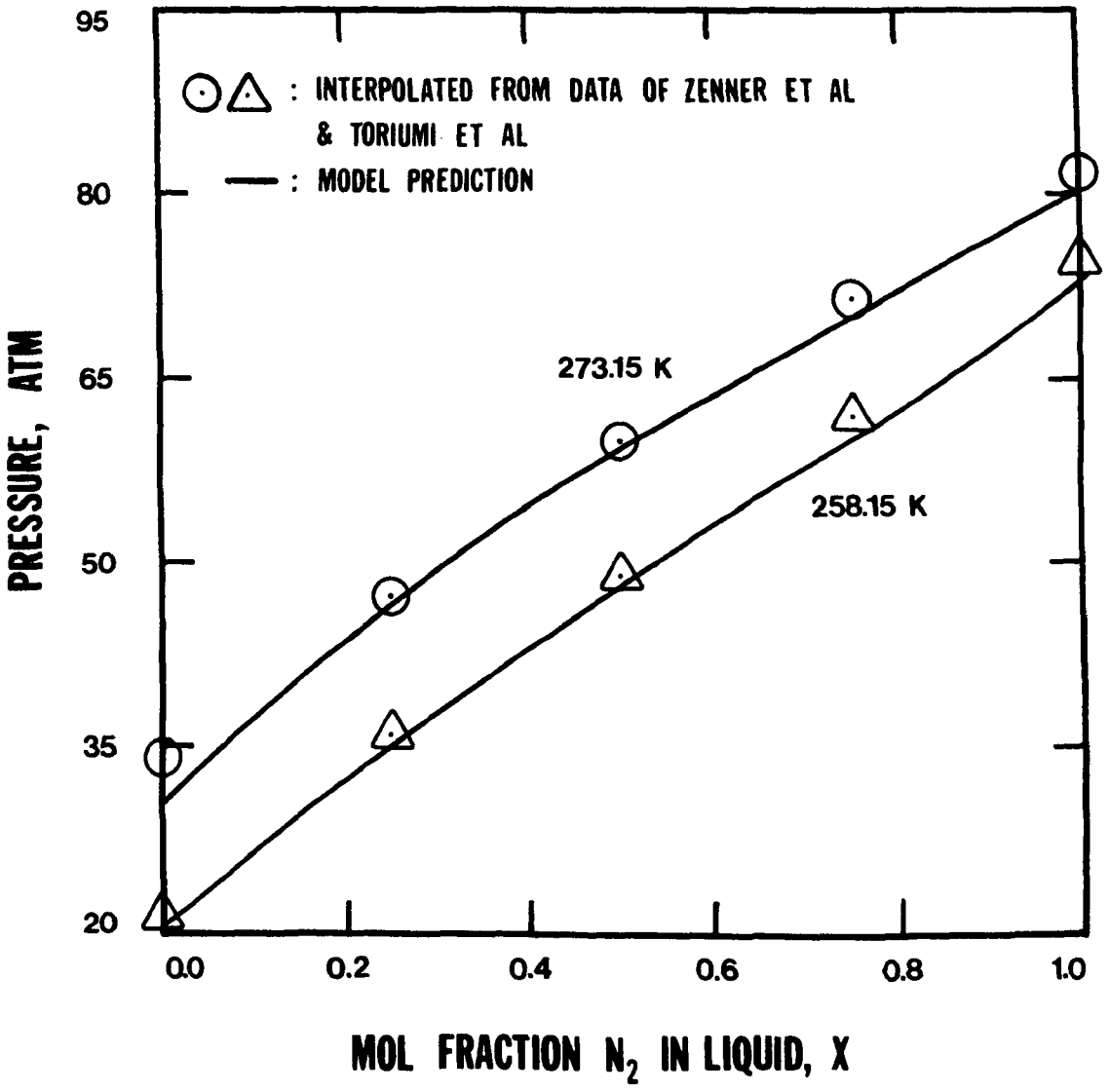

Figure 6. Comparison of Equilibrium Experimental and Predicted Pressures for the Carbon Dioxide-Nitrogen Mixtures.

Table 8 Comparisons of Experimental Vapor-Liquid Equilibrium Data with Model Correlations for Carbon Dioxide (1) - Hydrogen Sulfide (2) Mixtures

288.71°K

x_2	P_{exptl} (atm)	P_{calc} (atm)	DP (atm)	$y_{2,exptl}$	$y_{2,calc}$	Dy
0.948	20.41	19.99	-0.42	0.770	0.748	-0.022
0.815	27.22	27.46	0.24	0.540	0.531	-0.009
0.640	34.02	34.00	-0.02	0.395	0.395	0.000
0.419	40.83	41.69	0.86	0.272	0.261	-0.011

$DP = P_{calc} - P_{exptl}$

$Dy = y_{2,calc} - y_{2,exptl}$

Average percent deviation for pressure = 1.3
Average percent deviation for y_2 = 2.1

Experimental data of Sobocinski and Kurata (1969)

266.48°K

0.887	13.61	14.19	0.58	0.590	0.573	-0.017
0.630	20.41	19.97	-0.44	0.340	0.356	0.016
0.164	27.22	26.47	-0.75	0.095	0.128	0.033

$DP = P_{calc} - P_{exptl}$

$Dy = y_{2,calc} - y_{2,exptl}$

Average percent deviation for pressure = 3.1
Average percent deviation for y_2 = 14.1

Experimental data of Sobocinski and Kurata (1969)

(continued)

Table 8 (continued)

244.26°K						
x_2	P_{exptl} (atm)	P_{calc} (atm)	DP (atm)	$y_{2,exptl}$	$y_{2,calc}$	Dy
0.915	6.80	6.95	0.15	0.572	0.563	-0.009
0.235	13.61	13.52	-0.09	0.120	0.144	0.024

$DP = P_{calc} - P_{exptl}$

$Dy = y_{2,calc} - y_{2,exptl}$

Average percent deviation for pressure = 1.4
Average percent deviation for y_2 = 10.8

Experimental data of Sobocinski and Kurata (1969)

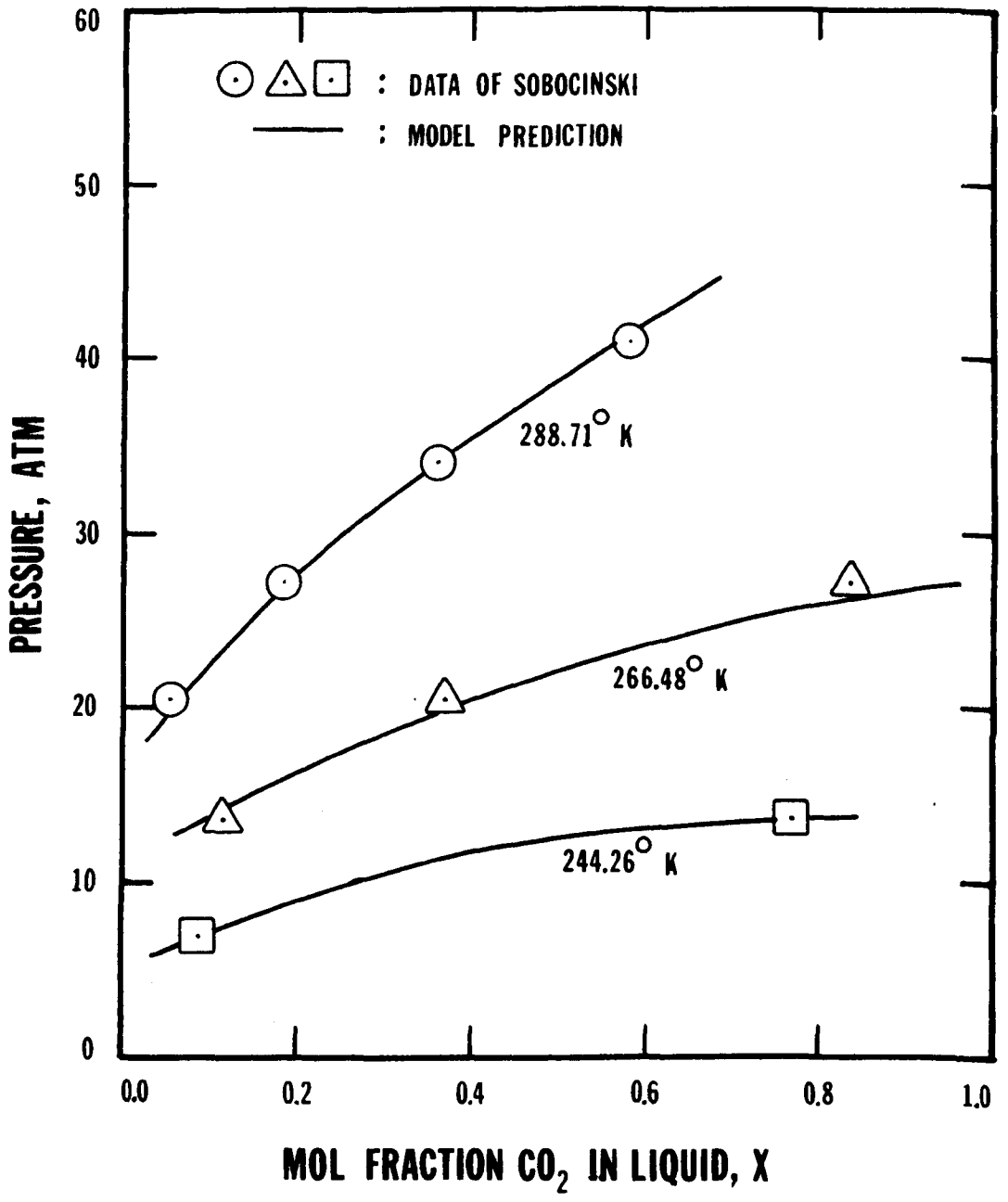

Figure 7. Comparison of Equilibrium Experimental and Predicted Pressures for Carbon Dioxide-Hydrogen Sulfide Mixtures.

Table 9 Comparisons of Interpolated Experimental Vapor-Liquid Equilibrium Data with Model Correlations for Nitrogen (1) - Hydrogen Sulfide (2) Mixtures

273.15°K

x_1	P_{exptl} (atm)	P_{calc} (atm)	DP (atm)
0.000	10.7	10.05	-0.65
0.002	14.0	14.11	0.11
0.004	18.5	18.54	0.04
0.006	23.0	23.30	0.30
0.008	28.0	28.36	0.36
0.010	33.5	33.68	0.18
0.012	39.0	39.21	0.21
0.014	44.4	44.89	0.49
0.016	50.0	50.67	0.67
0.018	55.7	56.47	0.77
0.020	61.4	62.22	0.82
0.022	66.8	67.87	1.07
0.024	72.3	73.32	1.02

$DP = P_{calc} - P_{exptl}$

Average percent deviation for pressure = 1.5

Experimental data interpolated from data of Robinson and Besserer (1972)

258.15°K

0.000	6.2	6.47	0.27
0.004	16.4	16.85	0.45
0.008	29.4	29.54	0.14
0.012	43.8	43.93	0.13
0.016	58.3	59.10	0.80
0.020	72.8	73.85	1.05
0.024	85.7	86.88	1.18

$DP = P_{calc} - P_{exptl}$

Average percent deviation for pressure = 1.7

Experimental data interpolated from data of Robinson and Besserer (1972)

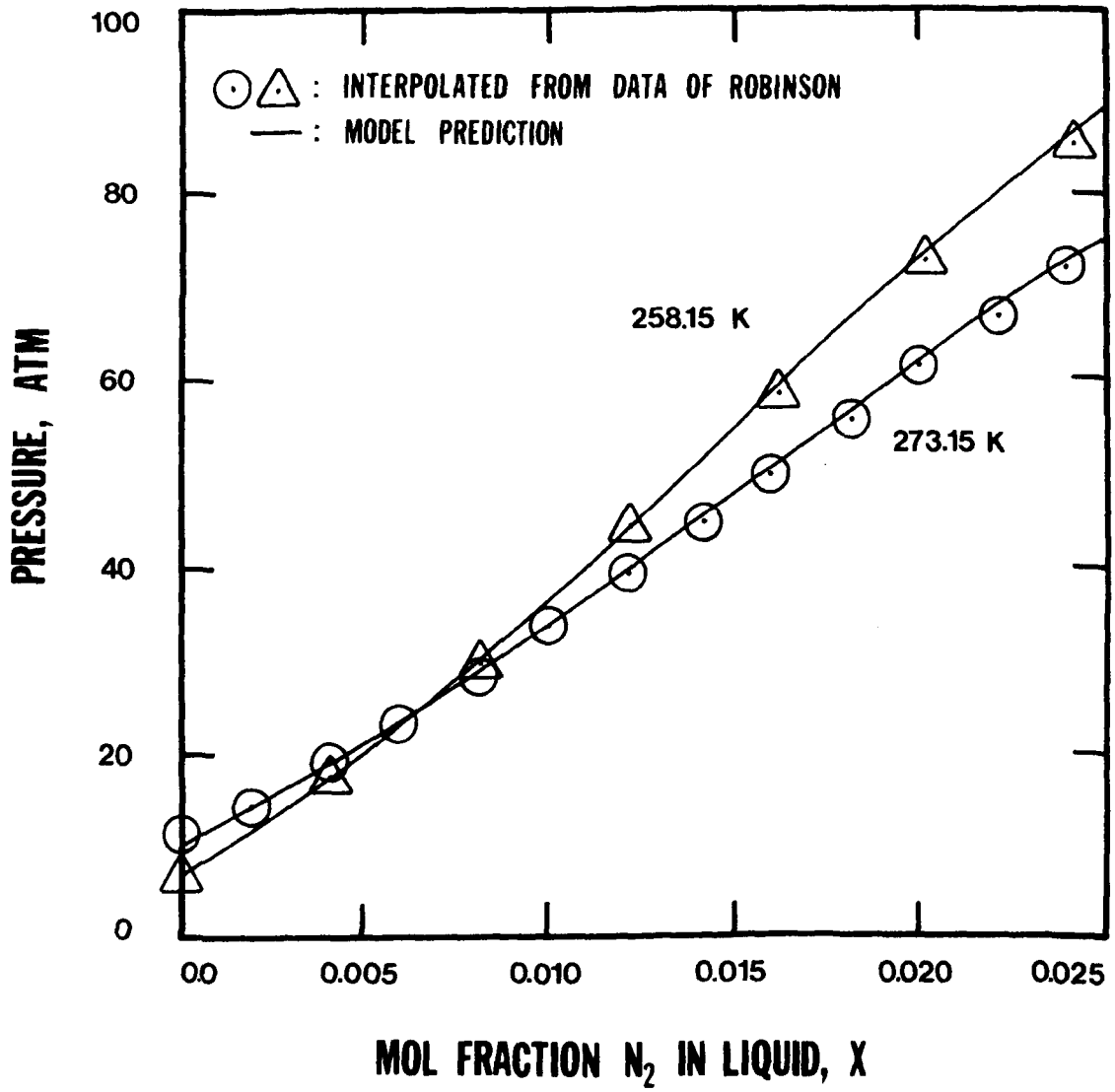

Figure 8. Comparison of Equilibrium Experimental and Predicted Pressures for Nitrogen-Hydrogen Sulfide Mixtures.

Summary

Margules parameters for six binary mixtures have been determined from vapor-liquid equilibrium data found in the literature. Constituents of these mixtures are taken from the group methanol, hydrogen sulfide, carbon dioxide and nitrogen. Parameters for the three nitrogen-free binary mixtures were found to be inversely proportioned to temperature, while parameters for the three nitrogen containing mixtures did not follow such a relationship. Since the model is to be tested against multicomponent equilibrium data taken at 273.15 K and 258.15 K. Margules parameters for each of the six binary mixtures were evaluated at these temperatures and are given in Table 10. The fits of binary equilibrium data to that predicted using these parameters are excellent.

Table 10 Margules parameters from Parameter Optimization Procedure GMAR

Binary	A_{12}	A_{21}	D_{12}
	273.15°K		
Methanol (1) - CO_2(2)	1.3395	0.6427	0.6940
Methanol (1) - N_2(2)	5.2000	1.1446	2.2000
Methanol (1) - H_2S(2)	1.0758	0.5374	0.9891
CO_2(1) - N_2(2)	2.1228	0.3023	3.1223
CO_2(1) - H_2S(2)	0.5705	0.5777	0.5793
N_2(1) - H_2S(2)	0.8115	-66.5928	-72.8469
	258.15°K		
Methanol (1) - CO_2(2)	1.4174	0.6800	0.7342
Methanol (1) - N_2(2)	11.0000	1.1657	8.7000
Methanol (1) - H_2S(2)	1.1383	0.5686	1.0466
CO_2(1) - N_2(2)	0.6328	0.2849	0.7872
CO_2(1) - H_2S(2)	0.6037	0.6113	0.6130
N_2(1) - H_2S(2)	0.8990	-114.3787	-123.1370

EXPERIMENTAL EQUIPMENT AND PROCEDURE

The experimental apparatus used to obtain multicomponent vapor liquid equilibrium data was a modification of the system used by Bass (1978). A schematic diagram of the apparatus is shown in Figure 9. The stainless steel cell had a volume of 1084 ml and was equipped with internal baffles. Valves used in the recycle line as well as those used for sampling and gas charging were teflon packed and rated for use at high pressure. Liquid in the cell was recirculated using a microflo pulsafeeder metering pump, model L20-S-3, manufactured by the Interpace Corporation. The diaphragm used in this pump eliminated any possibility of contamination. Pressure in the equilibrium cell was measured using a 16-inch Heise gauge graduated in 0.5 psi increments up to 1250 psia. The gauge had a guaranteed accuracy of 0.1 percent of the full scale. An Ashcroft type 1327 portable dead weight tester was used to confirm calibration of the gauge. Temperatures were measured using a copper-constantan thermocouple and a digital temperature indicator calibrated against known temperatures. The entire high pressure apparatus was housed in a Harris industrial freezer which provided the refrigeration. A Thermistemp temperature controller, a fan and a heater controlled the temperature in the cell within 0.1°C.

REAGENTS

Methanol was Fisher Spectranalyzed® with a stated purity of 99.95 percent. Carbon dioxide and nitrogen used in the research had

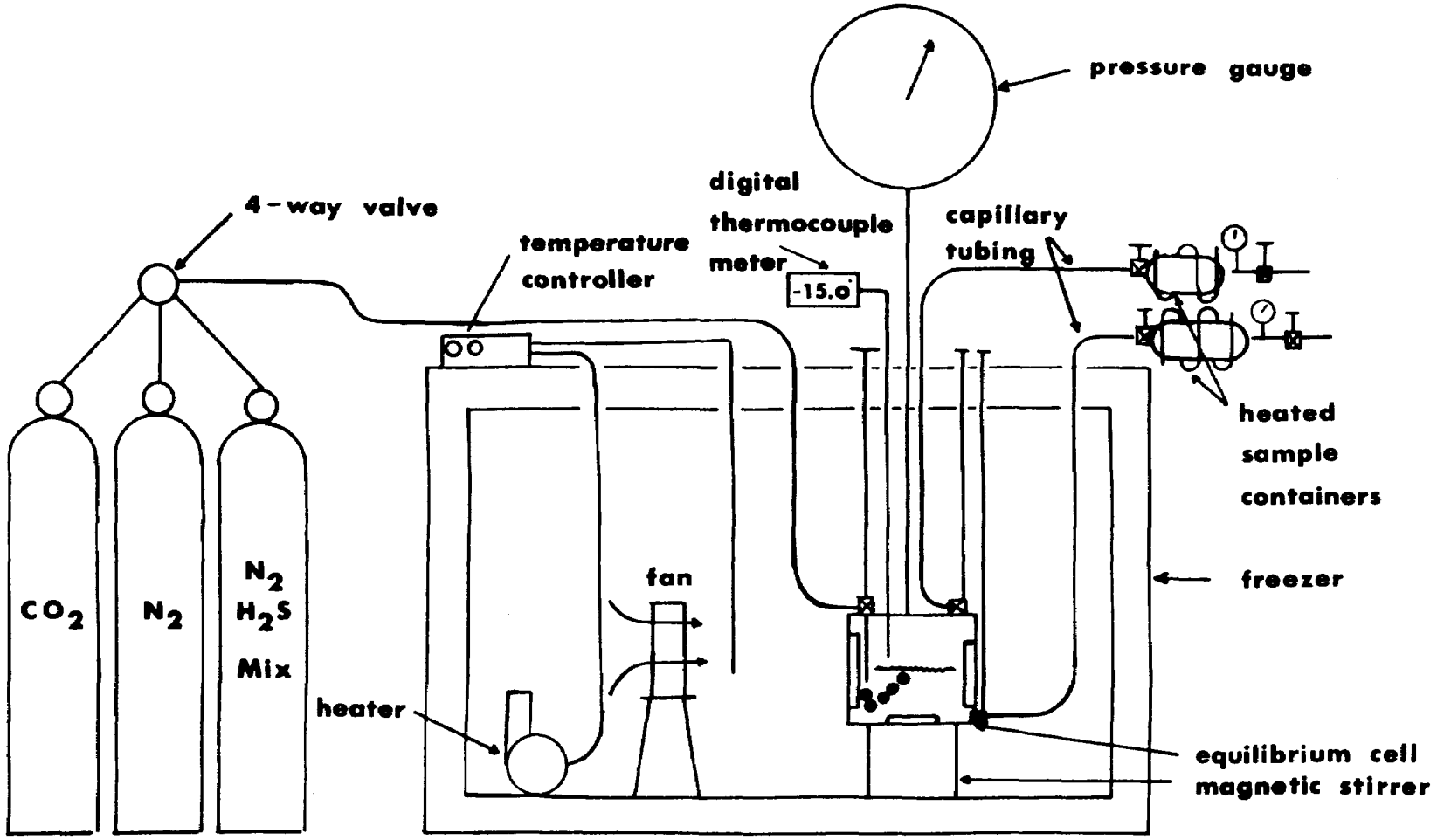

Figure 9. Experimental Apparatus.

a stated purity of 99.99 percent and 99.999 percent, respectively. These gases were supplied by Airco Inc. A mixture of 15.1 percent hydrogen sulfide in nitrogen, supplied by Air Products, was used.

ANALYSIS

Analyses of liquid and vapor samples taken during a run were done on a Tracor model 550 gas chromatograph equipped with a thermal conductivity detector, a temperature programmer and a heated gas sampling valve. Component separation was achieved in a stainless steel column, 3 meters in length and 3.2 mm in diameter, packed with Porapak QS. The signal from the gas chromatograph was analyzed using Southern Analytical's Supergrator-3 digital integrator and a Leeds and Northrup strip chart recorder.

CALIBRATIONS

Calibration of the gas chromatograph-supergrator combination was done by injecting known amounts of components into the gas chromatograph and noting the corresponding areas integrated by the supergrator. For each amount of every component the corresponding area was obtained for at least five replicate injections. The mean and the standard deviation were calculated for the replicate areas. The mean area was the response of the gas chromatograph-supergrator for the amount of the particular component under consideration and became part of the calibration data for that component. The percent standard deviations of the replicate areas provided a measure of the precision of the replicate areas obtained. The percent standard devia-

tion of the replicate areas was calculated at each calibration point for all four components. The average of these values is reported as the average percent standard deviation for area for each component in the following paragraphs. Calibration data in the form of g-moles of a component and the corresponding area integrated by the gas chromatograph-supergrator combination were fit with linear equations for all four components. Determination of unknown compositions were performed using these linear equations for the four components.

For methanol calibration, different concentrations of methanol in distilled, deionized water were prepared. Varying amounts of samples at each concentration were injected into the gas chromatograph. Sample injections were done using a Hamilton microliter syringe. All injections involved a sample volume greater than 2 microliters. The smallest graduation on the syringe was 0.1 microliter. It was observed that for methanol the average percent standard deviation for the area was less than 0.6. For the calibration of carbon dioxide, nitrogen and hydrogen sulfide, gaseous injections at various pressures were made using the gas sampling valve. The pressure gauge used for this purpose had a least count of 0.034 atm. The average percent standard deviations for the area for carbon dioxide, nitrogen and hydrogen sulfide were 0.49, 0.53 and 1.79, respectively.

TEST DATA: METHANOL - CO_2 MIXTURES

For the purpose of verifying the proposed experimental procedure, vapor-liquid equilibrium data were taken for methanol-carbon dioxide mixtures at 298.15 K. On the basis of excellent comparison of these

data with those of Katayama et al. (1975), the experimental apparatus and procedure were judged sound. The comparison is shown in Figure 10 and Table 11. The average deviation of CO_2 mole fraction of carbon dioxide between the two sets of data was 5.4%.

MULTICOMPONENT PROCEDURE

The first step in taking multicomponent vapor-liquid equilibrium data was to fill the equilibrium cell with about 390 ml of methanol. The refrigeration system was turned on to achieve the desired temperature in the cell, and the three gases were added to generate the desired overall composition and pressure. Liquid in the cell was recirculated for six hours and then allowed to sit unagitated for at least twelve hours prior to sampling. Samples were allowed to expand through the capillary tubing into the evacuated sample containers. Sampling was done quickly and the cell pressure was seldom disturbed by more than 0.48 atm. The vapor sample container was pressurized to approximately 1.36 atm with helium and then both containers were monitored to insure that the methanol in the samples did not approach the point of condensation. The contents of each container were analyzed a minimum of five times using the gas chromatograph.

MULTICOMPONENT MEASUREMENTS AND PREDICTIONS

Multicomponent vapor-liquid equilibrium data were taken for methanol-carbon dioxide-nitrogen-hydrogen sulfide mixtures at 258.15 K and 273.15 K. Data are given in Tables 12 and 13. Four data points were taken at 258.15 K and four more were obtained at 273.15 K. At

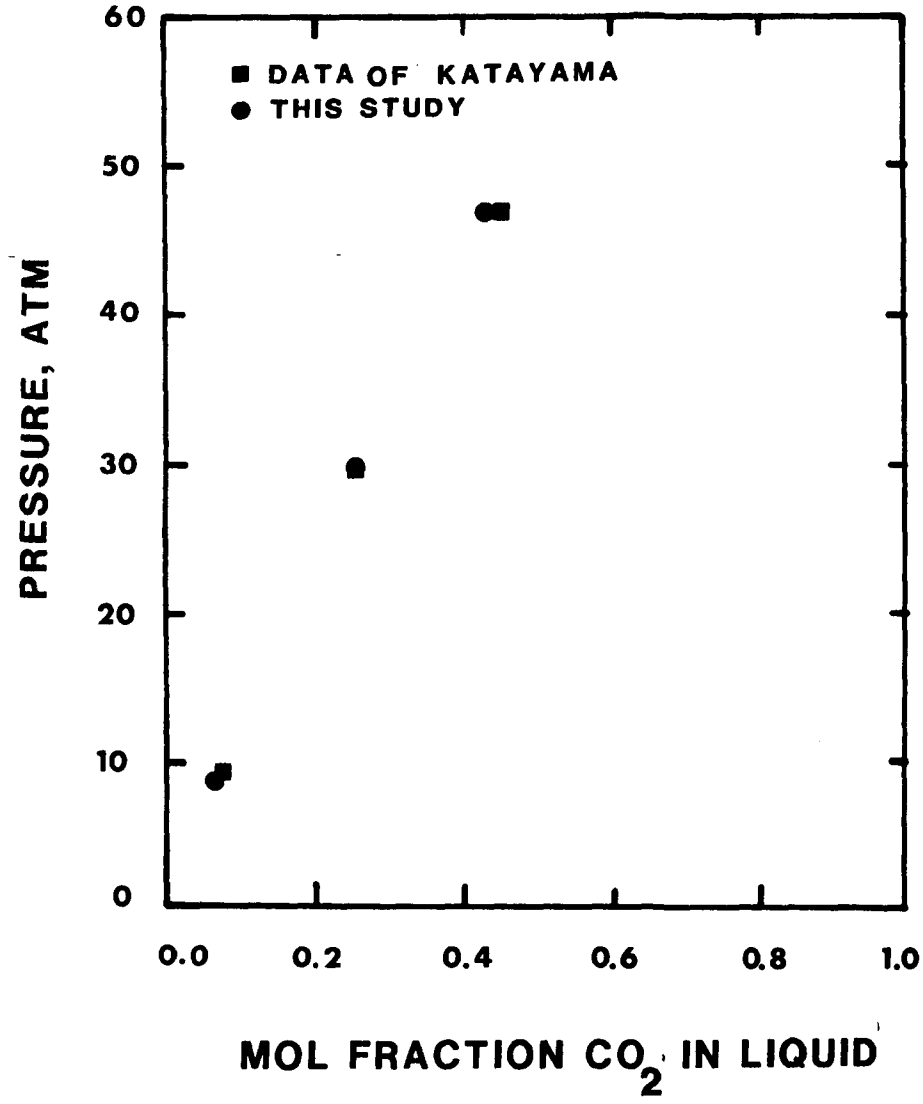

Figure 10. Comparison of Experimentally Determined Equilibrium Pressures with Those of Katayama et al. (1975) for Methanol-CO_2 Mixtures at 298.15 K.

Table 11 Comparison of Experimental Vapor-Liquid Equilibrium Data with Those of Katayama et al. (1975) for Methanol-CO_2 mixtures at 298.15 K.

P (atm)	x_2[a]	x_2[b]
9.39	0.070	0.065
29.62	0.256	0.250
46.97	0.450	0.420

Note: Average percent deviation for x_2 = 5.4.

[a]Data of Katayama et al. (1975).

[b]Data from this investigation.

each data point, vapor and liquid compositions were determined by gas chromatographic analysis; five repetitions were conducted on each of the vapor and liquid samples. The gas chromatographic analysis provided the absolute amounts for the four components in the system. Since it was the composition that was being sought, replicates of every analysis were normalized so that each replicate indicated the same amount of carbon dioxide. Carbon dioxide was chosen for this role because, over the entire data set, it was the component that was most significant in both the liquid and the vapor phases. After normalization, percent deviations for all the other components were calculated. For liquid sample analysis over the entire data set, the average percent standard deviation for methanol, nitrogen and hydrogen sul-

Table 12 Experimental Vapor-Liquid Equilibrium Data for Methanol-Carbon Dioxide-Nitrogen-Hydrogen Sulfide Mixtures at 258.15 K

P,atm	x_{CH_3OH}	x_{CO_2}	x_{N_2}	x_{H_2S}	y_{CH_3OH}	y_{CO_2}	y_{N_2}	y_{H_2S}
9.34	0.9081	0.0736	0.0029	0.0153	N.D.[a]	0.5400	0.4000	0.052
20.75	0.7680	0.2100	0.0031	0.0189	N.D.[a]	0.6111	0.3654	0.0235
29.64	0.6462	0.3312	0.0052	0.0209	N.D.[a]	0.5892	0.4004	0.0104
40.10	0.7419	0.2346	0.0078	0.0157	N.D.[a]	0.4580	0.5420	N.D.[a]

[a]N.D. = not detected.

Table 13 Experimental Vapor Liquid Equilibrium Data for Methanol-Carbon Dioxide-Nitrogen-Hydrogen Sulfide Mixtures at 273.15 K

P,atm	x_{CH_3OH}	x_{CO_2}	x_{N_2}	x_{H_2S}	y_{CH_3OH}	y_{CO_2}	y_{N_2}	y_{H_2S}
9.2	0.8997	0.0850	0.0019	0.0134	N.D.[a]	0.6853	0.2839	0.0308
21.2	0.7433	0.2339	0.0018	0.0211	N.D.[a]	0.8007	0.1648	0.0345
29.0	0.6961	0.2832	0.0033	0.0175	N.D.[a]	0.7720	0.2026	0.0218
39.8	0.6872	0.2849	0.0074	0.0204	N.D.[a]	0.5847	0.3760	0.0393

[a]N.D. = not detected

fide was 0.8, 5.1 and 3.0, respectively. In the vapor samples, the amount of methanol present was too small to be detected. In the vapor sample analysis, the average percent standard deviation for nitrogen and hydrogen sulfide was 0.7 and 5.1, respectively.

The experimental temperature and liquid phase composition were used in program BUBLT to predict equilibrium system pressure and vapor composition. Comparisons of predicted and experimental results at 258.15 K and 273.15 K are given in Tables 14 and 15, respectively. Over the entire data set, the average deviation of pressure was 7.9% and the average deviations for mole fractions in the vapor were 7.1% for carbon dioxide, 11.7% for nitrogen and 24.8% for hydrogen sulfide. All percent deviations used experimental values as a basis. The high percent deviation obtained for hydrogen sulfide was partly due to the relative insensitivity of the thermal conductivity detector in the gas chromatograph to hydrogen sulfide, especially at low concentration.

Figures 11 and 12 compare the system pressure predicted by the model and the experimental pressure at 258.15 K and 273.15 K, respectively. Figures 13 and 14 compare the predicted vapor composition and the experimental vapor composition at 258.15 K and 273.15 K, respectively. These figures show excellent agreement between model predictions and experimental data.

Clearly, the model satisfies many of the objectives of this research project. Namely, it is now possible to predict equilibrium behavior for mixtures of CO_2-H_2S-N_2 and methanol over a limited temperature range. Additional research is needed to expand the range of the model, to adapt it to general bubble

Table 14 Comparison of Model Predictions with Experimental Pressure and Vapor Compositions for Methanol Carbon Dioxide-Nitrogen-Hydrogen Sulfide Mixtures at 258.15 K

P(atm)			y_{CH_3OH}			y_{CO_2}			y_{N_2}			y_{H_2S}		
exptl	model	DP[a]	exptl	model	Dy[b]	exptl	model	Dy[b]	exptl	model	Dy[b]	exptl	model	Dy[b]
9.34	9.10	-0.24	N.D.[c]	0.0017	-	0.5400	0.5885	0.0485	0.4000	0.3822	-0.0178	0.0520	0.0276	-0.0244
20.75	19.31	-1.44	N.D.[c]	0.0009	-	0.6111	0.6794	0.0683	0.3654	0.3018	-0.0636	0.0235	0.0180	-0.0055
29.64	31.53	1.89	N.D.[c]	0.0007	-	0.5892	0.6306	0.0414	0.4004	0.3577	-0.0427	0.0104	0.0110	0.0006
40.10	41.62	1.52	N.D.[c]	0.0006	-	0.4580	0.4223	-0.0357	0.5420	0.5720	0.0300	N.D.[c]	0.0051	-

[a] $DP = P_{model} - P_{exptl}$

[b] $Dy = y_{model} - y_{exptl}$

[c] N.D. = not detected

Table 15 Comparison of Model Predictions with Experimental Pressure and Vapor Compositions for Methanol-Carbon Dioxide-Nitrogen-Hydrogen Sulfide Mixtures at 273.15 K

P(atm)			y_{CH_3OH}			y_{CO_2}			y_{N_2}			y_{H_2S}		
exptl	model	DP[a]	exptl	model	Dy[b]	exptl	model	Dy[b]	exptl	model	Dy[b]	exptl	model	Dy[b]
9.2	12.05	2.85	N.D.[c]	0.0037	-	0.6853	0.6414	-0.0439	0.2839	0.3227	0.0388	0.0308	0.0322	0.0014
21.2	22.14	0.94	N.D.[c]	0.0023	-	0.8007	0.8284	0.0277	0.1648	0.1385	-0.0263	0.0345	0.0308	-0.0037
29.0	30.77	1.77	N.D.[c]	0.0019	-	0.7720	0.7357	-0.0363	0.2026	0.2442	0.0416	0.0218	0.0183	-0.0035
39.8	39.11	-0.69	N.D.[c]	0.0017	-	0.5847	0.6286	0.0439	0.3760	0.3561	-0.0199	0.0393	0.0136	-0.0257

[a] $DP = P_{model} - P_{exptl}$

[b] $Dy = y_{model} - y_{exptl}$

[c] N.D. = not detected

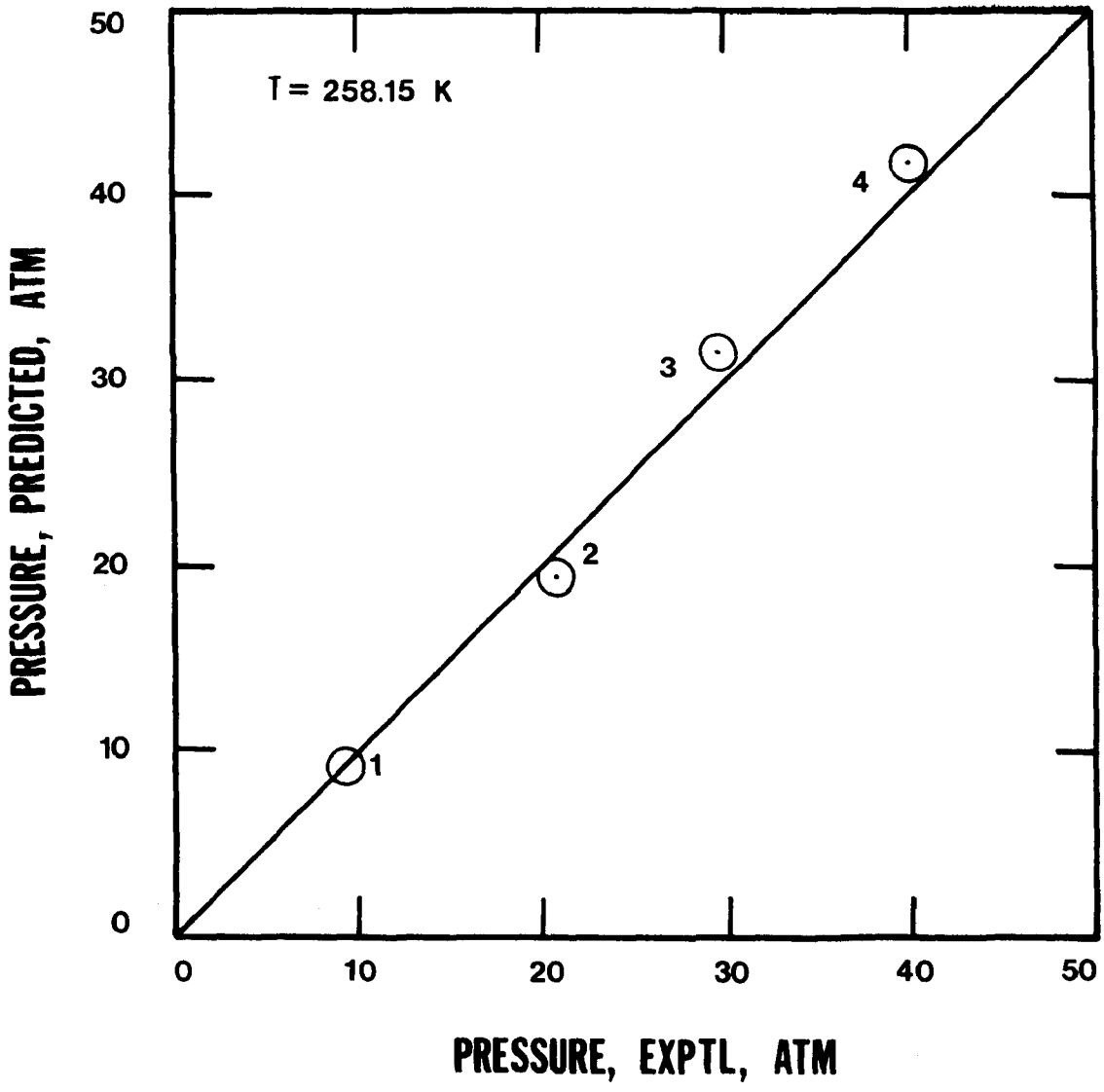

Figure 11. Comparison of Predicted and Measured Four-Component Mixtures at 258.15 K.

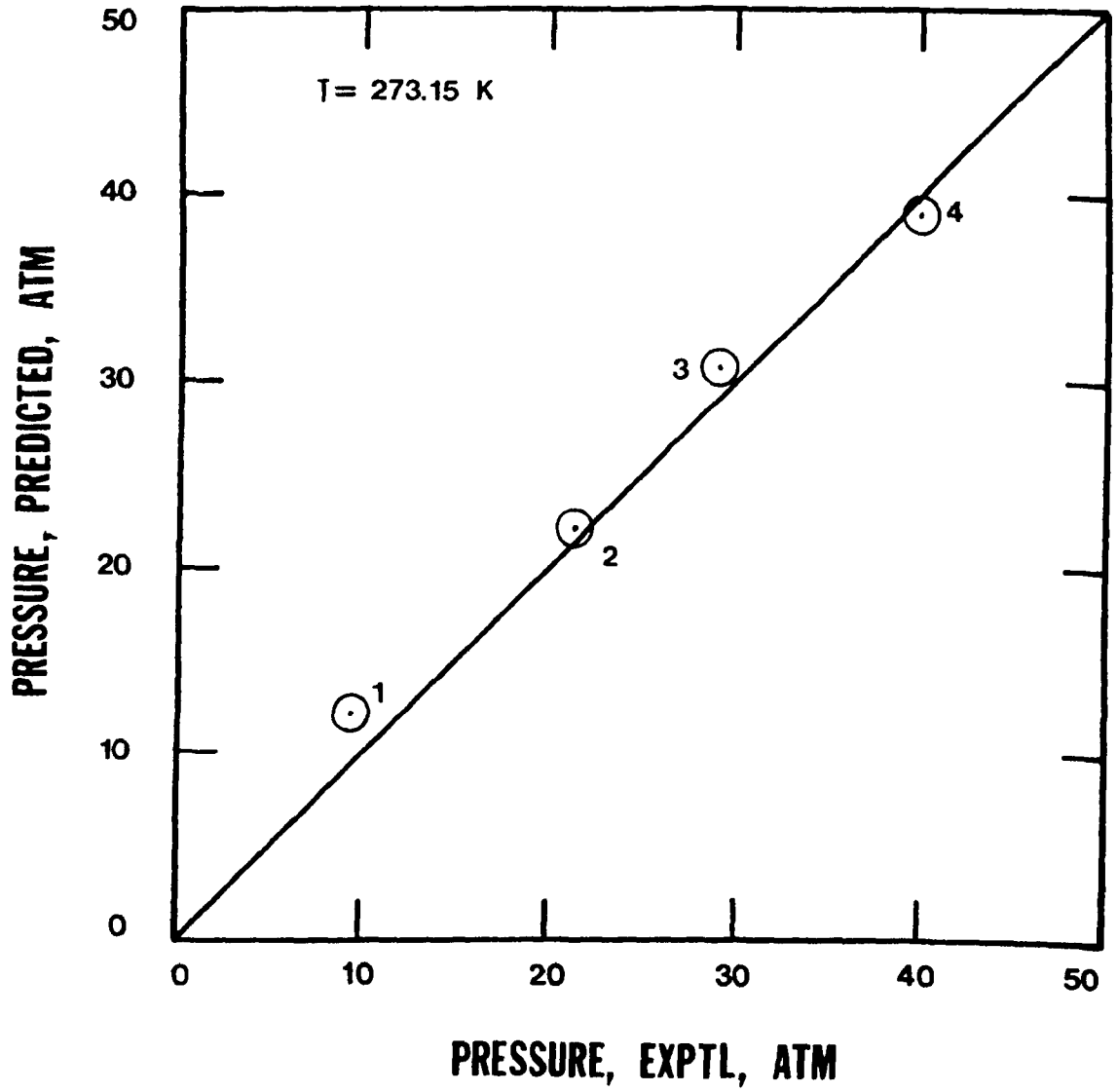

Figure 12. Comparison of Predicted and Measured Pressures for Four-Component Mixtures at 273.15 K.

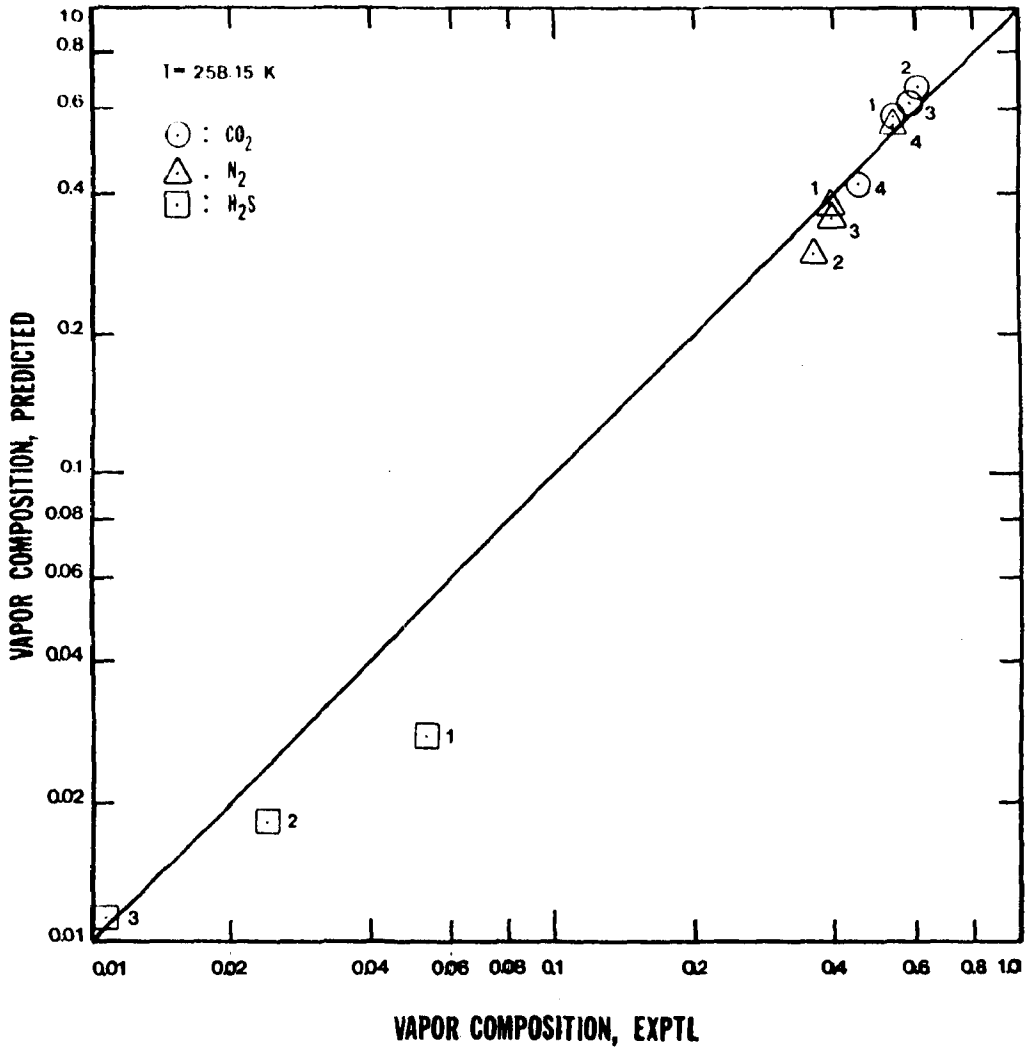

Figure 13. Comparison of Predicted and Experimental Vapor Compositions for Four-Component Mixtures at 258.15 K.

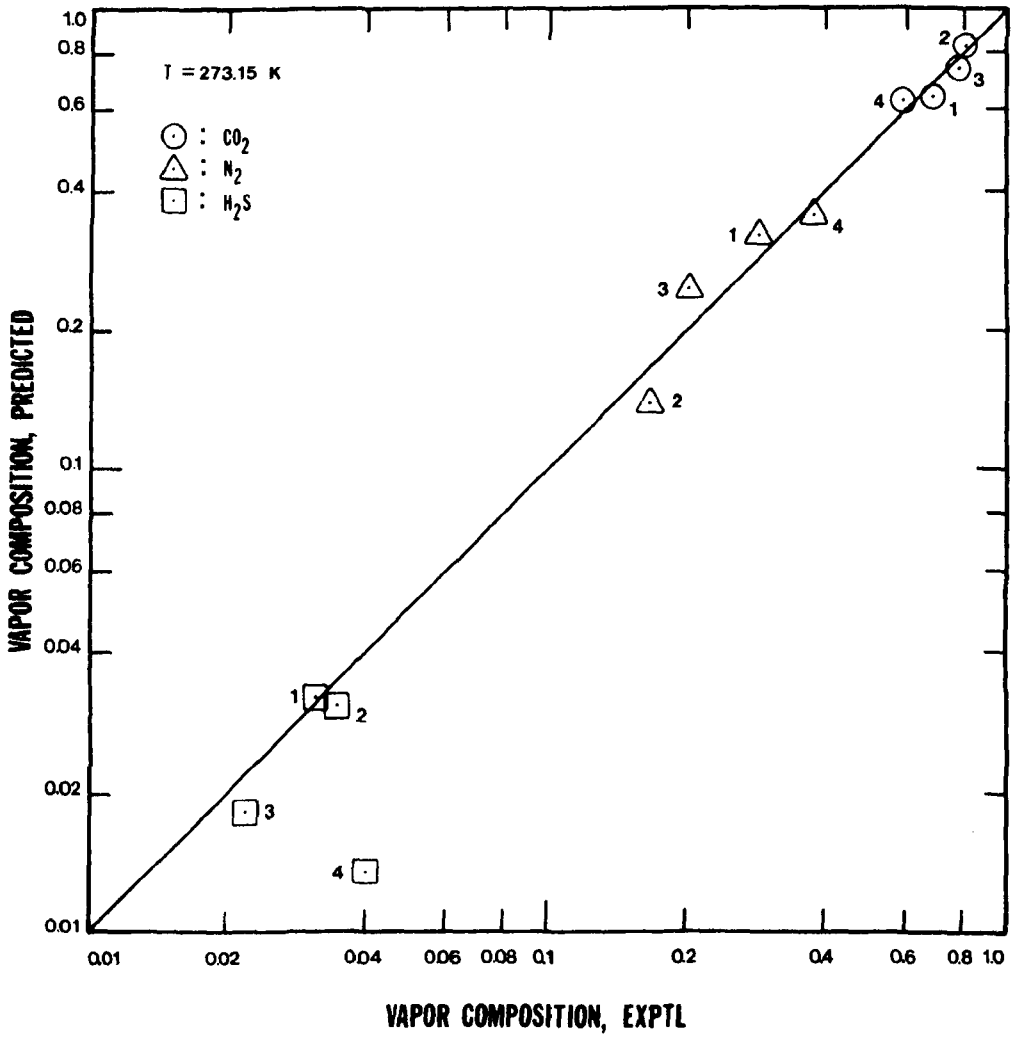

Figure 14. Comparison of Predicted and Experimental Vapor Compositions for Four-Component Mixtures at 273.15 K.

point, dewpoint and flash calculations, and to include additional key constituents of crude coal gas.

CONCLUSIONS

1. A thermodynamic model was developed which successfully correlated vapor-liquid equilibrium data for the six binary mixtures that can be formed from carbon dioxide, hydrogen sulfide, nitrogen and methanol. The model uses the Soave modification of the Redlich-Kwong equation of state to describe the gas phase, the four-suffix Margules equation to express activity coefficients, and pure liquids at the temperature and pressure of the system as reference states. Margules parameters were evaluated from a parameter search procedure known as GMAR. These parameters were found to be functions of temperature, with the functionality varying according to the binary mixture.
2. An experimental equilibrium cell, complete with sampling devices and gas chromatographic analysis capabilities, was constructed. The apparatus was checked by a favorable comparison of experimentally measured equilibrium data to literature data.
3. Experimental vapor-liquid equilibrium data were obtained for methanol-carbon dioxide-nitrogen-hydrogen sulfide mixtures at 258.15 K and 273.15 K. Pressures in these experiments ranged from 6 to 40 atm.
4. A multicomponent version of the vapor-liquid equilibrium model was used to predict vapor compositions and equilibrium pressures based on measured liquid compositions and system temperature. There was excellent agreement between experimental and predicted pressures and carbon dioxide and nitrogen vapor mole fractions. There was fair

agreement between experimental and predicted hydrogen sulfide mole fractions; this was believed due to poor chromatograph sensitivity to low hydrogen sulfide concentrations.

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16. ABSTRACT The report describes a thermodynamic model, developed to predict the equilibrium behavior of carbon dioxide, hydrogen sulfide, nitrogen, and methanol mixtures. The model uses the four-suffix Margules equation to describe liquid-phase nonidealities and the Soave modification of the Redlich-Kwong equation of state to describe the gas phase. Model parameters were obtained from previously published binary vapor/liquid equilibrium data. Vapor/liquid equilibrium data were obtained experimentally for CO2/H2S/N2/methanol mixtures at temperatures of 258.15 K and 273.15 K and pressures of 6-40 atm. Model predictions of equilibrium pressure and vapor compositions from specifications of temperature and liquid compositions compared favorably with experimentally measured values.

17. KEY WORDS AND DOCUMENT ANALYSIS

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