Solubilities of Carbon Dioxide, Hydrogen Sulfide and Nitrogen Mixtures in Methanol

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Previously published data for the six binary combinations that can be formed from CO_2, H_2S, N_2 and methanol are used to obtain parameters of the four-suffix Margules equation describing liquid solution behavior. The vapor phase is described by the Soave modification of the Redlich-Kwong equation of state. Isothermal binary data are fit well by these equations. The effects of temperature on the Margules parameters are significant and, except for N_2-containing mixtures, the parameters were taken to be inversely proportional to absolute temperature.

Experimental data were obtained for multicomponent mixtures of CO_2, H_2S, N_2 and methanol. Model predictions were tested against these data. Comparisons of predicted and measured values of bubble point pressure and equilibrium vapor compositions are satisfactory.

SCOPE

In acid gas removal operations, descriptions of equilibrium characteristics of the constituents of the process gas and the chosen solvent are required for analysis or design. The key components to be separated from the crude gas by such systems are usually carbon dioxide and hydrogen sulfide. Methanol has been used as a solvent in a number of such processes, particularly those coupled with coal gasification reactors. Nitrogen may exist in varying amounts in the process gas stream and it is also frequently chosen as a stripping gas for solvent regeneration. This work considers, therefore, the four components CO_2, H_2S, N_2 and methanol in the development of a thermodynamic model describing phase equilibrium behavior of acid gases in methanol.

The model is developed to have the potential for incorporating the effects of additional components on system behavior. Bubble point predictions using this model are tested against new experimental data on quaternary mixtures of CO_2, H_2S, N_2 and methanol. The results of these comparisons show that the model can be incorporated into simulation packages describing absorber and stripper performance.

CONCLUSIONS AND SIGNIFICANCE

It is shown that the Soave modification of the Redlich-Kwong equation of state and the four suffix Margules equation can be used to describe vapor and liquid phase behavior for binary combinations of CO_2, H_2S, N_2 and methanol. Parameters for each of these equations are determined from published binary equilibrium data. These data cover pressure, temperature and composition ranges typically encountered in acid gas removal systems that use methanol as a solvent.

Multicomponent system behavior can be predicted using the parameters estimated from binary equilibriuim data. Predictive capabilities are tested by favorable comparisons with multicomponent equilibrium data obtained for CO_2-H_2S-N_2-methanol mixtures.

Removal of CO_2, H_2S and other sulfur gases from a crude natural gas or a synthetic gas produced by coal gasification is carried out most often in a process involving absorption of these constituents in a solvent that is subsequently regenerated by stripping. Since the soluble components are acidic, the units in which they are taken out of the unrefined gas are referred to as acid gas removal systems. Although both physical and chemical solvents have been used successfully in acid gas removal, the current trend in coal gasication related operations appears to be towards greater utilization of physical solvents. An excellent discussion of solvent selection and characteristics is given by Savage (1980).

Refrigerated methanol is used in several commercial coal gasification facilities, e.g., the Kosovo coal gasification plant in Yugoslavia and the Sasol facilities in South Africa. Also, the North Carolina State University coal gasification-gas cleaning pilot plant currently is using refrigerated methanol in extensive studies focused on environmental aspects of coal gasification.

Despite commericalization of methanol-based acid gas removal systems, little information has been published on solubility characteristics of constituents of crude coal gas in methanol. Without such information absorber and stripper designs would have to be based on empirical extensions of single-component solubilities and would not reflect possible interactions of system constituents.

The purpose of this study is to begin development of a thermodynamic model that can be used to describe phase equilibrium behavior of the key components in an acid gas removal

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TABLE 1. COMPOSITION OF RAW GAS FROM COAL GASIFICATION (FISCH AND SYKES, 1973)

Component	With O_2 (vol. %)	With Air (vol. %)
CO_2	31.0	10.0
CO	15.0	19.0
H_2	45.0	22.0
CH_4	8.0	0.5
N_2	0.2	48.0
A	0.2	—
H_2S	6800 ppmv	0.5
COS	400 ppmv	150 ppmv

system using refrigerated methanol as solvent. The developed model must be of a form that can include additional system components. Methanol acid gas removal systems operate in a temperature range from 200 to 270°K and pressure range from 1 to 35 atm. Composition of the crude gas produced in coal gasification varies with the gasifier but may be typified by values in Table 1. Since CO_2 and H_2S are the key solutes to be absorbed and subsequently stripped from methanol with nitrogen, the four component system CO_2-H_2S-N_2-methanol was chosen for study.

FUNDAMENTAL EQUATIONS

Expressions relating temperature, pressure and compositions in coexisting phases can be obtained by beginning with the fundamental thermodynamic relationship stating that fugacities of a component in coexisting phases are equal at equilibrium. For vapor-liquid equilibrium,

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

Two methods can be used to express these fugacities in terms of system temperature, pressure and composition of each phase. The first follows from an exact thermodynamic treatment of the system and requires use of an equation of state to describe both liquid and vapor phases. Although the relative simplicity of this approach is appealing, it is limited to systems consisting of nonpolar and nonassociating components for which a single equation of state can be applied to both liquid and vapor phases.

In a second approach, liquid and vapor phases are treated separately. Vapor phase fugacity is evaluated from:

$$f_i^V = \phi_i\, y_i\, P \tag{2}$$

where the fugacity coefficient ϕ_i is a measure of the vapor phase deviation from ideality; it may be evaluated from an appropriate equation of state.

Fugacities of components in the liquid phase are defined in terms of a deviation from ideal solution behavior as given by Raoult's or Henry's laws:

$$f_i^L = \gamma_i (f_i^L)_{\text{ideal}} = \gamma_i\, x_i\, f_i^o \tag{3}$$

where γ_i defines the deviation of the solution from ideal behavior and f_i^o is the fugacity of the reference state at the system conditions. If the ideal solution is defined in terms of Raoult's law:

$$f_i^o = (f_i^L)_{\text{pure}} = P_i^*\, \phi_i^*\, \exp\left[\int_{P_i^*}^{P} (v_i^L/RT)\, dP\right] \tag{4}$$

where P_i^* and ϕ_i^* are functions of temperature and v_i^L is a function of temperature and pressure. Using this definition of the reference state $\gamma_i \rightarrow 1.0$ as $x_i \rightarrow 1.0$.

Accuracy of Eq. 4 clearly depends upon knowing P_i^* as a function of temperature. Unfortunately, system components are often at supercritical conditions so that hypothetical values of their vapor pressures must be estimated by extrapolation. In such instances, defining the reference state in terms of Henry's law may be preferable; that is

$$f_i^o = (f_i^L)_\infty = H_i \tag{5}$$

where H_i is the Henry's law constant at the system temperature and pressure. Equation 5 may be rewritten to illustrate the effect of pressure on H_i:

$$H_i = H_i^* \exp\left[\int_{P_{\text{ref}}}^{P} (\bar{v}_i^\infty/RT)\, dP\right] \tag{6}$$

where H_i^* is Henry's law constant evaluated at the system temperature and pressure P_{ref}. Use of Henry's law to define the reference state of a component whose critical temperature is less than the system temperature is usually favored over use of the Raoult's law definition. However, as O'Connell (1977) has noted, severe difficulties exist in using Henry's law for the reference state fugacity when the solvent consists of more than a single component. In essence, H_i^* and $\bar{v}_i^\infty$ would depend on solvent composition and extensive experimental data would be required to evaluate the respective composition-dependent functions.

Two decisions were made in beginning the current model development for phase equilibrium behavior. First, since methanol is a polar compound and methanol and CO_2 are believed to associate in the vapor phase (Hemmaplardh and King, 1972), use of an equation of state to calculate liquid fugacities was not attempted; Eq. 3 was used for this purpose. Second, it was decided that more flexibility would result from defining reference liquid state conditions by the Raoult's law convention. Although the Henry's law convention has attractive features, it appears that inclusion of additional components in the system model is made easier by the Raoult's law definition of ideality.

MODEL DEVELOPMENT

Combining Eqs. 1, 2 and 3 the basic phase equilibrium relationship is:

$$\phi_i\, y_i\, P = \gamma_i\, x_i\, f_i^o \tag{7}$$

Utilization of this expression requires that ϕ_i be expressed in terms of vapor composition, temperature and pressure, that γ_i be expressed in terms of liquid composition and temperature (this assumes pressure does not affect liquid solution behavior), and that f_i^o be expressed in terms of temperature and pressure. Methods used to obtain such expressions for this study are outlined in the next section.

Fugacity Coefficients

Expressions for fugacity coefficients may be obtained from equations of state such as Redlich-Kwong, Benedict-Webb-Rubin, virial and Peng-Robinson; the modification of the Redlich-Kwong equation of state by Soave (1972) was chosen for this study. The Soave (SRK) expression is:

$$P = \frac{RT}{v - b} - \frac{\alpha a}{v(v + b)} \tag{8}$$

where the constants a, b, and α are given as follows:

$$a = 0.42747\, R^2\, T_c^2/P_c \tag{8a}$$

$$b = 0.08664\, RT_c/P_c \tag{8b}$$

$$\alpha = \left[1 + \{0.48508 + 1.55171\omega - 0.15613\omega^2\}\left\{1 - \left(\frac{T}{T_c}\right)^{0.5}\right\}\right]^2 \tag{8c}$$

For a gas mixture the following mixing rules apply:

$$\alpha a = \sum_{i=1}^{N} \sum_{j=1}^{N} y_i\, y_j\, \alpha_{ij}\, a_{ij} \tag{8d}$$

$$\alpha_{ij}\, a_{ij} = (\alpha_i\, \alpha_j\, a_i\, a_j)^{1/2}\, (1 - K_{ij}) \tag{8e}$$

$$b = \sum_{i=1}^{N} y_i\, b_i \tag{8f}$$

TABLE 2. BINARY INTERACTION CONSTANTS FOR THE SOAVE MODIFICATION OF THE REDLICH-KWONG EQUATION OF STATE

System	K_{ij}	Source
Methanol—CO_2	0.0628	This work
Methanol—N_2	0.080	This work
Methanol—H_2S	−4.000	This work
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)

TABLE 3. PURE COMPONENT CONSTANTS FROM REID ET AL. (1977)

Component	T_c (°K)	P_c (atm)	V_c (cc/mol)	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

TABLE 4. RELATIONSHIPS OF MULTICOMPONENT MARGULES PARAMETERS TO BINARY AND TERNARY PARAMETERS

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

where

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

C^*_{ijk} = ternary constant

The only parameter in Eq. 8 that requires information other than that obtained from pure component data is K_{ij}. Soave (1972) and Graboski and Daubert (1978) indicate that K_{ij} is approximately zero for nonpolar hydrocarbons. Furthermore, Lin and Daubert (1980) suggest that the interaction coefficient as defined by Prausnitz (1969) may be used as an approximation of K_{ij}. Values of K_{ij} for the six binary mixtures encountered in systems of methanol, hydrogen sulfide, carbon dioxide and nitrogen are given in Table 2, along with how they were determined. Pure component constants required in Eq. 8 are given in Table 3.

Fugacity coefficients for constituents of a gas mixture following the SRK equation of state are given by:

$$\ln \phi_i = \frac{b_i}{b}(z - 1) - \ln (z - B) - \frac{A}{B}\left[\frac{2\sum_{j=1}^{N} y_j\, \alpha_{ij}\, a_{ij}}{\alpha a} - \frac{b_i}{b}\right] \ln\left(1 + \frac{B}{z}\right) \qquad (9)$$

where

$$A = \frac{\alpha a\, P}{R^2\, T^2} \qquad (9a)$$

$$B = \frac{bP}{RT} \qquad (9b)$$

$$z = Pv/RT \qquad (9c)$$

The compressibility constant z is calculated from Eq. 9 after the vapor molar volume is determined by solving Eq. 8 for its largest real root.

Prior to using modifications to the Redlich-Kwong equation of state suggested by Soave (1972), the unmodified version was tested. The modified version was significantly better when used in vapor-liquid equilibrium calculations.

Activity Coefficients

Activity coefficients can not 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. A variety of equations have been used for this purpose, including Wilson, Van Laar and UNIQUAC equations. In this case, however, a recommendation by Adler et al. (1966) was followed; they suggested use of a special case of the Wohl expansion model (1953) which results in the four-suffix Margules equation. In this approach 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 model allows activity coefficients to be expressed as a function including three adjustable parameters

$$\ln \gamma_i = x_j^2[A_{ij} + 2(A_{ji} - A_{ij} - D_{ij})\, x_i + 3D_{ij}\, x_i^2] \qquad (10)$$

Activity coefficients for constituents of a multicomponent solution are given by:

$$\ln \gamma_i = 4 \sum_{j=1}^{N} \sum_{k=1}^{N} \sum_{l=1}^{N} x_j\, x_k\, x_l\, \beta_{ijkl} - 3 \sum_{i=1}^{N} \sum_{j=1}^{N} \sum_{k=1}^{N} \sum_{l=1}^{N} x_i\, x_j\, x_k\, x_l\, \beta_{ijkl} \qquad (11)$$

where values of β_{ijkl} depend upon binary parameters A_{ij}, A_{ji} and D_{ij} and a ternary parameter C^*. Table 4 gives relationships between these parameters and β_{ijkl}.

Clearly it is necessary to have binary parameters reflecting liquid solution behavior for all possible pairs of components constituting a multicomponent system before Eq. 11 can be used. Moreover, all ternary system parameters C^*_{ijk} must be known for use of Eq. 11.

Six binary combinations may be formulated from the components methanol, carbon dioxide, hydrogen sulfide and nitrogen. These are methanol-carbon dioxide, methanol-hydrogen sulfide, methanol-nitrogen, carbon dioxide-hydrogen sulfide, carbon dioxide-nitrogen and hydrogen sulfide-nitrogen. The four possible ternary combinations for these components are methanol-carbon dioxide-hydrogen sulfide, methanol-carbon dioxide-nitrogen, methanol-hydrogen sulfide-nitrogen and hydrogen sulfide-carbon dioxide-nitrogen.

Three parameters for each binary mixture were evaluated from binary experimental *x-P-T* data using a number of techniques. The parameters used in the final solution model were those that resulted in a minimization of the deviation between experimental and predicted pressures for each binary mixture. Details of the techniques in parameter evaluation will be provided in a later section.

Adler et al. (1966) studied the effect of C^* on the deviation of predicted vapor composition from estimated values for a number of ternary systems. They found C^* to be very near zero in all cases. Based on this conclusion, and the lack of ternary data, C^* was assumed zero in this work.

In using the Margules equation to correlate activity coefficients for binary solutions and predict activity coefficients for quaternary solutions it was recognized that more recently developed solution models may, in the long run, be superior. However, in attempting to use the Wilson equations for this purpose significant difficulties were encountered with parameter estimation. And, while work with the Wilson equation has not been abandoned, the Margules equation has given very good results.

Liquid Reference State Fugacities

Recall that the chosen approach defines the reference state as the pure component at the system temperature and pressure and, therefore, evaluation of mixture liquid fugacities requires estimates of pure component liquid fugacities. These were obtained in a variety of ways depending upon the nature of the component.

Methanol. The relationship given by Equation 4 was used to calculate the reference state fugacity for methanol. Required vapor pressures were estimated from the Antoine equation:

$$\log_{10}\left[P^*_{CH_3OH}(\mathrm{mm\ Hg})\right] = 7.87862 - 1473.11/[T(^\circ\mathrm{K}) - 43.247] \qquad (12)$$

where the constants were determined from the data of Eubank (1970). The liquid molar volume for methanol used in Eq. 4 was calculated from the following corresponding state correlation of Chueh and Prausnitz described in detail in Reid, Prausnitz and Sherwood (1977)

$$1/v_i^L = \rho_s\left[1 + \frac{9z_c\, N_r\,(P - P_i^*)}{P_c}\right]^{1/9} \qquad (13)$$

where

$$N_r = (1.0 - 0.89)\,[\exp(6.9547 - 76.2853\,T_r + 191.3060\,T_r^2 - 203.5472\,T_r^3 + 82.7631\,T_r^4)] \qquad (13a)$$

$$\rho_s = \rho_c/(V_r^{(0)} + \omega V_r^{(1)} + \omega^2 V_r^{(2)}) \qquad (13b)$$

$$V_r^{(j)} = a_j + b_j T_r + c_j T_r^2 + d_j T_r^3 + e_j/T_r \qquad (13c)$$

Constants for Eq. 13 are given in Table 5. Using the above correlation for the liquid molar volume and evaluating the integral in Eq. 4, the following expression is obtained for the reference fugacity of methanol:

$$f^0 = P^*\,\phi^*\,\exp\left\{\frac{P_c}{8RT\,\rho_s\,z_c}\left[\left(1 + \frac{9z_c\,N_r(P - P^*)}{P_c}\right)^{8/9} - 1\right]\right\} \qquad (14)$$

CO_2 and H_2S. A reduced states correlation developed by Robinson and Chao (1971) was used to estimate pure component fugacities of carbon dioxide and hydrogen sulfide. The correlation, which follows, has three parameters estimated by functions chosen according to the range of reduced temperatures in the system.

$$\log\frac{f_i^0}{P} = \log\nu^{(0)} + \omega\log\nu^{(1)} \qquad (15)$$

$$\log\nu^{(0)} = B_0 + B_1\,P_r + B_2\,P_r^2 - \log P_r \qquad (15a)$$

$$B_0 = -20.651608 + 84.517272\,T_r - 15.376424\,T_r^2 + 152.65216\,T_r^3 - 84.899391\,T_r^4 + 24.84688\,T_r^5 - 2.9786581\,T_r^6 \qquad (15a\text{-}1)$$

$$\text{If } 0.8 > T_r \geq 0.3 \quad B_1 = \left(\frac{0.293}{2.303\,T_r}\right)^{[1+(1-T_r)^{0.286}]} \qquad (15a\text{-}2)$$

$$\text{If } 0.9 > T_r \geq 0.8 \quad B_1 = 0.321895\,T_r - 0.184316 \qquad (15a\text{-}3)$$

$$\text{If } 1.8 \geq T_r \geq 0.9 \quad B_1 = 58.16962 - 326.54444\,T_r + 775.11716\,T_r^2 - 1006.8122\,T_r^3 + 773.32667\,T_r^4 - 351.56938\,T_r^5 + 87.677429\,T_r^6 - 9.2617986\,T_r^7 \qquad (15a\text{-}4)$$

$$\text{If } 0.8 > T_r \geq 0.3 \quad B_2 = 0 \qquad (15a\text{-}5)$$

$$\text{If } 0.9 > T_r \geq 0.8 \quad B_2 = 0.0549369\,(0.8 - T_r) \qquad (15a\text{-}6)$$

$$\text{If } 1.0 > T_r \geq 0.9 \quad B_2 = 0.67334 \times 10^{-3} - 0.685226 \times 10^{-2}\,T_r \qquad (15a\text{-}7)$$

$$\text{If } T_r \geq 1.0 \quad B_2 = 0.72203901 - 2.7182597\,T_r + 3.984423\,T_r^2 - 2.8712448\,T_r^3 + 1.0202739\,T_r^4 - 0.14314712\,T_r^5 \qquad (15a\text{-}8)$$

$$\log\nu^{(1)} = \log\nu_{0.6}^{(1)} + (P_r - 0.6)\left(\frac{\partial\log\nu^{(1)}}{\partial P_r}\right) \qquad (15b)$$

$$\log\nu_{0.6}^{(1)} = -660.08698 + 7766.7774\,T_r - 40007.379\,T_r^2 + 116582.6\,T_r^3 - 209756.24\,T_r^4 + 238673.14\,T_r^5 - 167856.45\,T_r^6 + 66762.602\,T_r^7 - 11504.984\,T_r^8 \qquad (15b\text{-}1)$$

$$\frac{\partial\log\nu^{(1)}}{P_r} = -0.28997623 + 0.96418856\,T_r - 1.3344703\,T_r^2 + 0.82575807\,T_r^3 - 0.18939410\,T_r^4 \qquad (15b\text{-}2)$$

Nitrogen. The Chao-Seader equation was used to estimate the fugacity of pure nitrogen, the chosen reference state.

$$\log_{10}(f_i^0/P) = 2.7365534 - 1.9818310\,T_r - 0.51487289\,T_r + 0.942470988\,T_r^2 - 0.002814385\,T_r^3 + P_r(0.021495843\,T_r - 0.029474696) - \log_{10}P_r + \omega_i \qquad (16)$$

Model Structure

The thermodynamic model can be used in either bubble point or dew point calculations. In both types of calculations pure component properties T_c, P_c, V_c and ω are required for all components in the system; in addition, Margules parameters for all possible binary combinations of system constituents are required. Bubble point calculations then require specification of liquid composition and system temperature or pressure and result in an estimation of the equilibrium vapor composition and system pressure or temperature. In dew point calculations vapor composition and system temperature or pressure are specified, and equilibrium liquid composition and system pressure or temperature are determined.

TABLE 5. CONSTANTS FOR EQ. 17.

j	a_j	b_j	c_j	d_j	e_j	f_j
0	0.11917	0.009513	0.21091	−0.06922	0.07480	−0.084475
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

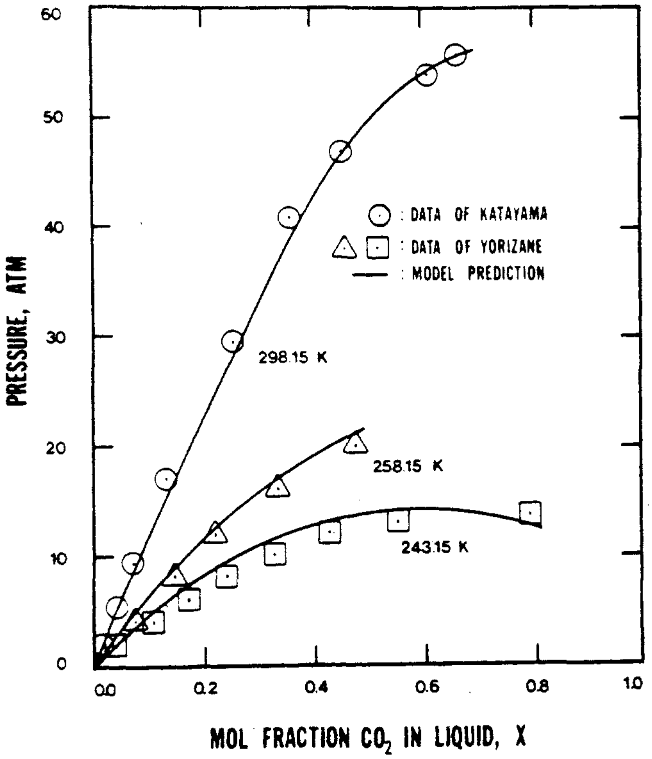

Figure 1. Comparison of the experimental pressure and the predicted pressure for the methanol-carbon dioxide system.

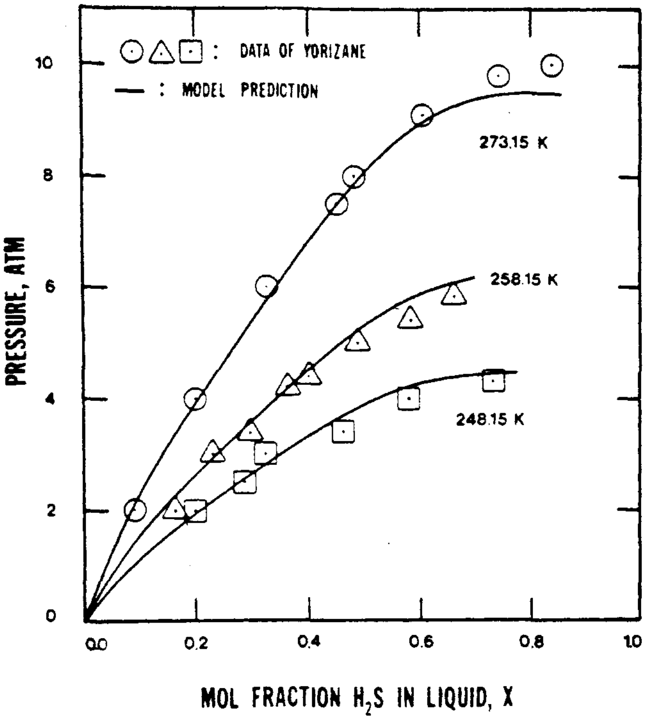

Figure 2. Comparison of the experimental pressure and the predicted pressure for the methanol-hydrogen sulfide system.

Computer programs were developed to accomplish both bubble point and dew point calculations. Their structure was set so that system temperature was specified and system pressure calculated, although the reverse arrangement is possible. Logic flow diagrams and listings of these programs are given by Matange (1980).

EVALUATION OF MARGULES PARAMETERS

As described earlier, the four-suffix Margules equation was used to describe the deviation of liquid solution from Raoult's law. For each of the six binary combinations of methanol, carbon dioxide, hydrogen sulfide and nitrogen, three parameters were needed: A_{ij}, A_{ji}, and D_{ij}. Thus, a total of 18 Margules parameters were required for the solution model. These were evaluated for the six binary combinations from phase equilibrium data found in the literature.

Details of parameter search procedures used in this study are given by Matange (1980). Two types of data were used: *x-y-P-T* data and *x-P-T* data. When *x-y-P-T* data are available, activity coefficients may be evaluated at each data point using the equation:

$$\gamma_i = \frac{\phi_i\, y_i\, P}{x_i\, f_i^0} \qquad (17)$$

More commonly, data were found in the *x-P-T* format, usually in the form of total pressure measurements with varying liquid compositions at a fixed temperature. These data can be used in a parameter search routine that combines bubbles point calculations with the data to determine optimum Margules parameters. In essence, the approach was to adjust values of the Margules parameters for a given binary system until the sum of the squares of the difference between calculated and experimental pressures was minimized.

As mentioned earlier, the interaction parameters K_{ij} required by the SRK equation of state were not available for the binary mixtures containing methanol. The values shown for these systems in Table 2 were determined using a procedure outlined by Evelein and Moore (1979). In this procedure, Margules parameters were evaluated using the least squares search procedure described above for several values of K_{ij}. The value of K_{ij} which gave the smallest value in the sum of the squares of the differences between calculated and experimental pressures was chosen. The dependence of the sum of the errors squared on K_{ij} was small and no attempt was made to refine this part of the parameter search procedure.

Margules parameters are dependent on temperature and, therefore, different values should be obtained in fitting each isothermal data set. Adler et al. (1966) found these parameters to

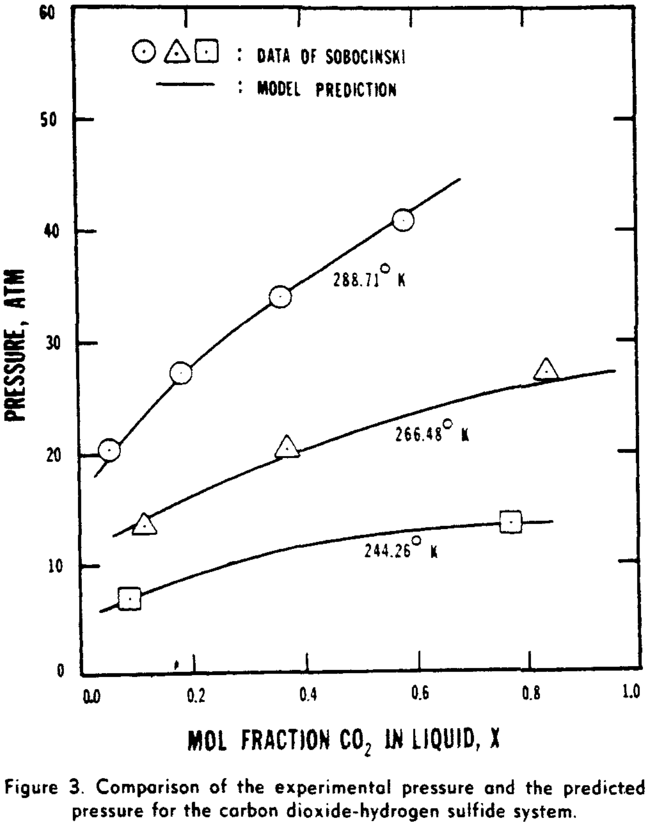

Figure 3. Comparison of the experimental pressure and the predicted pressure for the carbon dioxide-hydrogen sulfide system.

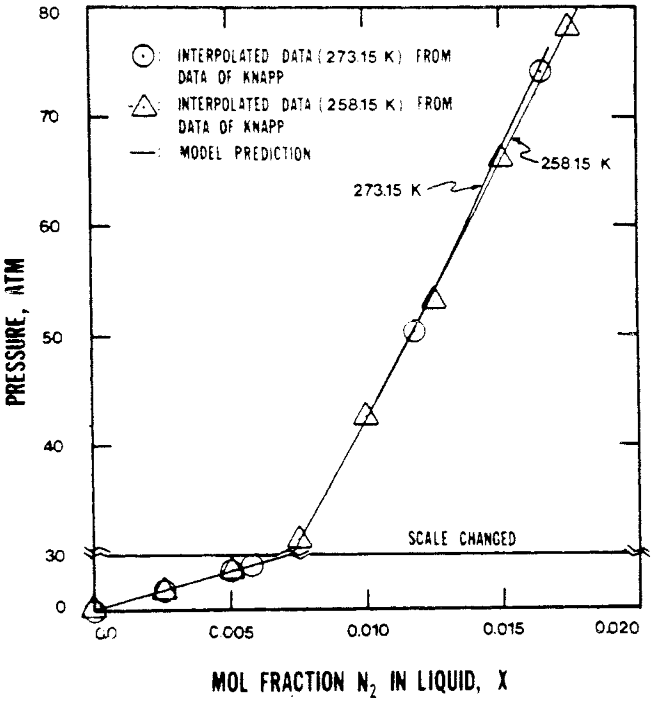

Figure 4. Comparison of the experimental pressure and the predicted pressure for the methanol-nitrogen system.

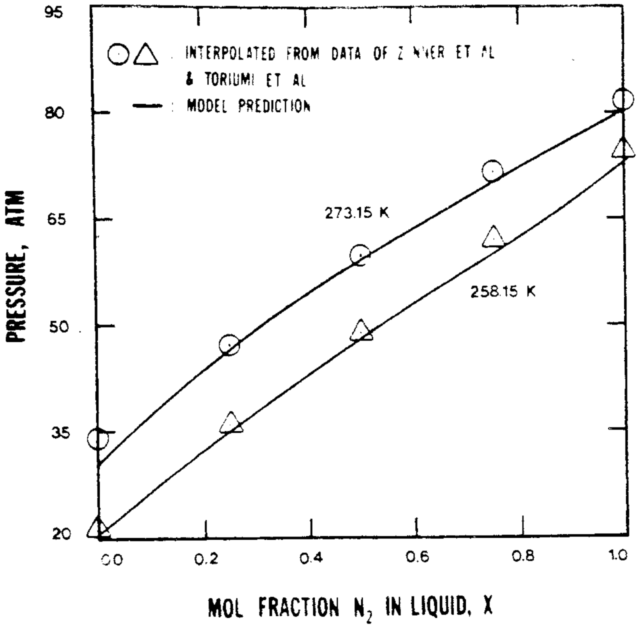

Figure 5. Comparison of the experimental pressure and the predicted pressure for the carbon dioxide-nitrogen system.

be inversely proportional to absolute temperature for a large number of binary mixtures. Assuming the Margules parameters to follow this relationship for methanol-carbon dioxide, methanol-hydrogen sulfide and carbon dioxide-hydrogen sulfide binary combinations was satisfactory and allowed utilization of all data to determine optimum parameters. Binary mixtures containing nitrogen could not be handled by this approach and three parameters per binary mixture were evaluated for each isothermal data set. Data from the cited references along with a comparison with the model predictions are available from the authors.

Methanol-Carbon Dioxide. The data of Katayama et al. (1975) at 298.15°K and of Yorizane et al. (1969) at 258.15 and 243.15°K were used to evaluate Margules parameters. Optimal values of these parameters were used to construct the comparison plots of experimental and model pressures shown in Figure 1. The correlation of these data gave an average deviation of 9.7% for pressure and 0.06% for the vapor mole fractions provided by Katayama et al. (1975).

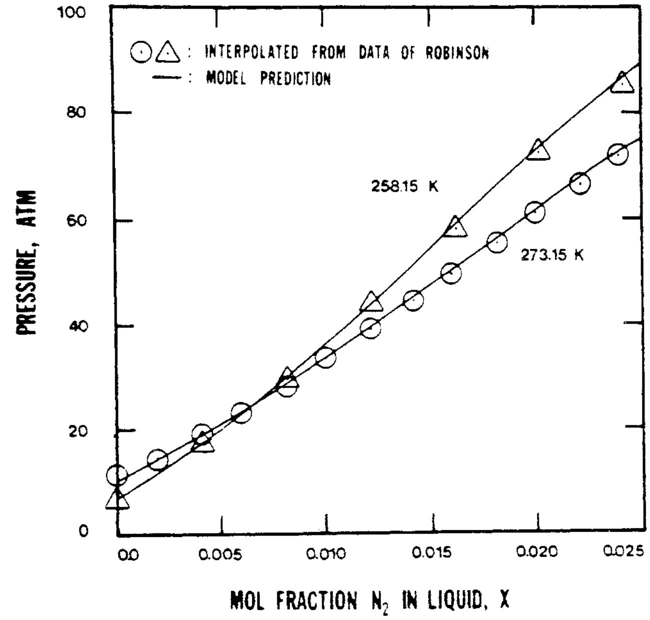

Figure 6. Comparison of the experimental pressure and the predicted pressure for the nitrogen-hydrogen sulfide system.

Methanol-Hydrogen Sulfide. The data of Yorizane et al. (1969) at 273.15, 258.15 and 248.15°K were used to evaluate Margules parameters. Figure 2 allows comparisons of experimental and model values.

Carbon Dioxide-Hydrogen Sulfide. The data of Sobocinski and Kurata (1959) at 288.71, 266.48 and 244.26°K were used to evaluate Margules parameters. Figure 3 gives comparisons of experimental, and model predictions.

Binary Mixtures Containing Nitrogen. None of the three binary combinations containing nitrogen exhibited a simple relationship between temperature and Margules parameters. Although data on each of the binary mixtures nitrogen-methanol, nitrogen-carbon dioxide and nitrogen-hydrogen sulfide were found at a number of temperatures, none were found at the specific temperatures to be used in multicomponent experiments providing information with which the thermodynamic model can be tested. Therefore, Margules parameters were determined at the temperatures of interest by interpolating published data. Comparisons of model fits with interpolated experimental values are given for these three mixtures in Figures 4, 5, and 6. Until an explicit relationship between Margules parameters and temperature is developed for mixtures containing nitrogen, these parameters will have to be evaluated at the temperature of interest. Although tedious, the procedures for these evaluations are straightforward and were outlined earlier.

Summary of Binary Analysis

Phase equilibrium data were used to evaluate Margules parameters for the six binary combinations that can be formed from the four components methanol, carbon dioxide, hydrogen sulfide and nitrogen. Parameters for systems containing nitrogen exhibited anomalous behavior in their dependence on temperature, whereas parameters for other mixtures were found to be inversely proportional to temperature. These results are summarized in Table 6 along with average deviations between predictions using model parameters and measured values.

One of the objectives of this study is to test the model developed against experimentally determined multicomponent equilibrium data. The next section describes the experimental apparatus and procedures used to obtain multicomponent data which give a quantitative comparison with model predictions.

TABLE 6. MARGULES PARAMETERS EVALUATED IN THIS STUDY

Mixture	$A_{12}T$	$A_{21}T$	$D_{12}T$	$\%E_p$	$\%E_y$
methanol (1)-CO_2(2)	365.88	175.55	189.57	9.7	0.06
methanol (1)-H_2S(2)	293.85	146.79	279.17	4.4	
CO_2(1)-H_2S(2)	155.83	157.80	158.24	1.9	8.0
methanol (1)-N_2(2)	1420.38*	312.65*	600.93*	1.2	
methanol (1)-N_2(2)	2839.65†	300.93†	2245.91†	0.9	
CO_2(1)-N_2(2)	579.84*	82.57*	852.86*	3.0	
CO_2(1)-N_2(2)	163.36†	73.55†	203.22†	1.7	
N_2(1)-H_2S(2)	221.66*	−18189.82*	−19898.13*	1.5	
N_2(1)-H_2S(2)	232.08†	−29526.86†	−31787.82†	1.7	

* At 273.15°K.
† At 258.15°K.

TABLE 7. COMPARISON OF TEST DATA WITH THAT OF KATAYAMA ET AL. (1975) FOR METHANOL (1)—CARBON DIOXIDE (2) MIXTURES AT 298.15°K

P(atm)	x_2(Katayama et al.)	x_2(This Study)
9.4	0.070	0.065
29.6	0.256	0.250
47.0	0.450	0.420

EXPERIMENTAL

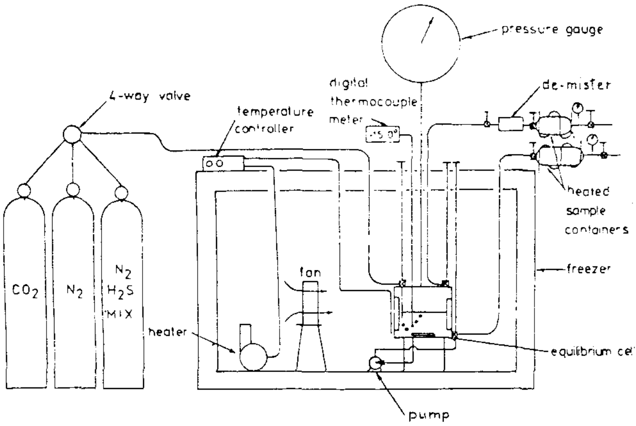

Figure 7. Experimental apparatus.

The apparatus used to obtain multicomponent vapor-liquid equilibrium data was a modification of that used by Bass (1978) and is shown in Figure 7. 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 high pressure use. Liquid in the cell was circulated using a microflo pulsafeeder diaphragm metering pump. Pressure in the equilibrium cell was measured using a 406-mm (16-in.) Heise gauge graduated in 3.5 kPa (0.5 psi) increments up to 85 atm. The gauge had a guaranteed accuracy of 0.1% of the full scale; an Ashcroft type 1327 portable dead weight tester was used to confirm the calibration of the gauge. Temperatures were measured using a copper-constantan thermocouple and a digital calibrated temperature indicator. The entire high pressure apparatus was housed in an industrial freezer which provided the refrigeration. A temperature controller, fan and heater held the temperature in the cell to within 0.1°C of a set point.

Purities of chemicals used were as follows: methanol, 99.95%; carbon dioxide, 99.99%; nitrogen, 99.999%; H_2S, a 15.1% mixture in N_2. All of these reagents were obtained commercially.

Compositions of liquid and vapor samples were determined by gas chromatographic analysis. The chromatograph had a thermal conductivity detector, temperature programmer and heated gas sampling valve. Columns in the chromatograph were 3.18 mm in diameter and 3 m in length; they were packed with Porapak 'QS'. The temperatures used were 35°C for separation of N_2 and H_2S, and 100°C for CO_2 and methanol. A digital integrator was used to evaluate the data provided by the chromatograph which were also recorded on a strip chart recorder. Details of chromatograph calibration are given by Matange (1980).

TABLE 8. EXPERIMENTAL VAPOR-LIQUID EQUILIBRIUM DATA FOR THE METHANOL-CARBON DIOXIDE-NITROGEN-HYDROGEN SULFIDE MIXTURES

T(°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}
258.15	9.3	0.908	0.074	0.003	0.015	*	0.544	0.403	0.052
258.15	20.8	0.768	0.210	0.003	0.019	*	0.611	0.365	0.024
258.15	29.6	0.646	0.331	0.005	0.021	*	0.589	0.400	0.010
258.15	40.1	0.742	0.235	0.008	0.016	*	0.458	0.542	*
273.15	9.2	0.900	0.085	0.002	0.013	*	0.685	0.284	0.031
273.15	21.2	0.743	0.234	0.002	0.021	*	0.801	0.165	0.035
273.15	29.0	0.696	0.283	0.003	0.018	*	0.774	0.204	0.022
273.15	39.8	0.687	0.285	0.007	0.020	*	0.585	0.376	0.039

* Species not detected.

TABLE 9. COMPARISON OF MODEL PREDICTIONS WITH EXPERIMENTAL PRESSURES (ATM) AND VAPOR COMPOSITION FOR METHANOL (1)-CARBON DIOXIDE (2)-NITROGEN (3)-HYDROGEN SULFIDE (4) MIXTURES

T(°K)	P_{exp}	P_{mod}	ΔP	y_1^E	y_1^M	y_2^E	y_2^M	Δy_2	y_3^E	y_3^M	Δy_3	y_4^E	y_4^M	Δy_4
258.15	9.3	9.1	−0.2	*	0.0017	0.544	0.588	0.044	0.403	0.382	−0.021	0.052	0.028	−0.024
258.15	20.8	19.3	−1.5	*	0.0019	0.611	0.679	0.068	0.365	0.302	−0.063	0.024	0.018	−0.006
258.15	29.6	31.5	1.9	*	0.0007	0.589	0.631	0.042	0.400	0.358	−0.042	0.010	0.011	0.001
258.15	40.1	41.6	1.5	*	0.0006	0.458	0.422	−0.036	0.542	0.572	0.030	*	0.005	—
273.15	9.2	12.0	2.8	*	0.0037	0.685	0.641	−0.044	0.284	0.323	0.039	0.031	0.032	0.001
273.15	21.2	22.1	0.9	*	0.0023	0.801	0.828	0.027	0.165	0.139	−0.026	0.034	0.031	−0.003
273.15	29.0	30.8	1.8	*	0.0019	0.774	0.736	−0.038	0.204	0.244	0.040	0.022	0.018	−0.004
273.15	39.8	39.1	−0.7	*	0.0017	0.585	0.629	0.044	0.376	0.356	−0.020	0.039	0.014	−0.025

Δ ≡ model − experimental.
* ≡ species not detected.

The first step in obtaining multicomponent vapor-liquid equilibrium data was to add about 0.39 liter of methanol to the equilibrium cell. The refrigeration system was turned on to achieve a desired temperature in the cell and the three gases were added to generate a desired composition and pressure. The 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 evacuated sample bombs. Sampling was done quickly and the cell pressure was seldom disturbed by more than 0.48 atm. The vapor sample bomb was pressurized to approximately 1.4 atm with helium and then both bombs were heated to 140°C for five hours. Pressures in the bombs were monitored to insure that the methanol in the samples did not approach the point of condensation. The contents of each bomb were analyzed a minimum of five times to determine a sample composition.

DISCUSSION OF EXPERIMENTAL RESULTS

The experimental apparatus and procedure described in the proceeding section were tested by comparing equilibrium data of methanol and carbon dioxide mixtures with three data points reported by Katayama et al. (1975). This comparison is shown in Table 7 and indicates favorable correspondence of the two sets of experimental data.

Vapor-liquid equilibrium data were then taken for methanol-carbon dioxide-hydrogen sulfide-nitrogen mixtures at 258.15 and 273.15°K. These data are given in Table 8. As previously mentioned, each sample bomb was subjected to at least five replicates. All replicates were normalized according to carbon dioxide content. For all liquid samples, the average percent standard deviations for methanol, nitrogen and hydrogen sulfide concentrations were 0.8, 5.1 and 3.0, respectively. Methanol was not detected in the vapor samples; nitrogen and hydrogen sulfide had average percent standard deviations in concentrations of 0.7 and 5.1, respectively.

The multicomponent vapor-liquid equilibrium model was used to estimate system pressure and vapor composition from measured system temperature and liquid composition data given in Table 8. Results of these bubble point calculations and their comparison with measured quantities are provided in Table 9. The average deviation between model and predicted experimental pressures was 7.9%. Comparisons between experimentally measured and model predicted vapor more fractions are somewhat difficult to make because of the variations in composition range among the constituents, and because vapor mole fractions are constrained to sum to 1.0; i.e., an error in the mole fraction of one constituent is distributed among the other constituents.

Table 9 shows that predictions of CO_2, N_2 and H_2S vapor mole fractions had maximum deviations from measured values of 0.068, 0.063 and 0.025 mole fraction units, respectively. Average deviations were 0.043, 0.035 and 0.009 mole fraction units. It should be noted that the two largest deviations from model values occurred from CO_2 and N_2 vapor mole fractions in the same experiment: 0.068 and −0.063 mole fraction units. It is believed that this correspondence is due to the restriction requiring mole fractions to sum to 1.0.

The comparison between model and experimental values described above indicates that the model does a good job in predicting equilibrium pressures and a somewhat poorer job is predicting equilibrium vapor compositions. This is probably due to a combination of factors including both experimental errors and model inaccuracies. Recall that model parameters were difficult to evaluate and there were no vapor composition data included in these evaluations. Furthermore, the liquid and vapor compositions in the experimental data reported here were evaluated subject to the standard deviations outlined earlier. The vapor composition provides the most logical source of difficulty because of an inability to measure the low concentrations of methanol in the samples. While methanol content is small, it could have a major influence on the given values of hydrogen sulfide, whose mole fraction in the vapor was also small.

CONCLUSIONS

The thermodynamic model developed in this paper may be used to describe phase equilibrium behavior of methanol, carbon dioxide, hydrogen sulfide and nitrogen mixtures. Margules parameters determined by fitting the model to the six binary combinations of these constituents may be used to describe the multicomponent system without further adjustment. It is to be expected that predictions of equilibrium pressures in a bubble point calculation may be somewhat more accurate than predictions of equilibrium vapor compositions.

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NOMENCLATURE

a, b = constants in SRK equation of state
A_{ij}, A_{ji}, D_{ij} = binary Margules parameters
DP = $P_{model} - P_{exp}$
Dy = $y_{model} - y_{exp}$
$\%E_P$ = $(DP/P_{exp}) \times 100\%$
$\%E_y$ = $(Dy/y_{exp}) \times 100\%$
f_i = fugacity of i
f_i^0 = fugacity of i in reference state
H_i = Henry's constant for i
k_{ij}, K_{ij} = binary interaction constants in Redlich-Kwong and SRK equation of state, respectively
n_i = moles of i
N = number of components in mixture
P = pressure
P_r = reduced pressure
P_{c_i} = critical pressure of i
P_i^* = vapor pressure of i
R = gas constant
T = temperature
T_r = reduced temperature
v = molar volume
V = total volume
V_c = critical volume
v_i^L = liquid molar volume of i
$\bar{v}_i^L$ = partial molar volume of i in liquid
x_i = mole fraction of i in liquid phase
y_i = mole fraction of i in gas phase
z = compressibility factor $\equiv Pv/RT$

Greek Symbols

α = constant in SRK equation of state
β_{ijk} = constant in Margules equation
γ_i = activity coefficient of i
ϕ_i = fugacity coefficient of i
ϕ_i^* = fugacity coefficient of saturated i
ω = Pitzer acentric factor

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Connection between Relative Gain and Control Loop Stability and Design

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The objective of this paper is to point out the relationship between the relative gain array (RGA) and control system stability and design. Rigorous stability limits are presented for a general 2 × 2 system for several cases involving both steady state and dynamic interactions. These stability limits explicitly involve the RGA. Two specific examples of interaction in distillation models are also discussed.

SCOPE

One of the most useful control tools that has appeared in the control literature is the Bristol (1966) relative gain array (RGA). The RGA has been used to assess interaction between control loops and the use of the RGA by industry has grown steadily. The RGA has the potential of giving insight into very complex control problems with a minimum of computational effort. As originally presented, the RGA involved only steady-state considerations. More recently several investigators have considered dynamic extensions of the RGA.

A legitimate question that has been raised with the traditional RGA is how can a steady-state interaction measure give an accurate indication of the dynamic behavior of control systems. The purpose of this paper is to help provide an answer to this important question. The primary focus of this paper is on control system stability although controller design is also treated. For an interacting 2 × 2 process modeled with transfer functions, rigorous relationships for control system stability which involve the RGA explicitly are presented for several cases. In addition, for two specific distillation column examples the relationship between a dynamic extension of the RGA and control system design is examined. It is shown that there is a strong connection between the RGA and control system stability and design.

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