

STANDARD STATE FUGACITY COEFFICIENTS, FOR THE HYPOTHETICAL VAPOR
BY BRIDGING FROM THE REAL GAS FUGACITY COEFFICIENTS
THROUGH THE GIBBS-DUHEM EQUATION

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PREFACE

A generalized method for determining the standard state fugacity coefficients for hypothetical vapors was developed by bridging from the fugacity coefficient of the real gaseous component to that of the hypothetical gaseous component through the Gibbs-Duhem equation. Binary systems of hydrogen sulfide with methane, ethane, propane and n-pentane selected from the literature formed the basis for the correlation.

The application of this method for the development of a similar correlation for the standard state fugacity coefficients of hypothetical liquids is outlined.

I sincerely appreciate the aid of Professor W. C. Edmister in suggesting the topic of this thesis and in guiding it to its completion. I am also grateful to Professor Edmister for arranging his schedule to the convenience of the author as a "drive in" student.

I am greatly indebted to Mr. A. N. Stuckey, Jr. for his suggestions and aid toward the completion of this work, particularly his work in calculating the fugacity coefficients on the IBM-650 digital computer.

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CHAPTER I

INTRODUCTION

The technological advances in the petroleum and chemical industries during the recent past have demonstrated the need for composition dependent distribution ratios, or K-values, for components in coexisting equilibrium liquid-vapor phases. The necessity of a quantitative expression defining the distribution of a component in a mixture between the vapor and liquid phases became apparent early in the century when the invention of the internal combustion engine created an interest in natural gasoline and the "front end" components of crude oil as a fuel. Raoult's law expressed in equation form as

$$p_i = P_i^o x_i \quad (\text{I-1})$$

where

- p_i = partial pressure of component i
- P_i^o = vapor pressure of pure component i
- x_i = mole fraction of component i in liquid

and Dalton's law expressed in equation form as

$$p_i = y_i P \quad (\text{I-2})$$

where

- y_i = mole fraction of component i in vapor
- P = system pressure

supplied the basis for the first efforts to create an expression for the equilibrium distribution ratio. Giving this equilibrium distribution ratio the symbol, K , and defining it as the ratio of the mole fraction of a component in the vapor to its mole fraction in the liquid, a quantitative expression for K is written as.

$$K_i = y_i/x_i \quad (I-3)$$

where

K_i = equilibrium distribution ratio of component i

Substitution of the values of x and y supplied by Raoult's and Dalton's laws give this expression for K

$$K_i = P_i^0/P \quad (I-4)$$

Note that this K -value is a function only of the component identity, the temperature and the pressure of the system.

Because of the fortuitous circumstances that the hydrocarbons considered formed nearly ideal solutions, the operating pressures were low and loose product specifications permitted low product purity, the liquid and vapor phases approached the performance of Raoult's and Dalton's laws. The K -values so derived served the industry adequately for many years.

As the demand for purer products increased, the industry was forced to raise its operating pressures. At these higher pressures deviations from the Raoult's-Dalton's Law K increased until it did not adequately define the equilibrium ratio. To correct for this fugacities were substituted for pressures. This has for its basis the criterion for equilibrium that at a given system temperature and pressure the

chemical potential of a given component is the same in both phases. This is equivalent to equal fugacities of the component in both phases. This is stated analytically as

$$\bar{f}_i^L = \bar{f}_i^V \quad (\text{I-5})$$

where

\bar{f}_i^L = fugacity of component i in liquid mixture

\bar{f}_i^V = fugacity of component i in vapor mixture

and then assuming that the Lewis and Randall rule (which is based on Amagat's law of additive volumes) applies

$$\bar{f}_i^L = x_i f_i^L \quad \text{and} \quad \bar{f}_i^V = y_i f_i^V \quad (\text{I-6})$$

hence,

$$x_i f_i^L = y_i f_i^V \quad (\text{I-7})$$

and substitution into equation I-3 gives for K

$$K_i = f_i^L / f_i^V \quad (\text{I-8})$$

Equation I-8 formed the basis for the MIT K charts of W. K. Lewis (29) and the Michigan K charts of G. G. Brown (8). These K-values assume ideal solutions in both phases, hence correct only for the non-ideality of the vapor phase. These charts were widely used during the 1930's and 1940's.

During the early 1940's catalytic cracking became a major process in the petroleum industry and during the late 1940's catalytic reforming came into the picture. With these processes came large quantities of aromatics and other hydrocarbons as well as significant

quantities of nonhydrocarbons such as hydrogen, hydrogen sulfide and carbon dioxide. Solutions of these new hydrocarbon types deviated from ideality.

At this time it became apparent that the ideal K-values must be modified by a composition factor. One of the first attempts was the Polyco charts prepared by Benedict, et al. (2,3,4) which used the molal average boiling point as a parameter characterizing the solution. A replot of these charts was published by The M. W. Kellogg Company (27).

DePriester (12) modified the Kellogg charts using two parameters, one for the vapor phase and the other for the liquid phase, and with additional experimental data reduced the number of charts from 144 to 24.

Edmister and Ruby (14) generalized the Kellogg charts by using reduced temperatures and pressures, and the boiling point ratio. In so doing they were able to reduce the number of charts to six while at the same time making them more usable.

Gamson and Watson (16) suggested a method of using the convergence of the K-values to unity in calculating an activity coefficient to account for the deviation from ideal behavior of the vapor and liquid phases. This procedure was further developed by Smith and Watson (45) and the charts published by Smith and Smith (44).

Prausnitz, Edmister and Chao (35) transformed equation I-3 to the form

$$K_i = \frac{y_i}{x_i} = \frac{\left[\frac{\bar{f}_i^L / P x_i}{f_i^L / P} \right] \left[f_i^L / P \right]}{\bar{f}_i^V / P y_i} = \frac{\gamma_i^L \mathcal{V}_i}{\phi_i} \quad (\text{I-9})$$

where

γ_i^L = activity coefficient of component i in liquid

ϕ_i = fugacity coefficient of component i in vapor

\mathcal{V}_i = fugacity coefficient of pure component i in liquid

These authors introduced the concept of calculating the liquid activity coefficient through the solubility parameter and regular solution theory of Hildebrand (20).

Pigg (32) simplified this work by the assumption that the term involving the solubility parameters in the Scatchard-Hildebrand equation was insensitive to temperature as well as pressure.

Chao and Seader (9) used this same equation to make a general correlation of a large quantity of data.

Pipkin (33) as suggested by Edmister (15) transformed equation I-9 by dividing the ϕ_i term and the \mathcal{V}_i term by the fugacity coefficient of pure component i in the vapor to

$$K_i = \frac{\gamma_i^L}{\gamma_i^V} K_{\text{ideal}} \quad (\text{I-10})$$

where K_{ideal} is the value defined by equation I-8. This equation was used in correlating methane binaries.

The reader is referred to the original papers for the methods used in developing the correlations. Stuckey (46), Pipkin (33) and Edmister (15) present excellent reviews of the subject.

Purpose of This Work

The purpose of this work is to develop the necessary information for calculating the activity coefficients of hydrogen sulfide - hydrocarbon binaries. In binary equilibria one of the components always exists in the vapor at pressures above its vapor pressure and one component exists in the liquid at pressures below its vapor pressure or at temperatures above its critical temperature. The standard states for the calculation of the activity coefficients of equation I-10 are therefore frequently hypothetical for the heavy component in the vapor and for the light component in the liquid. This work using a method proposed by Hoffman, et al. (22) and modified by Stuckey (46) bridges from the activity coefficient of the light component in the vapor phase through the Gibbs-Duhem equation to the activity coefficient of the heavy component in the vapor phase. The hypothetical vapor phase fugacity coefficient of the pure heavy component is then calculated from the derived vapor phase activity coefficient and the fugacity coefficient of the component in the vapor mixture. From the criterion of equilibrium that the fugacity of a component in the vapor mixture must be equal to its fugacity in the liquid mixture, the activity coefficient of the heavy component in the liquid is calculated. This calculated activity coefficient is then compared to the one calculated by the Scatchard-Hildebrand equation.

In summary this work accomplishes three things

1. Calculates the hypothetical fugacity coefficient of the heavy component in the vapor
2. Calculates the activity coefficient of the heavy component

in the liquid by bridging from the fugacity coefficient of this component in the vapor mixture.

3. Compares the activity coefficient calculated by the above procedure with that calculated by the Scatchard-Hildebrand equation.

CHAPTER II

DEVELOPMENT OF EQUATIONS

Chemical Potential

The free energy of a system defined in terms of temperature, pressure and the moles of the components present and stated mathematically is

$$dG = \left[\frac{\partial G}{\partial T} \right]_{P, n} dT + \left[\frac{\partial G}{\partial P} \right]_{T, n} dP + \sum_{n_1}^{n_N} \left[\frac{\partial G}{\partial n_i} \right]_{T, P, n_j} dn_i \quad (II-1)$$

where

G = free energy of the system

T = system temperature

P = system pressure

n = total number of components present

n = total number of moles present

n_i = total number of moles of component i present

n_j = total number of moles of components other than i present

$\sum_{n_1}^{n_N}$ = summation of all components from n_1 to n_N

A thermodynamic relationship for a closed system, i. e., one of constant mass, states that

$$dG = -SdT + VdP \quad (\text{II-2})$$

which gives

$$\left[\frac{\partial G}{\partial T} \right]_{P,n} = -S \quad \text{and} \quad \left[\frac{\partial G}{\partial P} \right]_{T,n} = V \quad (\text{II-3})$$

therefore

$$dG = -SdT + VdP + \sum \left[\frac{\partial G}{\partial n_i} \right]_{T,P,n_j} dn_i \quad (\text{II-4})$$

Similarly a definition for the internal energy (E) as a function of entropy (S), temperature (T), and the number of moles present (n) is written as

$$dE = \left[\frac{\partial E}{\partial S} \right]_{V,n} dS + \left[\frac{\partial E}{\partial V} \right]_{S,n} dV + \sum_{n_1}^{n_N} \left[\frac{\partial E}{\partial n_i} \right]_{S,V,n_j} dn_i \quad (\text{II-5})$$

and from the relationship for a closed system

$$dU = dQ - PdV$$

$$dE = TdS - PdV \quad (\text{II-6})$$

which gives

$$\left[\frac{\partial E}{\partial S} \right]_{V,n} = T \quad \text{and} \quad \left[\frac{\partial E}{\partial V} \right]_{S,n} = -P \quad (\text{II-7})$$

therefore the expression for dE is

$$dE = TdS - PdV + \sum \left[\frac{\partial E}{\partial n_i} \right]_{S,V,n_j} dn_i \quad (\text{II-8})$$

Writing the definition for the free energy of a system and differentiating gives

$$\begin{aligned}
 G &= U - TS + PV \\
 G &= H - TS \\
 dG &= dH - TdS - SdT
 \end{aligned}
 \tag{II-9}$$

or

$$dG = dE + PdV + VdP - TdS - SdT \tag{II-10}$$

Substituting equation II-4 and II-8 into equation II-10 gives

$$\sum \left[\frac{\partial G}{\partial n_i} \right]_{T,P,n_j} dn_i = \sum \left[\frac{\partial E}{\partial n_i} \right]_{S,V,n_j} dn_i \tag{II-11}$$

Defining the partial quantities as

$$\bar{G}_i = \left[\frac{\partial G}{\partial n_i} \right]_{T,P,n_j} \quad \text{and} \quad \bar{E}_i = \left[\frac{\partial E}{\partial n_i} \right]_{S,V,n_j} \tag{II-12}$$

gives from equation II-11

$$\bar{G}_i = \left[\frac{\partial G}{\partial n_i} \right]_{T,P,n_j} = \left[\frac{\partial E}{\partial n_i} \right]_{S,V,n_j} = \bar{E}_i \tag{II-13}$$

A similar analysis shows the partial enthalpy, \bar{H}_i , and work function, \bar{A}_i , equal to each other and to \bar{G}_i and \bar{E}_i . J. Willard Gibbs termed these partial quantities, chemical potential.

The criterion for equilibrium states that, at a constant system temperature and pressure, the chemical potential of component i in the vapor must be equal to its chemical potential in the liquid.

Stated symbolically

$$\mu_i^V = \mu_i^L \tag{II-14}$$

The chemical potential as such is difficult to use, however fugacity, a much more convenient term, can be related to the chemical potential through the free energy.

Fugacity

Integrating the second portion of equation II-3 at constant temperature gives

$$G_2 - G_1 = \int_{P_1}^{P_2} V dP \quad (\text{II-15})$$

where the subscripts 1 and 2 represent different points on the same isotherm.

For an ideal gas

$$G_2 - G_1 = RT \int_{P_1}^{P_2} d(\ln P) \quad (\text{II-16})$$

or

$$G_2 - G_1 = RT \ln(P_2/P_1) \quad (\text{II-17})$$

Equation II-17 applies to an ideal gas only. Fugacity is an expression for pressure that makes equation II-17 applicable to real gases. Therefore for real gases

$$G_2 - G_1 = RT \ln(f_2/f_1) \quad (\text{II-18})$$

Equation II-18 in differential form is

$$dG = RT d(\ln f) \quad (\text{II-19})$$

and defining the fugacity of component i in a mixture in a similar manner leads to

$$d\bar{G}_i = RT d(\ln \bar{F}_i) \quad (\text{II-20})$$

or

$$d\mu_i = d\bar{G}_i = RT d(\ln \bar{f}_i) \quad (\text{II-21})$$

Hence equating the fugacities of a component in both phases is the equal of chemical potentials as a criterion of equilibrium.

In terms of a real gas equation II-15 can be written in differential form as

$$(dG)_T = \frac{ZRT}{P} dP = ZRT d(\ln P) \quad (\text{II-22})$$

and substituting into equation II-19

$$ZRT d(\ln P) = RT d(\ln f) \quad (\text{II-23})$$

$\frac{ZRT}{RT} = \frac{d(\ln f)}{d(\ln P)}$
 $Z = \frac{d(\ln f)}{d(\ln P)}$

or rearranging, subtracting one from each side and integrating

$$\ln(f/P) = \int_0^P (Z - 1) d(\ln P) \quad (\text{II-24})$$

$Z - 1 = \frac{d(\ln f) - d(\ln P)}{d(\ln P)}$

where

$$\lim_{P \rightarrow 0} \frac{f}{P} = 1$$

$f = P$

or in terms of volume

$$\ln(f/P) = -\frac{1}{RT} \int_0^P \left[\frac{RT}{P} - \underline{V} \right] dP \quad (\text{II-25})$$

$\left(\frac{PV}{RT} - 1 \right) \left(\frac{RT}{P} \right) dP$
 $-\frac{1}{RT} (PV - RT) \frac{RT}{P} dP$
 $\frac{1}{P} dP$
 $RT \frac{PV}{RT} = PV$
 $\frac{PV}{RT} = Z$

f/P is by definition the fugacity coefficient of a pure substance.

Fugacity and Activity Coefficients

The fugacity coefficient of component i in a mixture is defined as

$$\phi_i = \bar{f}_i / P y_i \quad (\text{II-26})$$

and the activity coefficient as

$$\gamma_i = \bar{f}_i / f_i^* x_i \quad (\text{II-27})$$

The fugacity and activity coefficients are obtained from pressure, volume, temperature and composition data. The free energy of an ideal gas is given by the equation

$$G^* = H^* - TS^* \quad (\text{II-28})$$

where $*$ refers to the ideal gaseous state. The entropy for an ideal gaseous mixture is

$$S^* = \sum \tilde{n}_i S_i^* - R \sum \tilde{n}_i \ln \left[\frac{\tilde{n}_i}{\sum \tilde{n}_i} \right] \quad (\text{II-29})$$

Combining equations II-28 and II-29 gives for an ideal gas mixture

$$G^* = \sum \tilde{n}_i H_i^* - T \sum \tilde{n}_i S_i^* + RT \sum \tilde{n}_i \ln \left[\frac{\tilde{n}_i}{\sum \tilde{n}_i} \right] \quad (\text{II-30})$$

Since

$$\sum \tilde{n}_i G_i^* = \sum \tilde{n}_i H_i^* - T \sum \tilde{n}_i S_i^* \quad (\text{II-31})$$

equation II-30 reduces to

$$G^* = \sum \tilde{n}_i G_i^* + RT \sum \tilde{n}_i \ln \left[\frac{\tilde{n}_i}{\sum \tilde{n}_i} \right] \quad (\text{II-32})$$

and combining with equation II-15 leads to

$$G = \int_{P^*}^P V dP + \sum n_i G_i^* + RT \sum n_i \ln \left[\frac{n_i}{\sum n_i} \right] \quad (\text{II-33})$$

where G_1 and G_2 are equal to G^* and G respectively. Differentiating equation II-33 with respect to the moles of component i gives

$$\frac{\partial G}{\partial n_i} = \mu_i = \int_{P^*}^P \left[\frac{\partial V}{\partial n_i} \right] dP + RT \ln x_i + G_i^* \quad (\text{II-34})$$

By definition

$$\int_{P^*}^P \left[\frac{\partial V}{\partial n_i} \right] dP = \int_{P^*}^P \bar{V}_i dP = RT \ln(\bar{f}_i / f_i^*) \quad (\text{II-35})$$

applies to real gases. Combining this equation with equation II-34 gives

$$\mu_i = RT \ln(\bar{f}_i x_i / f_i^*) + G_i^* \quad (\text{II-36})$$

and choosing the ideal gas where $f_i^* = y_i P^*$ as the standard state and changing x_i to y_i gives

$$\mu_i = RT \ln(\bar{f}_i / P^*) + G_i^* \quad (\text{II-37})$$

Equating the right hand sides of equations II-34 and II-37

$$RT \ln(\bar{f}_i / y_i P^*) = \int_{P^*}^P \bar{V}_i dP \quad (\text{II-38})$$

or

$$RT \ln(\bar{f}_i / y_i P^*) = \int_{P^*}^P \frac{RT}{P} dP - \int_{P^*}^P \left[\frac{RT}{P} - \bar{V}_i \right] dP \quad (\text{II-39})$$

$RT \ln \frac{P}{P^*}$
 $PV = nRT$
 $n = \frac{PV}{RT}$

and integrating

$$\ln(\bar{f}_i/y_i P) = -\frac{1}{RT} \int_{P^*}^P \left[\frac{RT}{P} - \bar{v}_i \right] dP \quad (\text{II-40})$$

Allowing the lower limit of integration to become zero gives the fugacity coefficient of a real gas in a mixture as

$$\ln \phi_i = \ln(\bar{f}_i/y_i P) = -\frac{1}{RT} \int_0^P \left[\frac{RT}{P} - \bar{v}_i \right] dP \quad (\text{II-41})$$

Equation II-41 can be applied to a liquid mixture as well as a gaseous mixture.

The activity coefficient is obtained by subtracting equation II-25 from equation II-41 giving

$$\gamma_i^V = \ln(\bar{f}_i^V/y_i f_i^V) = -\frac{1}{RT} \int_0^P (\underline{v}_i^V - \bar{v}_i^V) dP \quad (\text{II-42})$$

The activity coefficient of the liquid is written in the same manner by substituting x_i for y_i and using the liquid volumes in place of the vapor volumes thus,

$$\gamma_i^L = \ln(\bar{f}_i^L/x_i f_i^L) = -\frac{1}{RT} \int_0^P (\underline{v}_i^L - \bar{v}_i^L) dP \quad (\text{II-43})$$

Application

From the criterion of equilibrium that $\bar{f}_i^L = \bar{f}_i^V$ and the definition of the K-value the equation for the calculation of K-values evolves by subtracting equation II-43 from equation II-42

$$\ln(\bar{f}_i^L/x_i f_i^L) - \ln(\bar{f}_i^V/y_i f_i^V) = -\frac{1}{RT} \int_0^P \left[(\underline{v}_i^L - \bar{v}_i^L) - (\underline{v}_i^V - \bar{v}_i^V) \right] dP \quad (\text{II-44})$$

or

$$K_i = \frac{y_i}{x_i} = \left[\frac{f_i^L}{f_i^V} \right] e^{-\frac{1}{RT} \int_0^P \left[(\bar{v}_i^L - \bar{v}_i^L) - (\bar{v}_i^V - \bar{v}_i^V) \right] dP} \quad (\text{II-45})$$

Defining K_{ideal} as f_i^L/f_i^V and solving for the activity coefficients from equations II-42 and II-43, equation II-45 reduces to

$$K_i = y_i/x_i = \left[\frac{\gamma_i^L}{\gamma_i^V} \right] K_{\text{ideal}} \quad (\text{II-46})$$

Equation II-45 is a rigorous thermodynamic relationship but is of limited usefulness because of the difficulty in obtaining partial molar volumes.) It is here that equations of state with their compromising simplifications are introduced to calculate fugacity coefficients and activity coefficients. In this work the relatively simple equation of state of Redlich and Kwong (41) is used to calculate vapor phase fugacity coefficients for both components in the vapor mixture and for the pure light component in the vapor. This equation is further discussed in Appendix B.

Pure liquid fugacity coefficients for the heavy component in the liquid were calculated by the Chao-Seader equation. This equation is discussed in Appendix C.

The liquid activity coefficients were calculated for both components in the liquid phase by use of the Scatchard-Hildebrand equation as discussed in Appendix D.

Gibbs-Duhem Equation

Substitution of equation II-13, defining the chemical potential in terms of \bar{E}_i , into equation II-8 gives

$$dE = TdS - PdV + \sum \mu_i dn_i \quad (\text{II-47})$$

Integrating equation II-47 at constant composition

$$E = TS - PV + \sum \mu_i n_i \quad (\text{II-48})$$

and then differentiating without any restrictions

$$dE = SdT + TdS - VdP - PdV + \sum \mu_i dn_i + \sum n_i d\mu_i \quad (\text{II-49})$$

Subtraction of equation II-47 from equation II-49 results in

$$\sum n_i d\mu_i = VdP - SdT \quad (\text{II-50})$$

At constant temperature and pressure

$$\left(\sum n_i d\mu_i = 0 \right)_{T,P} \quad (\text{II-51})$$

and dividing by $\sum n_i$ gives

$$\left(\sum x_i d\mu_i = 0 \right)_{T,P} \quad (\text{II-52})$$

This is one of the forms of the Gibbs-Duhem equation. Since the use of chemical potentials is inconvenient, equation II-52 is more usable in terms of activity coefficients.

The partial derivative of equation II-21 with respect to x_i at constant temperature gives

$$\left[\frac{\partial \mu_i}{\partial x_i} \right]_T dx_i = RT \left[\frac{\partial \ln \bar{f}_i}{\partial x_i} \right]_T dx_i \quad (\text{II-53})$$

and the same for equation II-52

$$\left[x_i \frac{\partial \mu_i}{\partial x_i} dx_i = 0 \right]_{T,P} \quad (\text{II-54})$$

Then for a binary mixture

$$x_1 \left[\frac{\partial \ln \bar{f}_1}{\partial x_1} \right] dx_1 + x_2 \left[\frac{\partial \ln \bar{f}_2}{\partial x_2} \right] dx_2 = 0 \quad (\text{II-55})$$

and since $dx_1 = -dx_2$

$$x_1 \left[\frac{\partial \ln \bar{f}_1}{\partial x_1} \right] = x_2 \left[\frac{\partial \ln \bar{f}_2}{\partial x_2} \right] \quad (\text{II-56})$$

Since the standard reference state fugacity is constant at constant temperature and pressure, and from the definition of the activity coefficient, equation II-56 becomes

$$x_1 \left[\frac{\partial \ln \gamma_1 x_1}{\partial x_1} \right] = x_2 \left[\frac{\partial \ln \gamma_2 x_2}{\partial x_2} \right] \quad (\text{II-57})$$

or

$$x_1 \left[\frac{\partial \ln \gamma_1}{\partial x_1} \right] + x_1 \left[\frac{\partial \ln x_1}{\partial x_1} \right] = x_2 \left[\frac{\partial \ln \gamma_2}{\partial x_2} \right] + x_2 \left[\frac{\partial \ln x_2}{\partial x_2} \right] \quad (\text{II-58})$$

and since

$$\frac{x_1 \partial \ln x_1}{\partial x_1} = \frac{x_2 \partial \ln x_2}{\partial x_2} = 1 \quad (\text{II-59})$$

equation II-56 becomes

$$x_1 \left[\frac{\partial \ln \gamma_1}{\partial x_1} \right]_{T,P} = x_2 \left[\frac{\partial \ln \gamma_2}{\partial x_2} \right]_{T,P} \quad (\text{II-60})$$

For a binary solution

$$\partial x_1 = \partial(1 - x_2) \quad (\text{II-61})$$

Therefore equation II-60 becomes

$$x_1 d \ln \gamma_1 = -x_2 d \ln \gamma_2 \quad (\text{II-62})$$

This is the form of the Gibbs-Duhem equation used later in this work to bridge from the activity coefficient of one component in a binary mixture to the activity coefficient of the other component.

CHAPTER III

METHOD OF PROCESSING DATA

Vapor-liquid equilibrium data for solutions of hydrogen sulfide and methane, ethane, propane and n-pentane were selected from the literature. This data was found either as x-y data, i. e., the composition of each phase determined at specified temperature and pressure conditions, or as P-V-T data, i. e., the pressure and temperature at which a solution of given composition exists in the vapor phase and in the liquid phase. The x-y data were used in this work. Where necessary the P-V-T data were replotted as pressure versus the composition of each phase at constant temperature. From these plots the necessary x-y data were obtained for each system at the selected isotherms.

Fugacity Coefficients of Vapor Phase

The fugacity coefficients of each component in the vapor phase mixture were calculated by the Redlich-Kwong equation of state as were the fugacity coefficients of the pure light component. These calculations were made on an IBM-650 digital computer. The Redlich-Kwong equation of state is discussed in Appendix B and an example of the calculating procedure is illustrated in Appendix H.

Activity Coefficients in the Vapor Phase

The activity coefficient of the pure light component in the vapor phase was calculated by dividing the fugacity coefficient of that component in the mixture by its fugacity coefficient in the pure state. The standard state was defined as that of the pure component at the same temperature and pressure conditions. Because of the conditions selected the standard state of the heavy component in the mixture becomes hypothetical, i.e., the pure heavy component cannot exist at the pressure and temperature chosen. Therefore, a hypothetical fugacity coefficient is necessary at these conditions to directly obtain an activity coefficient for the heavy component in the vapor. In this work, as suggested by Hoffman, et al. (22) and further developed by Stuckey (46), the activity coefficient of the heavy component in the vapor was calculated by bridging from the activity coefficient of the light component in the vapor by use of the Gibbs-Duhem equation in the form

$$\ln \gamma_2 = - \int_0^y \frac{y_1}{1 - y_1} d \ln \gamma_1 \quad (\text{III-1})$$

The logarithm of γ_1 , being determined as mentioned above from the Redlich-Kwong fugacity coefficients, was plotted versus the mole fraction of the light component in the vapor. The logarithm of γ_2 was calculated by a numerical integration of equation III-1 as shown in Appendix H. It is obvious from equation III-1 that reliable values of γ_2 will result only when sufficient data points exist at low concentrations of the light component to define adequately the curve of the right hand side of equation III-1. Where necessary,

these points were obtained by extrapolation of the data by a plot of $\log P$ versus y_1 to the vapor pressure of the heavy component at $y_1 = 0$. A sample calculation of γ_1 and the numerical integration to obtain γ_2 are illustrated in Appendix H.

Hypothetical Fugacity Coefficient in Vapor Phase

The hypothetical vapor phase fugacity coefficient was calculated by the equation

$$(f_2^V/P)_h = \frac{(\bar{f}_2^V/Py_2)}{\gamma_2^V} \quad (\text{III-2})$$

where (\bar{f}_2^V/Py_2) and γ_2^V are calculated as described above.

The hypothetical vapor fugacity coefficients so calculated are plotted in Figures 1 to 4 for several isotherms as a function of the reduced pressure. Figures 5 to 7 show the $(f_2^V/P)_h$ data replotted with even increments of reduced temperature as a parameter. These were obtained by first cross plotting the $(f_2^V/P)_h$ data of Figures 1-4 versus T_r at constant P_r , followed by the replots of Figures 5-7.

Liquid Phase Activity Coefficient

The activity coefficient of the heavy component in the liquid was calculated by bridging from the fugacity coefficient of this component in the vapor mixture. This can be done as a result of the criterion of equilibrium that

$$\bar{f}_i^L = \bar{f}_i^V \quad (\text{I-5})$$

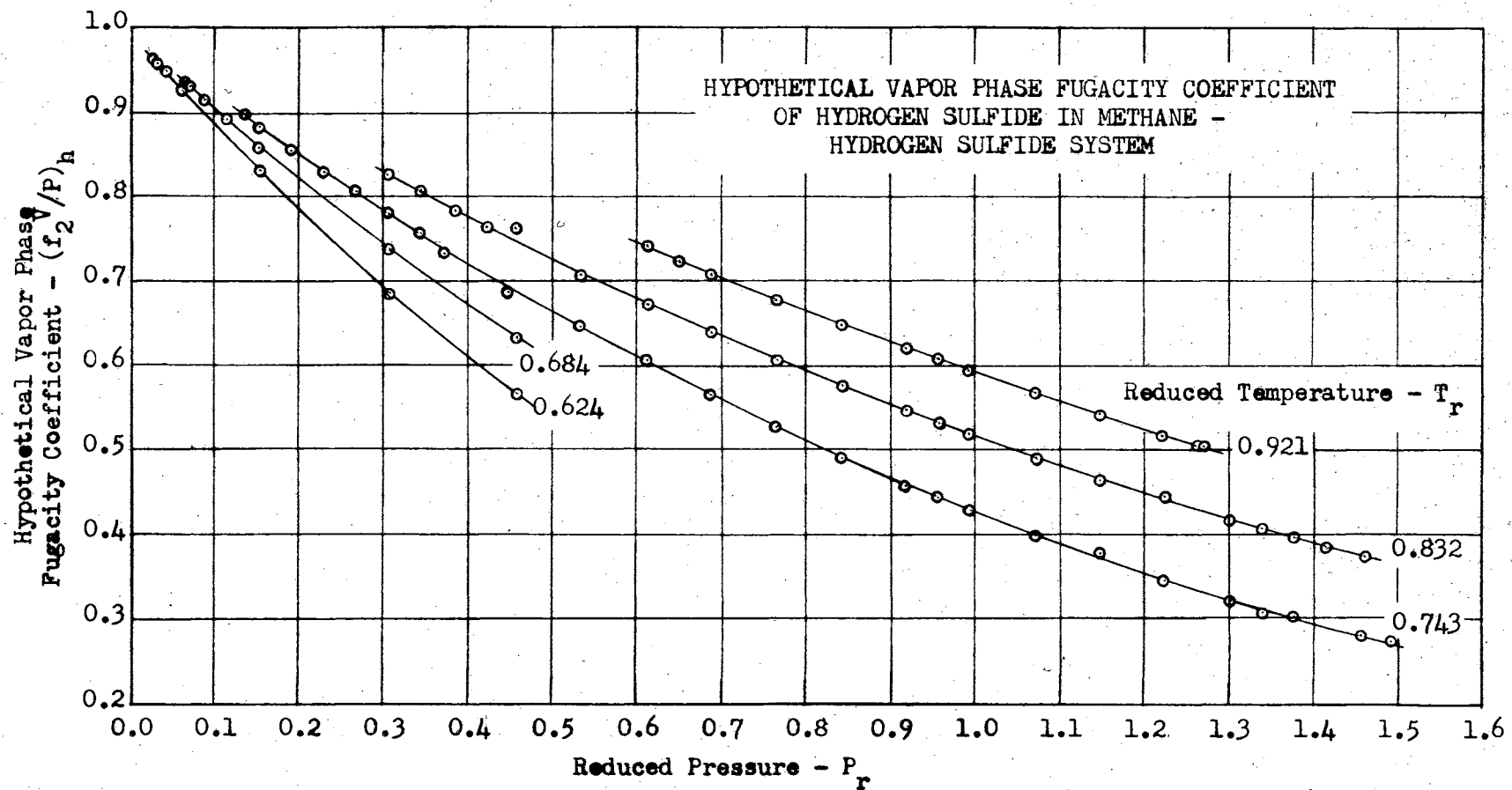


Figure 1

Hypothetical Vapor Phase Fugacity Coefficient of Hydrogen Sulfide
in Methane - Hydrogen Sulfide System (28,37)

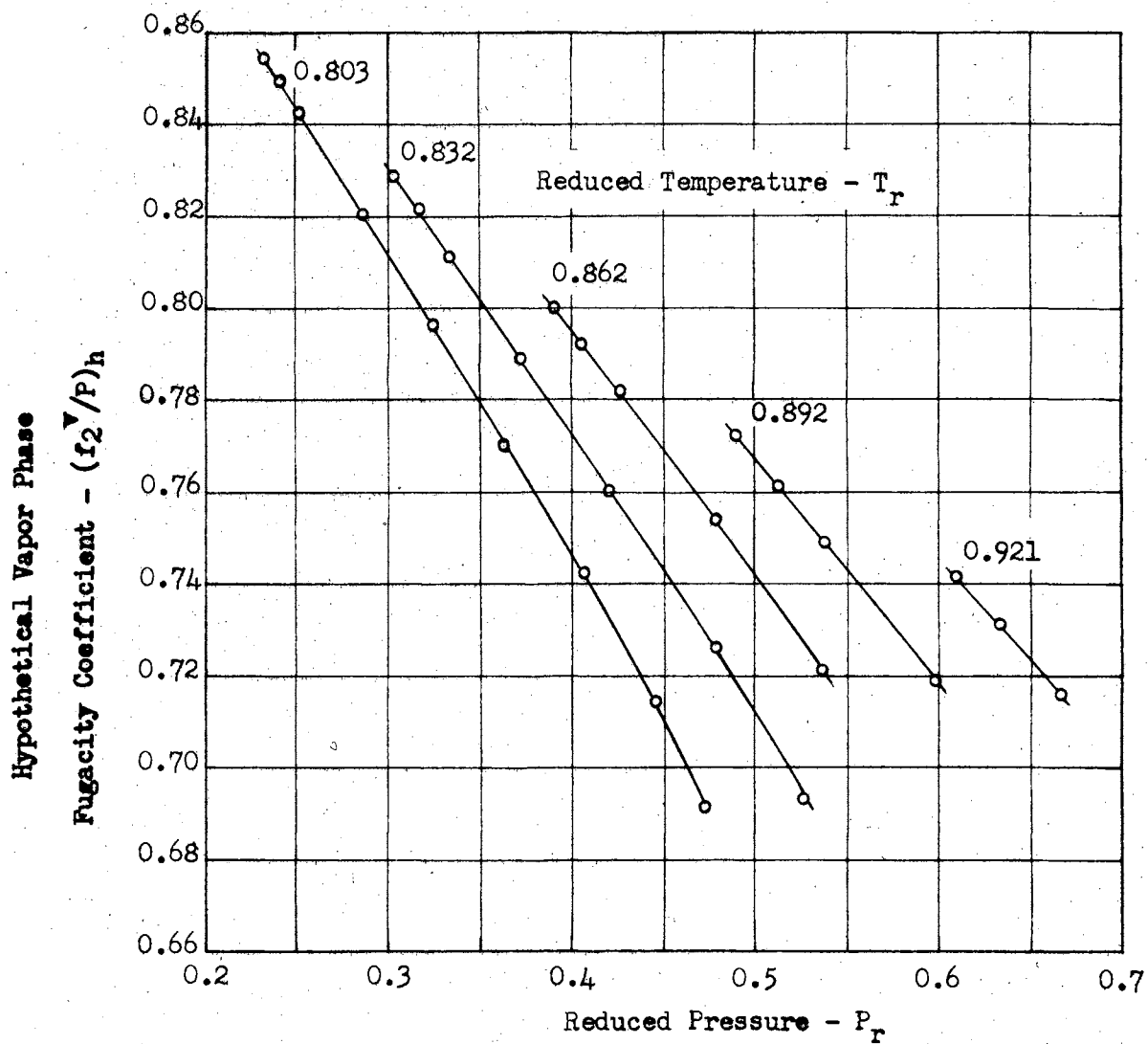


Figure 2

Hypothetical Vapor Phase Fugacity Coefficient of Hydrogen Sulfide in Ethane - Hydrogen Sulfide System (25)

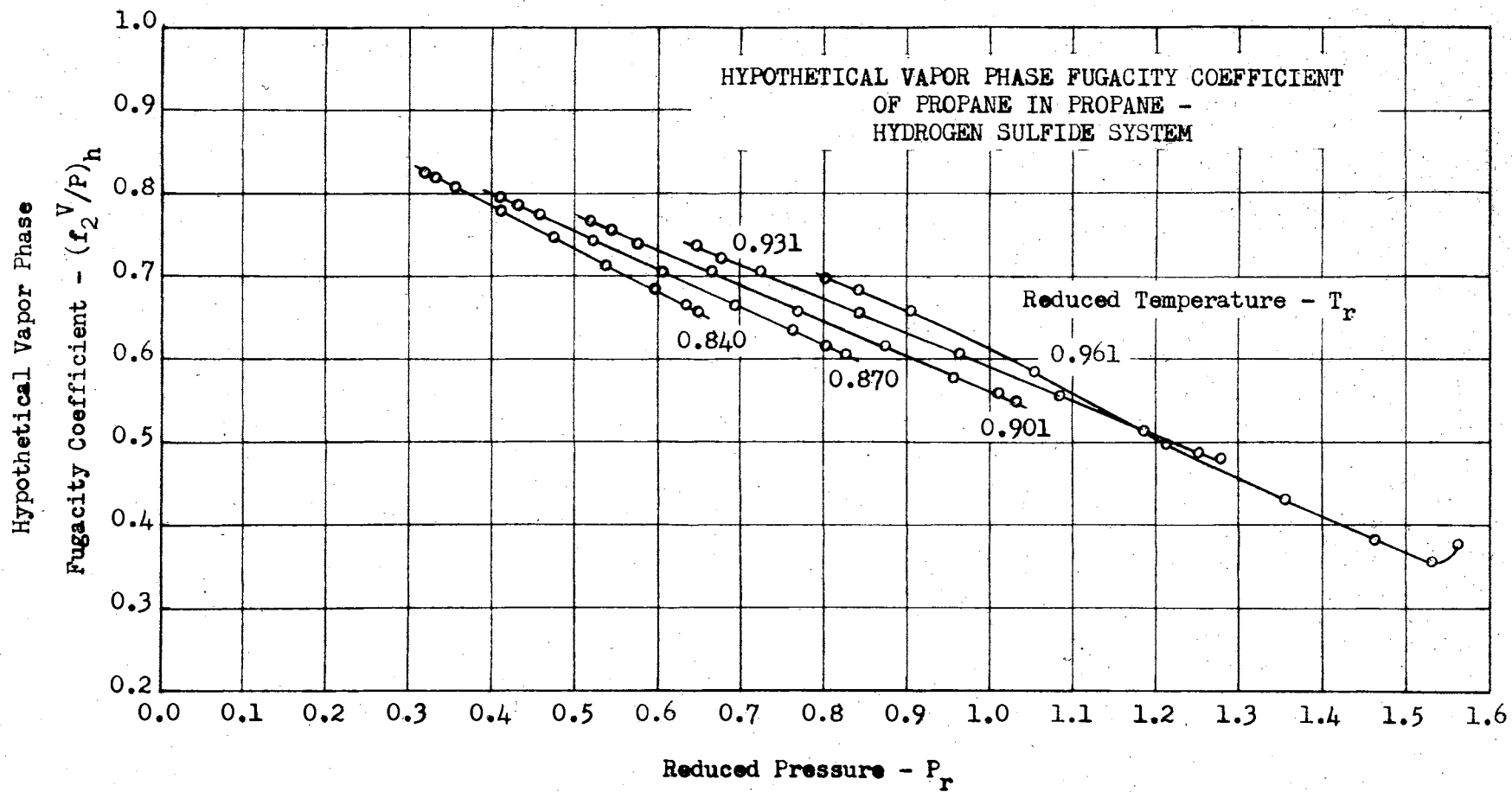


Figure 3
Hypothetical Vapor Phase Fugacity Coefficient of Propane in
Propane-Hydrogen Sulfide System (26)

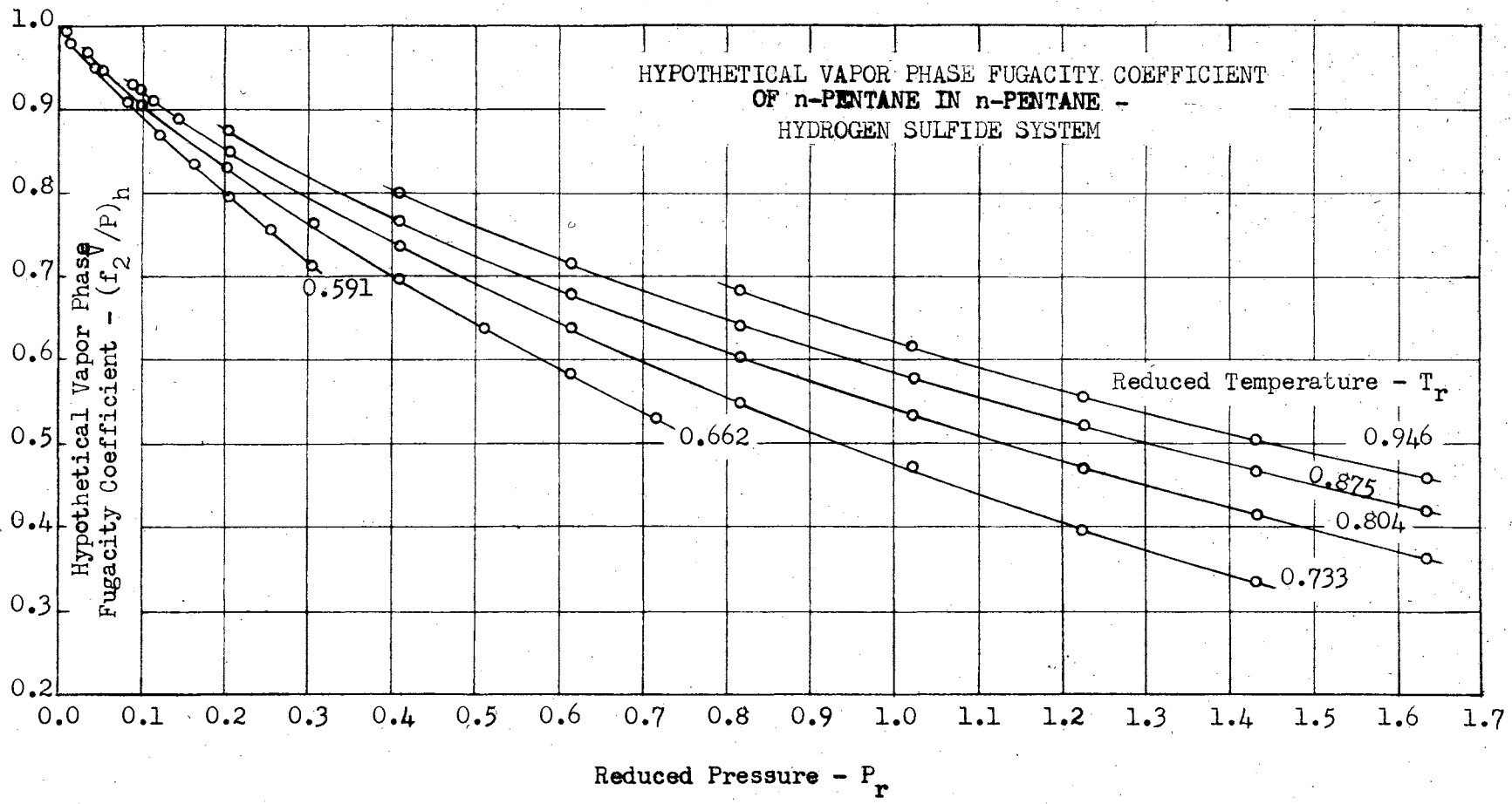


Figure 4

Hypothetical Vapor Phase Fugacity Coefficient of
n-Pentane in n-Pentane-Hydrogen Sulfide System (39)

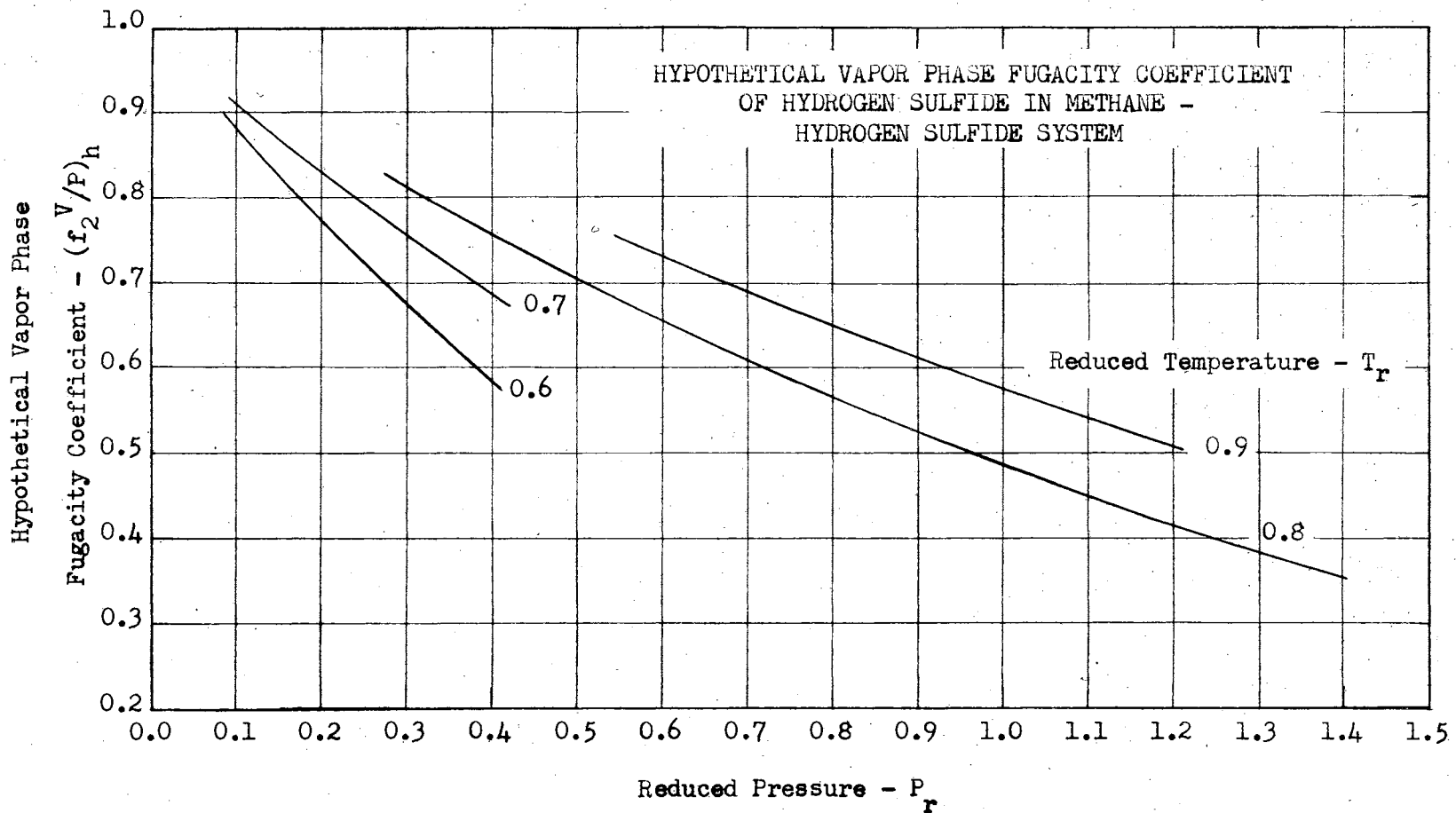


Figure 5

Hypothetical Vapor Phase Fugacity Coefficient of Hydrogen Sulfide in
Methane-Hydrogen Sulfide System

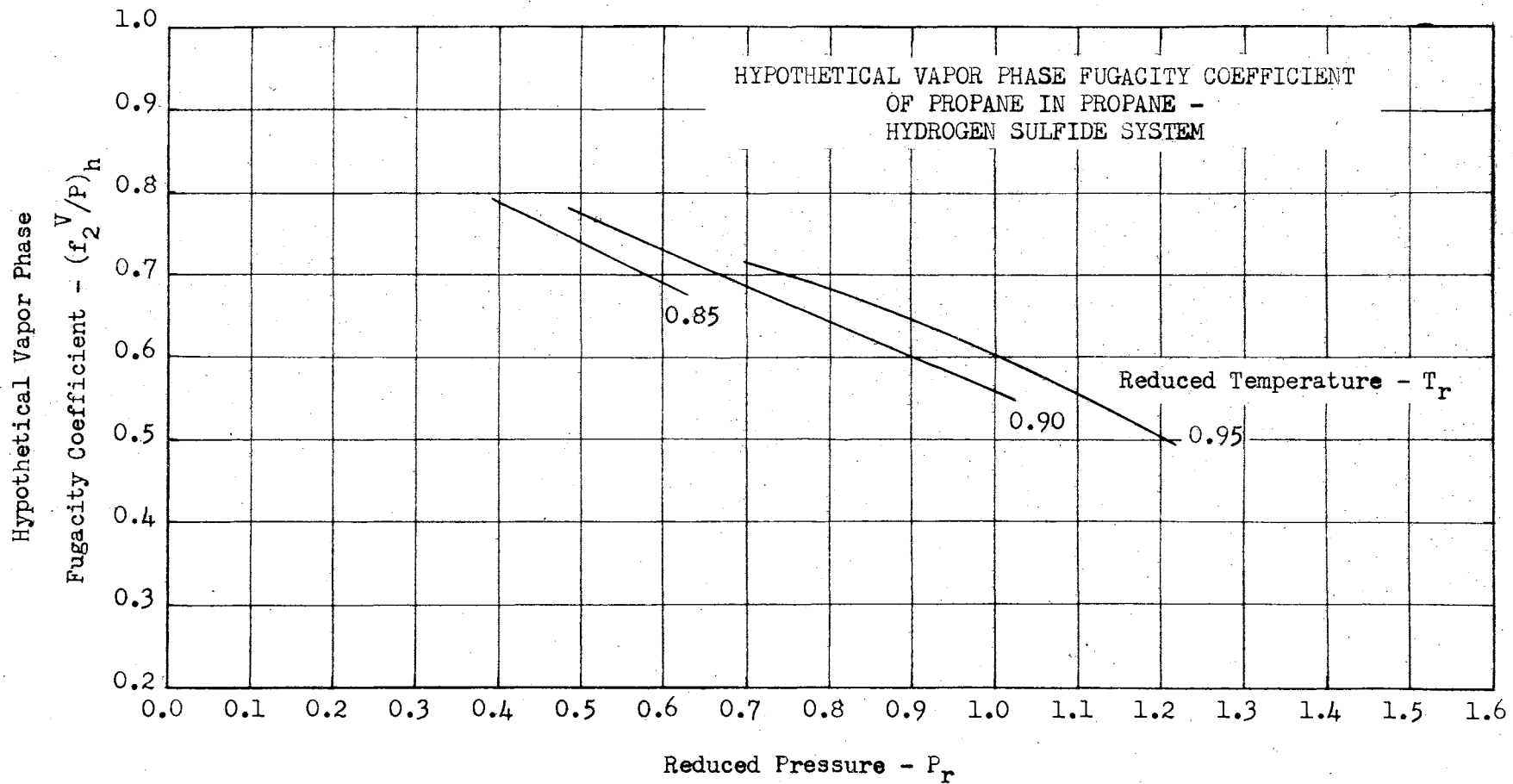


Figure 6

Hypothetical Vapor Phase Fugacity Coefficient of Propane in Propane-Hydrogen Sulfide System

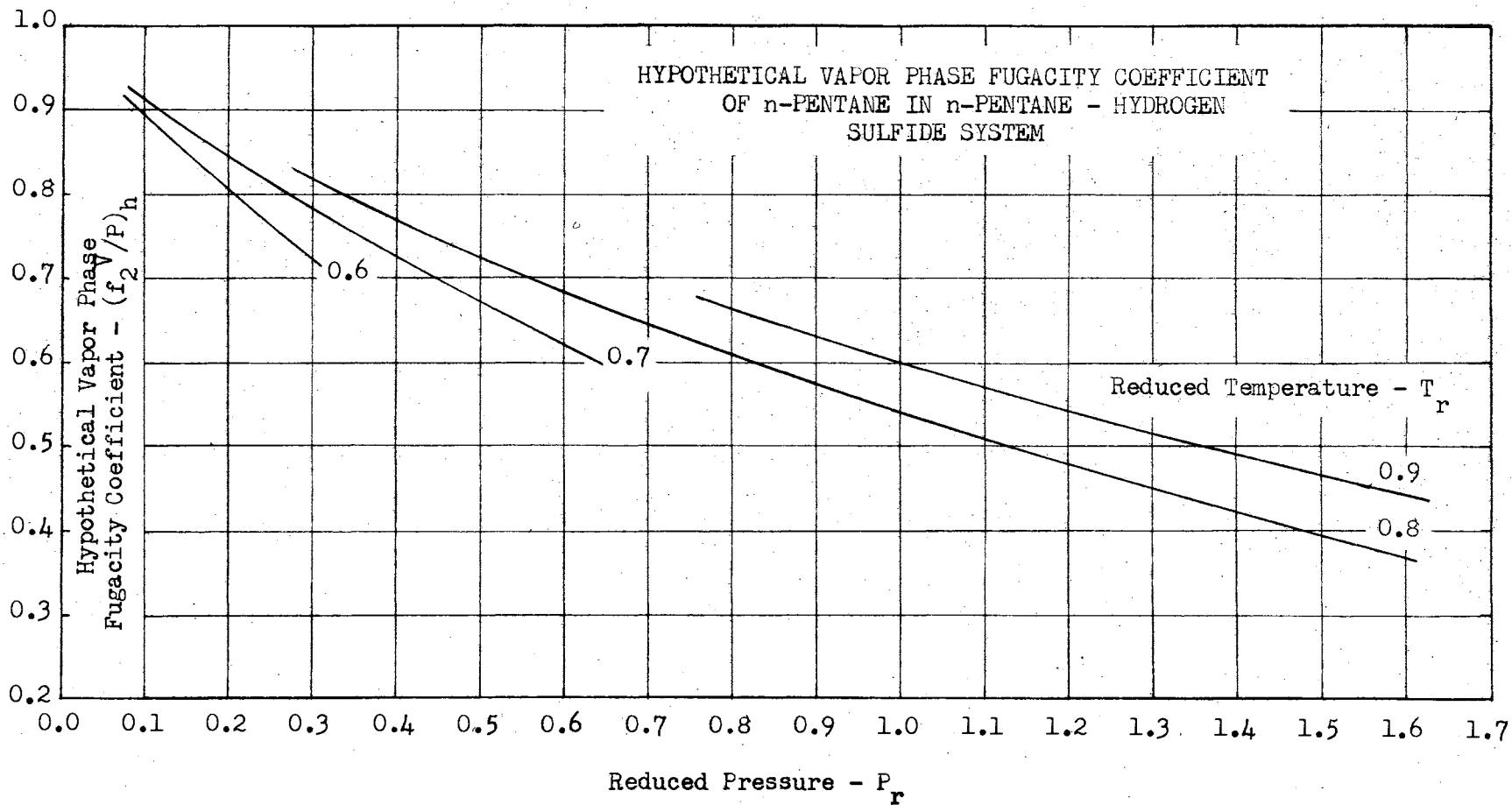


Figure 7

Hypothetical Vapor Phase Fugacity Coefficient of n-Pentane in
n-Pentane-Hydrogen Sulfide System

The calculating equation is

$$\gamma_2^L = \frac{(\phi_2)(y_2/x_2)}{(f_2^L/P)} \quad (\text{III-3})$$

The x-y data is from the experimental source, ϕ_2 from the Redlich-Kwong equation of state as previously discussed. The fugacity coefficient of the pure heavy component in the liquid was calculated from the Chao-Seader equation as discussed in Appendix C. A sample calculation is illustrated in Appendix H.

The values of γ_2^L so obtained are tabulated in Tables III to XXIII inclusive. An illustration of the calculation appears in Appendix H.

The liquid phase activity coefficients for both components were also calculated from the Scatchard-Hildebrand equation. This was done to obtain a comparison of the two methods of calculating the activity coefficient of the heavy component in the liquid phase. A comparison of the activity coefficient of hydrogen sulfide in the liquid phase of the methane-hydrogen sulfide system at 40°F. calculated by equation III-3 and the Scatchard-Hildebrand equation is shown in Figure 8. The Scatchard-Hildebrand equation is discussed in Appendix D and a sample calculation is illustrated in Appendix H.

To put the data in the form used by Pitzer (11), i. e., a fugacity coefficient for the simple fluid ($\omega = 0$) and a correction to the simple fluid for acentric factor, the data for the hypothetical vapor phase fugacity coefficient for hydrogen sulfide in the methane-hydrogen sulfide system from Figure 5 and that for the n-pentane in the n-pentane-hydrogen sulfide system from Figure 7 were used. The

equation

$$(f_2^V/P)_h = \left[(f_2^V/P)_h^{\circ} \right] \left[(f_2^V/P)_h \right]^{(1)} \quad (\text{III-4})$$

was solved simultaneously for $(f_2^V/P)_h^{\circ}$, the fugacity coefficient of the simple fluid, and $(f_2^V/P)_h^{(1)}$, the correction for acentric factor, at values of $(f_2^V/P)_h$ taken from Figures 5 and 7 at constant values of T_r and P_r . The acentric factors for hydrogen sulfide and n-pentane were used with the hypothetical vapor phase fugacity coefficients from Figure 5 and Figure 7 respectively. The hypothetical vapor phase fugacity coefficient so obtained for the simple fluid is plotted versus the reduced pressure at several isotherms in Figure 9. The correction for acentric factor is plotted similarly in Figure 10.

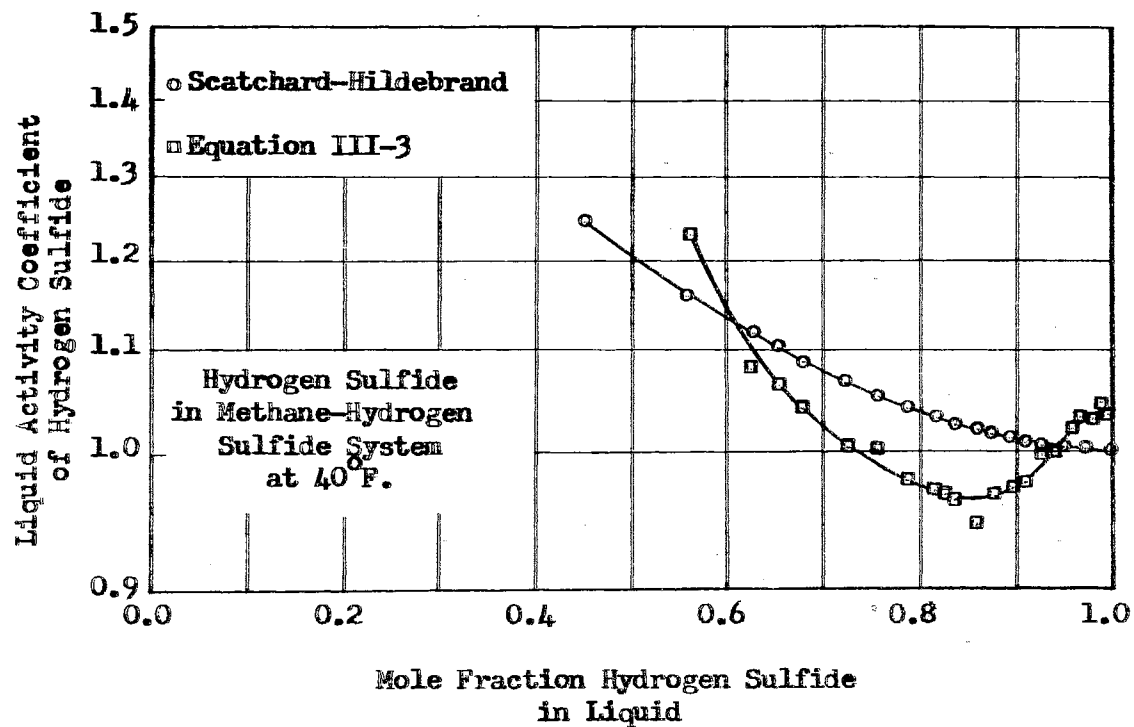


Figure 8

Comparison of the Liquid Activity Coefficient of Hydrogen Sulfide Calculated by the Scatchard-Hildebrand Equation with the One Calculated by Equation III-3

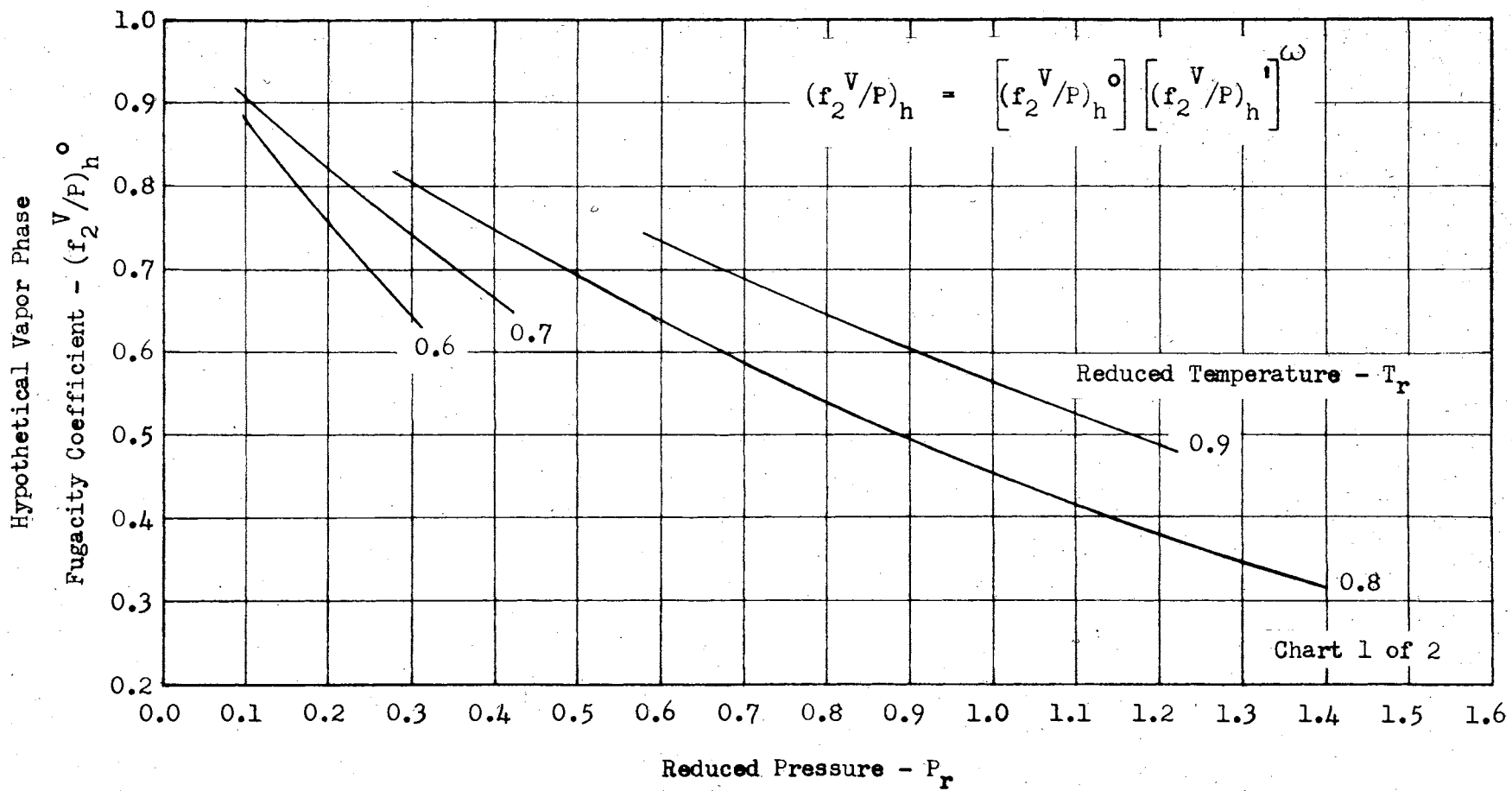


Figure 9
 Hypothetical Vapor Phase Fugacity Coefficient for the Simple Fluid

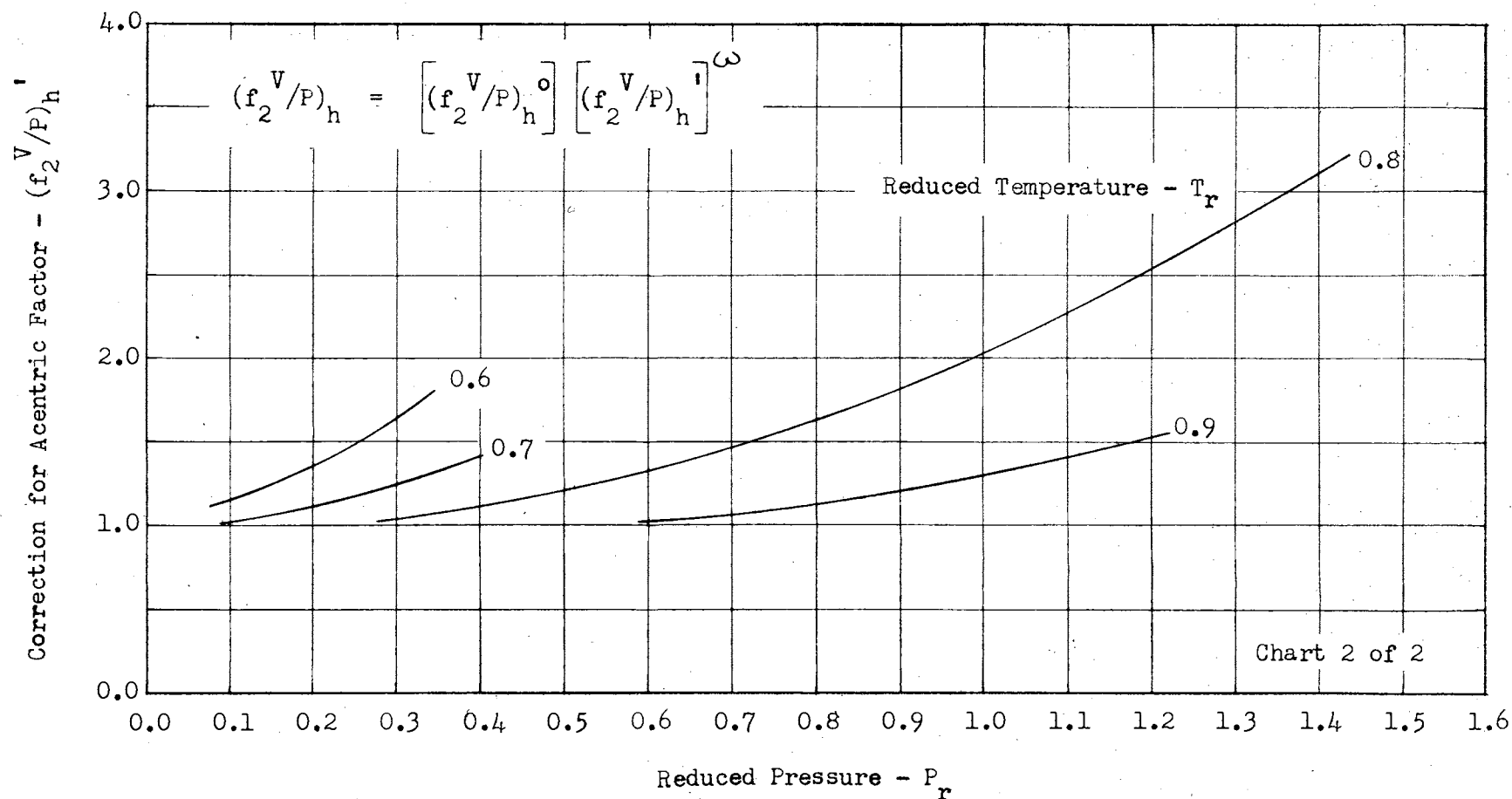


Figure 10
Correction to the Hypothetical Vapor Phase Fugacity Coefficient for Acentric Factor

CHAPTER IV

DISCUSSION OF RESULTS

Hoffman, et al. (22) first presented the idea of bridging from the activity coefficient of the real gaseous component to that of the hypothetical gas through the Gibbs-Duhem equation for the purpose of calculating the standard state for the hypothetical gas. For this they used the Van Laar equation, a particular solution of the Gibbs-Duhem equation, in the form

$$\log \gamma_i^V = \frac{a_{ij}^2}{\left[1 + \frac{a_{ij}^2 y_i}{a_{ji}^2 y_j} \right]^2} \quad (\text{IV-1})$$

The constants (a_{ij} & a_{ji}) of equation IV-1 were calculated by fitting the equation to the activity coefficient for the light component in the vapor phase calculated through the Cline Black equation of state (7). After evaluation of the constants the vapor phase activity coefficient of the heavy component was calculated by equation IV-1. The hypothetical vapor phase fugacity coefficient was calculated from this activity coefficient and the fugacity coefficient of the component in the mixture, calculated by the Cline Black equation, by means of equation III-2. Stuckey (46) proposed the numerical integration of equation III-1 used in this work as a simpler and less tedious method of bridging from the vapor phase activity coefficient

of the light component to that of the heavy component. Stuckey's method has the disadvantage of requiring sufficient data to extrapolate the $\log \gamma_1^V$ versus y_1 curve to zero concentration of the light component.

The form of the Gibbs-Duhem equation used is rigorous only at constant pressure and temperature. For a binary mixture in vapor-liquid equilibrium, it is not possible to vary the concentration of a component in the mixture without a corresponding change in either the temperature or pressure. The rigorous form of the Gibbs-Duhem equation at constant temperature is

$$\frac{d \ln \gamma_1}{d \ln y_1} - \frac{d \ln \gamma_2}{d \ln y_2} = \frac{\Delta V^m}{RT} \frac{dP}{dy_1} \quad (\text{IV-2})$$

The use of equation IV-2 requires volumetric data for evaluation. The error in neglecting the pressure effect of equation IV-2 is small and as pointed out by Thompson (47) is highly sensitive to small errors in the volumetric data. It therefore appears that at this stage of development that the added complexity of equation IV-2 may be neglected in these calculations.

Prausnitz (36) developed an empirical method of arriving at the hypothetical standard state by arbitrarily drawing a smooth curve from the vapor boundary of the two phase region of a PV plot and converging with the fluid portion of the curve at some high pressure. These curves were developed for acentric factors of 0.0, 0.2 and 0.4. Edmister (15) replotted Prausnitz's data in the form used by Pitzer (11), i. e., f/P as a function of the simple fluid and a simple fluid correction for acentric factor. Table I presents a comparison of the

hypothetical vapor phase fugacity coefficients as calculated by Edmister's plots of Prausnitz (15), Hoffman, et al. (22), and this work.

TABLE I
COMPARISON OF HYPOTHETICAL VAPOR PHASE
FUGACITY COEFFICIENT VALUES

$$\omega = 0.2925$$

T_r	P_r	Edmister- Prausnitz Values	Hoffman's Values	This Work
0.6	0.1	0.26	0.817	0.925
	0.3	0.12	0.600	0.741
0.7	0.1	0.52	0.900	0.908
	0.3	0.33	0.720	0.788
0.8	0.3	0.56	0.814	0.817
	0.7	0.38	0.614	0.656
	1.1	0.27	0.446	0.527
	1.3	0.24		0.467
0.9	0.7	0.54	0.695	0.702
	0.9	0.48	0.620	0.634
	1.1	0.42		0.575

A comparison of the values in Table I show that those of this work are considerably higher than the values of Prausnitz. This same trend was also observed by Stuckey (46). These values which were calculated at an acentric factor of 0.2925 (equivalent to a Z_c of 0.27), the point at which Hoffman, et al. (22) presented their data, are appreciably higher than Hoffman's values. Stuckey (46) found excellent agreement for his values of normal butane with those of Hoffman at $Z_c = 0.27$. An adequate explanation for these differences is not apparent. It can only be surmised that since both correlations are based on a rather meager amount of x-y data, additional data are required to determine the correct values.

Table II compares the hypothetical vapor phase fugacity coefficient of the simple fluid as developed by Stuckey (46) from ethane binaries and from this work on hydrogen sulfide binaries.

TABLE II
COMPARISON OF HYPOTHETICAL VAPOR PHASE FUGACITY
COEFFICIENTS OF THE SIMPLE FLUID

$$\omega = 0$$

<u>T_r</u>	<u>P_r</u>	<u>Hypothetical Vapor Phase Fugacity Coefficient for the Simple Fluid</u>	
		<u>Stuckey's Values</u>	<u>This Work</u>
0.7	0.4	0.65	0.66
0.8	0.4	0.74	0.75
	0.6	0.63	0.64
	0.8	0.55	0.54
0.9	0.6	0.75	0.74
	0.8	0.68	0.64

Excellent agreement is observed in the values of Table II. Thus as the acentric factor increases from zero the difference between Stuckey's values and those of this work become larger indicating possibly a need for a better method of correlation of the values for real fluids with those of the simple fluid.

Liquid Phase Analysis

The first step in making a similar analysis of the liquid phase is to calculate the activity coefficient of the real liquid component, i. e., the heavy component in the liquid phase. This work, as previously noted, calculates the activity coefficient of the heavy component in the liquid by

$$\gamma_2^L = \frac{(\phi_2)(y_2/x_2)}{(f_2^L/P)} \quad (\text{III-3})$$

where ϕ is calculated by the Redlich-Kwong equation of state (41) and (f_2^L/P) is calculated by the Chao-Seader equation (9). Hoffman, et al. (23) made a similar analysis using the Black equation of state to calculate ϕ_2 and the generalized fugacity coefficients of Lyderson, Greenkorn and Hougen to obtain (f_2^L/P) .

The Scatchard-Hildebrand equation (43) provides a means to directly obtain these activity coefficients. This equation is based upon the components in the liquid phase forming a 'regular solution' and as a result of simplification has the added restriction that all activity coefficients are equal to or greater than unity. The criterion of hydrocarbons behaving as 'regular solutions' seems justified when pressure and temperature conditions are such that the normal state of aggregation of the components is liquid. There is, however, a question of whether or not this is true of those liquid solutions encountered in vapor-liquid equilibria in which the light component in the liquid phase cannot exist in its pure state at the given temperature and pressure. This question is further increased when one of the components as in this work is a nonhydrocarbon and a polar compound.

A comparison of the activity coefficients calculated by the Scatchard-Hildebrand equation and by equation III-3 is illustrated in Figure 8 for hydrogen sulfide in the methane-hydrogen sulfide system at 40°F. The shape of the curves in Figure 8 is characteristic of the systems studied. Comparisons of the remaining systems appear

in Tables III through XXIII.

It is apparent from Figure 8 that considerable difference exists in the two methods of calculation. There is an apparent error in the values obtained from equation III-3 as the pure liquid is approached since at this point the activity coefficient is by definition unity. This error is attributed to the failure of the Redlich-Kwong equation of state and/or the Chao-Seader equation to fit the data perfectly. Even with these inherent inadequacies equation III-3 appears to be the preferable method of calculating the liquid phase activity coefficient of the heavy component of a binary mixture since it removes the restrictions of the Scatchard-Hildebrand equation that the solution must be 'regular' and that the activity coefficient must be equal to or greater than unity.

CHAPTER V

RESULTS, RECOMMENDATIONS AND CONCLUSIONS

Results

The ultimate goal in this investigation was to establish a means of determining the standard state fugacity coefficients for hypothetical vapors and liquids. Methods are available for calculating the fugacity coefficients of components in solution with one another. Knowing these two fugacity coefficients, the activity coefficients of a component in each phase is available as well as the ideal K-value, thus permitting calculation of the actual K-value by means of

$$K_i = \frac{\gamma_i^L}{\gamma_i^V} K_{ideal} \quad (I-10)$$

In this work on hydrogen sulfide binaries a standard state fugacity coefficient correlation for the hypothetical vapor has been successfully developed. These values are generalized using the acentric factor as an identifying parameter and are presented graphically in Figures 9 and 10.

Stuckey (46) and Hoffman, et al. (22) have presented similar data on hydrocarbon binaries. A comparison of their work with this nonhydrocarbon - hydrocarbon binary study indicates the possibility of correlating nonhydrocarbon - hydrocarbon solutions into the same framework used for strictly hydrocarbon solutions.

Further the Scatchard-Hildebrand equation (43) with its restrictions does not appear as applicable to calculation of the liquid phase activity coefficients as the method of bridging from the vapor fugacity coefficient of the heavy component in the mixture to the liquid fugacity coefficient. Since the heavy component is a real liquid its pure state fugacity coefficient can be calculated and then its activity coefficient found. This was the limit of this work.

Recommendations

To conclude the work the liquid phase analysis needs to be completed. From the activity coefficient of the heavy component in the liquid phase, the activity coefficient of the light component can be calculated by bridging through the Gibbs-Duhem equation as was done here for the vapor phase. The fugacity coefficient of the light component in the mixture is then calculated from its fugacity coefficient in the vapor as calculated by an equation of state and then bridging to the liquid using the criteria for equilibrium of equal fugacities of a component in each phase. Knowing the fugacity coefficient of the light component in the liquid solution and its activity coefficient, the standard state fugacity coefficient of the hypothetical liquid is back calculated.

Considerable more work is needed on nonhydrocarbon - hydrocarbon solutions to determine whether the methods used here for hydrogen sulfide - hydrocarbon solutions are also applicable to other nonhydrocarbon - hydrocarbon solutions and to heterogeneous solutions in general. Additional data is available in the literature for

carbon dioxide - hydrocarbon systems (1,13,31,34,38,48). Data is available for the hydrogen sulfide - carbon dioxide system (6). It is expected that analyses of these systems (1) hydrocarbon - hydrocarbon, (2) hydrogen sulfide - hydrocarbon, (3) carbon dioxide - hydrocarbon, and (4) carbon dioxide - hydrogen sulfide would give an excellent basis for a correlation involving the interaction effects of hydrocarbons with other materials.

Conclusions

The conclusions drawn in this work are:

1. The modified Hoffman procedure for calculating the standard state fugacity coefficient of the hypothetical vapor gives the best value available at this time. The method is applicable only if x-y data are available over the entire concentration range of the solution. In the event complete x-y data is not available Hoffman's (22) procedure using the Van Laar equation may be used.
2. The standard state fugacity coefficients of the hypothetical vapor can be generalized using the acentric factor of Pitzer and Curl (11) as an identifying parameter.
3. The activity coefficients for the heavy component in the liquid phase calculated by means of equation III-3 appear to be preferable to those calculated by means of the Scatchard-Hildebrand equation (43).

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APPENDIX A

DATA COMPILATION

TABLE III

SYSTEM: METHANE - HYDROGEN SULFIDE

Temperature: -40°F , Reduced Temperatures: Methane, 1.220; Hydrogen Sulfide, 0.624

Pressure psia	METHANE					HYDROGEN SULFIDE								
	P_r	Vapor Phase			Liquid Phase		P_r	Vapor Phase			Liquid Phase			
		y_1	ϕ_1	(f_1^V/P)	γ_1^V	x_1		$(\gamma_1^L)_{SH}$	ϕ_2	$(f_2^V/P)_h$	γ_2^V	(f_2^L/P)	$(\gamma_2^L)_{SH}$	$(\gamma_2^L)_d$
36.7	0.054	0.000					0.028							
37.8	0.056	0.030	0.9959	0.9894	1.007		0.029	0.9639	0.9639	1.000				
40.5	0.062	0.100	0.9947	0.9887	1.006		0.031	0.9614	0.9613	1.000				
53	0.079	0.300	0.9900	0.9852	1.005		0.041	0.9502	0.9498	1.000				
80	0.119	0.500	0.9815	0.9777	1.004		0.061	0.9274	0.9263	1.001				
200	0.297	0.754	0.9474	0.9449	1.003	0.0125	2.240	0.153	0.8333	0.8308	1.003	0.190	1.000	1.088
400	0.594	0.862	0.8937	0.8918	1.002	0.054	2.063	0.306	0.6915	0.6879	1.005	0.079	1.003	1.269
600	0.891	0.900	0.8427	0.8407	1.002	0.083	1.951	0.459	0.5697	0.5673	1.004	0.069	1.007	0.900

x-y Data Source: Kohn & Kurata, A.I.Ch.E. Journal 4, 211(1958)

TABLE IV

SYSTEM: METHANE - HYDROGEN SULFIDE

Temperature: 0°F, Reduced Temperatures: Methane, 1.337; Hydrogen Sulfide, 0.684

Pressure psia	METHANE						HYDROGEN SULFIDE							
	P_r	Vapor Phase			Liquid Phase		P_r	Vapor Phase			Liquid Phase			
		y_1	ϕ_1	(f_1^V/P)	γ_1^V	x_1		$(\gamma_1^L)_{SH}$	ϕ_2	$(f_2^V/P)_h$	γ_2^V	(f_2^L/P)	$(\gamma_2^L)_{SH}$	$(\gamma_2^L)_d$
82.3	0.122	0.000												
85	0.126	0.030	0.9946	0.9822	1.013		0.065	0.9364	0.9364	1.000				
92	0.137	0.100	0.9924	0.9807	1.012		0.070	0.9314	0.9313	1.000				
113	0.168	0.250	0.9864	0.9764	1.010		0.087	0.9167	0.9163	1.000				
148	0.220	0.400	0.9778	0.9692	1.009		0.113	0.8934	0.8924	1.001				
200	0.297	0.522	0.9662	0.9585	1.008	0.009	2.161	0.153	0.8600	0.8585	1.002	0.411	1.000	1.009
400	0.594	0.720	0.9248	0.9186	1.007	0.045	2.017	0.306	0.7421	0.7392	1.004	0.214	1.002	1.013
600	0.891	0.792	0.8865	0.8803	1.007	0.072	1.920	0.459	0.6348	0.6329	1.003	0.148	1.006	0.961

x-y Data Source: Kohn & Kurata, A.I.Ch.E. Journal 4, 211(1958)

TABLE V

SYSTEM: METHANE - HYDROGEN SULFIDE

Temperature: 40°F, Reduced Temperatures: Methane, 1.453; Hydrogen Sulfide, 0.743.

Pressure psia	METHANE							HYDROGEN SULFIDE							
	P _r	Vapor Phase				Liquid Phase			P _r	Vapor Phase			Liquid Phase		
		γ ₁	φ ₁	(f ₁ ^V /P)	γ ₁ ^V	x ₁	(γ ₁ ^L) _{SH}	φ ₂		(f ₂ ^V /P) _h	γ ₂ ^V	(f ₂ ^L /P)	(γ ₂ ^L) _{SH}	(γ ₂ ^L) _d	
169*		0.0000				0.0000									
200	0.297	0.1371	0.9898	0.9686	1.022	0.0057	2.097	0.153	0.8816	0.8814	1.000	0.738	1.000	1.037	
250	0.371	0.2783	0.9800	0.9607	1.020	0.0132	2.066	0.191	0.8543	0.8537	1.001	0.597	1.000	1.046	
300	0.446	0.3896	0.9700	0.9530	1.018	0.0212	2.035	0.230	0.8287	0.8276	1.001	0.501	1.000	1.031	
350	0.520	0.4604	0.9615	0.9455	1.017	0.0284	2.009	0.268	0.8038	0.8019	1.002	0.434	1.001	1.029	
400	0.594	0.5126	0.9535	0.9380	1.016	0.0354	1.983	0.306	0.7795	0.7773	1.003	0.381	1.001	1.034	
450	0.669	0.5551	0.9456	0.9306	1.016	0.0424	1.958	0.345	0.7558	0.7532	1.003	0.343	1.002	1.024	
500	0.743	0.5879	0.9381	0.9233	1.016	0.0493	1.934	0.383	0.7326	0.7298	1.004	0.312	1.002	1.018	
600	0.891	0.6394	0.9235	0.9089	1.016	0.0636	1.886	0.459	0.6878	0.6853	1.004	0.265	1.004	1.000	
700	1.040	0.6755	0.9098	0.8948	1.017	0.0783	1.840	0.536	0.6446	0.6435	1.002	0.231	1.006	0.983	
800	1.189	0.6989	0.8971	0.8811	1.018	0.0930	1.796	0.613	0.6023	0.6031	0.999	0.206	1.008	0.971	
900	1.337	0.7141	0.8855	0.8678	1.020	0.1083	1.752	0.689	0.5608	0.5647	0.993	0.186	1.011	0.967	
1000	1.486	0.7242	0.8749	0.8548	1.024	0.1250	1.707	0.766	0.5202	0.5275	0.986	0.171	1.014	0.959	
1100	1.634	0.7299	0.8656	0.8422	1.028	0.1433	1.661	0.842	0.4803	0.4913	0.978	0.162	1.019	0.935	
1200	1.783	0.7321	0.8579	0.8300	1.034	0.1635	1.613	0.919	0.4411	0.4572	0.965	0.148	1.024	0.954	
1250	1.857	0.7319	0.8548	0.8241	1.037	0.1750	1.588	0.957	0.4217	0.4441	0.950	0.143	1.027	0.958	
1300	1.931	0.7306	0.8523	0.8182	1.042	0.1868	1.563	0.995	0.4022	0.4285	0.939	0.138	1.031	0.966	
1400	2.080	0.7262	0.8491	0.8068	1.052	0.2137	1.508	1.072	0.3640	0.3992	0.912	0.131	1.040	0.968	
1500	2.229	0.7185	0.8490	0.7959	1.067	0.2450	1.451	1.149	0.3268	0.3791	0.862	0.122	1.052	0.999	
1600	2.377	0.7075	0.8523	0.7853	1.085	0.2798	1.395	1.225	0.2913	0.3458	0.842	0.118	1.067	1.003	
1700	2.526	0.6931	0.8589	0.7752	1.108	0.3240	1.331	1.302	0.2586	0.3206	0.807	0.113	1.089	1.039	
1750	2.600	0.6828	0.8650	0.7704	1.123	0.3492	1.299	1.340	0.2426	0.3093	0.784	0.111	1.102	1.065	
1800	2.674	0.6686	0.8751	0.7656	1.143	0.3758	1.260	1.378	0.2261	0.3011	0.751	0.109	1.118	1.081	
1900	2.823	0.6130	0.9275	0.7564	1.226	0.4401	1.202	1.455	0.1870	0.2814	0.665	0.105	1.159	1.231	
1949**	2.896	0.5500	1.0053	0.7521	1.337	0.5500	1.119	1.492	0.1611	0.2734	0.589		1.243		

* Vapor pressure of hydrogen sulfide. ** Estimated critical state

x-y Data Source: Reamer, Sage & Lacey, Ind. Eng. Chem. 43, 976(1951)

TABLE VI

SYSTEM: METHANE - HYDROGEN SULFIDE

Temperature: 100°F, Reduced Temperatures: Methane, 1.627; Hydrogen Sulfide, 0.832

Pressure psia	METHANE						HYDROGEN SULFIDE							
	P_r	Vapor Phase			Liquid Phase			P_r	Vapor Phase			Liquid Phase		
		y_1	ϕ_1	(f_1^V/P)	γ_1^V	x_1	$(\gamma_1^L)_{SH}$		ϕ_2	$(f_2^V/P)_h$	γ_2^V	(f_2^L/P)	$(\gamma_2^L)_{SH}$	$(\gamma_2^L)_d$
394*		0.0000												
400	0.594	0.0117	1.0123	0.9581	1.057	0.0007	2.010	0.306	0.8266	0.8266	1.000		1.000	
450	0.669	0.0963	1.0055	0.9532	1.055	0.0067	2.001	0.345	0.8055	0.8055	1.000	0.702	1.000	1.044
500	0.743	0.1642	0.9995	0.9482	1.054	0.0128	1.978	0.383	0.7851	0.7851	1.000	0.637	1.000	1.043
550	0.817	0.2203	0.9939	0.9433	1.054	0.0190	1.956	0.421	0.7653	0.7651	1.000	0.584	1.000	1.042
600	0.891	0.2688	0.9885	0.9385	1.053	0.0255	1.934	0.459	0.7461	0.7458	1.000	0.539	1.001	1.039
700	1.040	0.3416	0.9796	0.9291	1.054	0.0385	1.890	0.536	0.7087	0.7087	1.000	0.469	1.001	1.035
800	1.189	0.3976	0.9715	0.9199	1.056	0.0523	1.846	0.613	0.6728	0.6733	0.999	0.417	1.003	1.026
900	1.337	0.4396	0.9648	0.9109	1.059	0.0670	1.802	0.689	0.6379	0.6399	0.997	0.376	1.004	1.019
1000	1.486	0.4707	0.9597	0.9022	1.064	0.0828	1.757	0.766	0.6037	0.6073	0.994	0.344	1.006	1.013
1100	1.634	0.4923	0.9570	0.8937	1.071	0.0996	1.712	0.842	0.5697	0.5769	0.988	0.326	1.009	0.985
1200	1.783	0.5079	0.9563	0.8855	1.080	0.1182	1.665	0.919	0.5360	0.5485	0.977	0.295	1.012	1.015
1250	1.857	0.5130	0.9573	0.8815	1.086	0.1282	1.641	0.957	0.5190	0.5331	0.974	0.285	1.014	1.017
1300	1.931	0.5182	0.9583	0.8775	1.092	0.1390	1.616	0.995	0.5025	0.5192	0.968	0.276	1.017	1.019
1400	2.080	0.5240	0.9636	0.8698	1.108	0.1620	1.566	1.072	0.4690	0.4905	0.956	0.260	1.022	1.025
1500	2.229	0.5255	0.9730	0.8624	1.128	0.1885	1.512	1.149	0.4355	0.4640	0.939	0.247	1.030	1.030
1600	2.377	0.5195	0.9914	0.8552	1.159	0.2192	1.456	1.225	0.4004	0.4441	0.902	0.234	1.040	1.042
1700	2.526	0.5058	1.0222	0.8483	1.205	0.2532	1.401	1.302	0.3641	0.4190	0.869	0.224	1.052	1.059
1750	2.600	0.4947	1.0454	0.8449	1.237	0.2725	1.372	1.340	0.3451	0.4083	0.845	0.219	1.064	1.095
1800	2.674	0.4797	1.0750	0.8416	1.277	0.2940	1.342	1.378	0.3257	0.3982	0.818	0.214	1.070	1.122
1850	2.749	0.4580	1.1203	0.8384	1.336	0.3185	1.310	1.417	0.3050	0.3872	0.788	0.210	1.081	1.155
1900	2.823	0.4190	1.2036	0.8353	1.441	0.3578	1.265	1.455	0.2801	0.3766	0.744	0.206	1.101	1.230
1907**	2.833	0.3880	1.2770	0.8348	1.530	0.3880	1.233	1.460	0.2681	0.3750	0.715		1.117	

* Vapor pressure of hydrogen sulfide

** Estimated critical state

x-y Data Source: Reamer, Sage & Lacey, Ind. Eng. Chem. 43, 976(1951)

TABLE VII

SYSTEM: METHANE - HYDROGEN SULFIDE

Temperature: 160 °F, Reduced Temperatures: Methane, 1.802; Hydrogen Sulfide, 0.921

Pressure psia	METHANE						HYDROGEN SULFIDE							
	P_r	Vapor Phase				Liquid Phase		P_r	Vapor Phase			Liquid Phase		
		y_1	ϕ_1	(f_1^V/P)	γ_1^V	x_1	$(\gamma_1^L)_{SH}$		ϕ_2	$(f_2^V/P)_h$	γ_2^V	(f_2^L/P)	$(\gamma_2^L)_{SH}$	$(\gamma_2^L)_d$
778.9*		0.0000				0.0000								
800	1.189	0.0196	1.076	0.946	1.137	0.0031	1.941	0.613	0.7406	0.7406	1.000	0.716	1.000	1.017
850	1.263	0.0592	1.074	0.943	1.139	0.0098	1.918	0.651	0.7243	0.7243	1.000	0.677	1.000	1.017
900	1.337	0.0946	1.072	0.940	1.141	0.0167	1.895	0.689	0.7084	0.7083	1.000	0.644	1.000	1.013
1000	1.486	0.1553	1.069	0.934	1.145	0.0309	1.850	0.766	0.6775	0.6781	0.999	0.586	1.001	1.008
1100	1.634	0.2021	1.070	0.928	1.153	0.0459	1.805	0.842	0.6475	0.6490	0.998	0.553	1.002	0.979
1200	1.783	0.2367	1.076	0.923	1.167	0.0622	1.760	0.919	0.6177	0.6205	0.995	0.499	1.003	1.008
1250	1.857	0.2534	1.078	0.920	1.172	0.0720	1.731	0.957	0.6034	0.6079	0.993	0.482	1.005	1.007
1300	1.931	0.2646	1.085	0.917	1.183	0.0814	1.707	0.995	0.5884	0.5946	0.990	0.466	1.006	1.011
1400	2.080	0.2811	1.105	0.912	1.211	0.1021	1.655	1.072	0.5580	0.5690	0.981	0.437	1.009	1.022
1500	2.229	0.2775	1.167	0.907	1.286	0.1245	1.603	1.149	0.5209	0.5442	0.957	0.413	1.013	1.041
1600	2.377	0.2580	1.309	0.902	1.451	0.1547	1.540	1.225	0.4752	0.5180	0.917	0.385	1.020	1.083
1650	2.451	0.2295	1.474	0.900	1.638	0.1830	1.486	1.263	0.4457	0.5057	0.881	0.382	1.027	1.100
1660**	2.466	0.2090	1.580	0.899	1.756	0.2090	1.440	1.271	0.4349	0.5032	0.864		1.035	

* Vapor pressure of hydrogen sulfide ** Estimated critical state

x-y Data Source: Reamer, Sage & Lacey, Ind. Eng. Chem. 43, 976(1951)

TABLE VIII

SYSTEM: ETHANE - HYDROGEN SULFIDE

Temperature: 80°F, Reduced Temperatures: Ethane, 0.981; Hydrogen Sulfide, 0.803

Pressure psia	ETHANE						HYDROGEN SULFIDE							
	P_r	Vapor Phase			Liquid Phase			P_r	Vapor Phase			Liquid Phase		
		y_1	ϕ_1	(f_1^V/P)	γ_1^V	x_1	$(\gamma_1^L)_{SH}$		ϕ_2	$(f_2^V/P)_h$	γ_2^V	(f_2^L/P)	$(\gamma_2^L)_{SH}$	$(\gamma_2^L)_d$
305	0.430	0.000	0.8491	0.8488	1.000	0.000	0.234	0.8536	0.8536					
315	0.444	0.050	0.8442	0.8439	1.000	0.007	1.877	0.241	0.8488	0.8488	1.000	0.793	1.000	1.024
329	0.464	0.100	0.8373	0.8371	1.000	0.018	1.837	0.252	0.8420	0.8420	1.000	0.761	1.000	1.013
374	0.527	0.200	0.8154	0.8152	1.000	0.062	1.693	0.286	0.8203	0.8203	1.000	0.673	1.004	1.040
424	0.597	0.300	0.7909	0.7908	1.000	0.125	1.532	0.325	0.7960	0.7960	1.000	0.599	1.014	1.063
476	0.671	0.400	0.7654	0.7654	1.000	0.210	1.373	0.364	0.7702	0.7702	1.000	0.539	1.037	1.085
531	0.748	0.500	0.7381	0.7381	1.000	0.330	1.223	0.407	0.7421	0.7420	1.000	0.487	1.081	1.137
582	0.820	0.600	0.7122	0.7122	1.000	0.495	1.102	0.446	0.7142	0.7142	1.000	0.448	1.162	1.120
618	0.871	0.700	0.6934	0.6932	1.000	0.653	1.041	0.473	0.6915	0.6919	0.999	0.425	1.254	1.407

x-y Data Source: Kay & Brice, Ind. Eng. Chem. 45, 615(1953)

TABLE IX

SYSTEM: ETHANE - HYDROGEN SULFIDE

Temperature: 100°F, Reduced Temperatures: Ethane, 1.018; Hydrogen Sulfide, 0.832

Pressure psia	ETHANE						HYDROGEN SULFIDE							
	P_r	Vapor Phase			Liquid Phase			P_r	Vapor Phase			Liquid Phase		
		y_1	ϕ_1	(f_1^V/P)	γ_1^V	x_1	$(\gamma_1^L)_{SH}$		ϕ_2	$(f_2^V/P)_h$	γ_2^V	(f_2^L/P)	$(\gamma_2^L)_{SH}$	$(\gamma_2^L)_d$
396	0.558	0.000	0.8246	0.8244	1.000	0.000	0.3032	0.8284	0.8284	1.000				
414	0.583	0.050	0.8168	0.8166	1.000	0.012	1.832	0.3170	0.8206	0.8206	1.000	0.758	1.000	1.041
435	0.613	0.100	0.8077	0.8075	1.000	0.028	1.777	0.3331	0.8114	0.8114	1.000	0.724	1.001	1.038
487	0.686	0.200	0.7851	0.7850	1.000	0.076	1.634	0.3729	0.7885	0.7885	1.000	0.652	1.005	1.047
550	0.775	0.300	0.7576	0.7576	1.000	0.148	1.469	0.4211	0.7603	0.7602	1.000	0.583	1.019	1.072
624	0.879	0.400	0.7251	0.7251	1.000	0.260	1.293	0.4778	0.7257	0.7257	1.000	0.519	1.052	1.134
687	0.968	0.500	0.6974	0.6968	1.001	0.391	1.140	0.5260	0.6925	0.6930	0.999	0.476	1.106	1.194
737	1.038	0.600	0.7088	0.6733	1.053	0.500	1.097	0.5643	0.5590			0.447	1.160	1.000
776	1.093	0.700	0.6689	0.6537	1.023	0.665	1.037	0.5942	0.5517			0.427	1.255	1.158
785	1.106	0.730	0.6604	0.6488	1.018	0.710	1.026	0.6011	0.5515			0.423	1.283	1.214

x-y Data Source: Kay & Brice, Ind. Eng. Chem. 45, 615(1953)

TABLE X

SYSTEM: ETHANE - HYDROGEN SULFIDE

Temperature: 120°F, Reduced Temperatures: Ethane, 1.054; Hydrogen Sulfide, 0.862

Pressure psia	ETHANE							HYDROGEN SULFIDE							
	P_r	Vapor Phase				Liquid Phase			P_r	Vapor Phase			Liquid Phase		
		y_1	ϕ_1	(f_1^V/P)	γ_1^V	x_1	$(\gamma_1^L)_{SH}$	ϕ_2		$(f_2^V/P)_H$	γ_2^V	(f_2^L/P)	$(\gamma_2^L)_{SH}$	$(\gamma_2^L)_d$	
510	0.719	0.000	0.7977	0.7976	1.000	0.000		0.391	0.7999	0.7999	1.000				
530	0.747	0.050	0.7900	0.7899	1.000	0.014	1.800	0.406	0.7920	0.7920	1.000	0.736	1.000	1.036	
556	0.783	0.100	0.7799	0.7798	1.000	0.033	1.738	0.426	0.7816	0.7816	1.000	0.704	1.001	1.034	
625	0.881	0.200	0.7533	0.7533	1.000	0.093	1.573	0.479	0.7537	0.7537	1.000	0.632	1.008	1.052	
702	0.989	0.300	0.7236	0.7235	1.000	0.177	1.405	0.538	0.7211	0.7211	1.000	0.569	1.026	1.078	
785	1.106	0.400		0.6911		0.290	1.248	0.601				0.515	1.062		
870	1.226	0.500	0.7025	0.6571	1.069	0.446	1.124	0.666	0.5584			0.471	1.130	1.071	
893	1.258	0.520	0.6859	0.6477	1.059	0.503	1.093	0.684	0.5485			0.460	1.158	1.152	

x-y Data Source: Kay & Brice, Ind. Eng. Chem. 45, 615(1953)

TABLE XI

SYSTEM: ETHANE - HYDROGEN SULFIDE

Temperature: 140°F, Reduced Temperatures: Ethane, 1.090; Hydrogen Sulfide, 0.892

Pressure psia	ETHANE							HYDROGEN SULFIDE							
	P_r	Vapor Phase				Liquid Phase			P_r	Vapor Phase			Liquid Phase		
		y_1	ϕ_1	(f_1^V/P)	γ_1^V	x_1	$(\gamma_1^L)_{SH}$	ϕ_2		$(f_2^V/P)_h$	γ_2^V	(f_2^L/P)	$(\gamma_2^L)_{SH}$	$(\gamma_2^L)_d$	
640	0.902	0.000	0.7726	0.7725	1.000	0.000		0.490	0.7721	0.7721	1.000				
670	0.944	0.050	0.7623	0.7623	1.000	0.018	1.764	0.513	0.7611	0.7611	1.000	0.714	1.000	1.031	
702	0.989	0.100	0.7515	0.7514	1.000	0.041	1.693	0.538	0.7493	0.7493	1.000	0.683	1.002	1.029	
781	1.100	0.200	0.7249	0.7246	1.000	0.106	1.528	0.598	0.7193	0.7194	1.000	0.621	1.010	1.037	
886	1.248	0.300				0.211	1.342	0.678				0.555	1.034		
955	1.345	0.350	0.7426	0.6658	1.115	0.299	1.236	0.731	0.5813			0.519	1.064	1.038	
994	1.400	0.375	0.7160	0.6528	1.097	0.365	1.176	0.761	0.5644			0.501	1.090	1.109	

x-y Data Source: Kay & Brice, Ind. Eng. Chem. 45, 615(1953)

TABLE XII

SYSTEM: ETHANE - HYDROGEN SULFIDE

Temperature: 160°F, Reduced Temperatures: Ethane, 1.127; Hydrogen Sulfide, 0.921

Pressure psia	ETHANE						HYDROGEN SULFIDE							
	P_r	Vapor Phase			Liquid Phase		P_r	Vapor Phase			Liquid Phase			
		y_1	ϕ_1	(f_1^V/P)	γ_1^V	x_1		$(\gamma_1^L)_{SH}$	ϕ_2	$(f_2^V/P)_h$	γ_2^V	(f_2^L/P)	$(\gamma_2^L)_{SH}$	$(\gamma_2^L)_d$
797	1.123	0.000	0.7469	0.7468	1.000	0.000	0.610	0.7415	0.7415	1.000				
827	1.165	0.050	0.7381	0.7378	1.000	0.017	1.747	0.633	0.7314	0.7314	1.000	0.693	1.000	1.020
871	1.227	0.100	0.7254	0.7247	1.001	0.045	1.664	0.667	0.7162	0.7162	1.000	0.661	1.002	1.021
992	1.398	0.200		0.6893		0.149	1.431	0.760				0.588	1.029	
1065	1.500	0.250	0.7581	0.6684	1.134	0.233	1.304	0.815	0.5989			0.553	1.040	1.059
1080	1.522	0.260	0.7480	0.6642	1.126	0.246	1.288	0.827	0.5929			0.546	1.044	1.065

x-y Data Source: Kay & Brice, Ind. Eng. Chem. 45, 615(1953)

TABLE XIII

SYSTEM: PROPANE - HYDROGEN SULFIDE

Temperature: 100°F, Reduced Temperatures: Propane, 0.840; Hydrogen Sulfide, 0.832

Pressure psia	HYDROGEN SULFIDE					PROPANE								
	P_r	Vapor Phase			Liquid Phase		P_r	Vapor Phase			Liquid Phase			
		y_1	ϕ_1	(f_1^V/P)	γ_1^V	x_1		$(\gamma_1^L)_{SH}$	ϕ_2	$(f_2^V/P)_h$	γ_2^V	(f_2^L/P)	$(\gamma_2^L)_{SH}$	$(\gamma_2^L)_d$
189.1	0.145	0.0000				0.000								
197	0.151	0.050	0.9394	0.9143	1.027	0.012	1.422	0.319	0.8245	0.8245	1.000	0.770	1.000	1.030
205	0.157	0.100	0.9343	0.9109	1.026	0.027	1.414	0.332	0.8175	0.8172	1.000	0.742	1.000	1.019
218	0.167	0.1633	0.9269	0.9053	1.024	0.053	1.401	0.353	0.8064	0.8060	1.000	0.701	1.000	1.017
252.5	0.193	0.2986	0.9086	0.8904	1.020	0.136	1.360	0.409	0.7778	0.7766	1.002	0.611	1.004	1.034
292	0.224	0.4342	0.8875	0.8734	1.016	0.246	1.304	0.473	0.7469	0.7440	1.004	0.535	1.014	1.047
332	0.254	0.5641	0.8659	0.8561	1.011	0.375	1.238	0.538	0.7179	0.7117	1.009	0.476	1.038	1.051
370	0.283	0.6755	0.8459	0.8397	1.007	0.548	1.152	0.599	0.6926	0.6817	1.016	0.433	1.106	1.148
392	0.300	0.7817	0.8330	0.8301	1.003	0.687	1.087	0.635	0.6824	0.6648	1.026	0.411	1.216	1.157
401.5	0.307	0.8984	0.8266	0.8260	1.001	0.928	1.007	0.650	0.6849	0.6560	1.044	0.403	1.730	2.432
394		1.0000				1.000								

x-y Data Source: Kay & Rambosek, Ind. Eng. Chem. 45, 221(1953)

TABLE XIV

SYSTEM: PROPANE - HYDROGEN SULFIDE

Temperature: 120°F, Reduced Temperatures: Propane, 0.870; Hydrogen Sulfide, 0.862

Pressure psia	HYDROGEN SULFIDE							PROPANE							
	P_r	Vapor Phase				Liquid Phase			P_r	Vapor Phase			Liquid Phase		
		y_1	ϕ_1	(f_1^V/P)	γ_1^V	x_1	$(\gamma_1^L)_{SH}$	ϕ_2		$(f_2^V/P)_h$	γ_2^V	(f_2^L/P)	$(\gamma_2^L)_{SH}$	$(\gamma_2^L)_d$	
242.9	0.186	0.0000				0.000		0.393							
254	0.194	0.050	0.9322	0.9001	1.036	0.020	1.406	0.411	0.7951	0.7950	1.000	0.750	1.000	1.027	
266	0.204	0.100	0.9258	0.8954	1.034	0.042	1.395	0.431	0.7856	0.7853	1.000	0.717	1.000	1.029	
282.5	0.216	0.1633	0.9172	0.8889	1.032	0.072	1.381	0.458	0.7728	0.7725	1.000	0.678	1.001	1.028	
322	0.246	0.2986	0.8968	0.8735	1.027	0.148	1.344	0.522	0.7434	0.7420	1.002	0.602	1.004	1.016	
374.5	0.287	0.4342	0.8716	0.8531	1.022	0.267	1.285	0.607	0.7058	0.7016	1.006	0.525	1.016	1.038	
427	0.327	0.5641	0.8456	0.8325	1.016	0.419	1.210	0.692	0.6712	0.6640	1.011	0.467	1.049	1.078	
471	0.361	0.6755	0.8234	0.8153	1.010	0.564	1.140	0.763	0.6455	0.6327	1.020	0.429	1.112	1.119	
498	0.381	0.7817	0.8084	0.8046	1.005	0.703	1.078	0.807	0.6355	0.6140	1.035	0.409	1.227	1.142	
510	0.391	0.8984	0.8007	0.7999	1.001	0.941	1.005	0.826	0.6395	0.6016	1.063	0.401	1.763	2.746	
503	0.385	1.0000				1.000									

x-y Data Source: Kay & Rambosek, Ind. Eng. Chem. 45, 221(1953)

TABLE XV -

SYSTEM: PROPANE - HYDROGEN SULFIDE

Temperature: 140°F, Reduced Temperatures: Propane, 0.901; Hydrogen Sulfide, 0.892

Pressure psia	HYDROGEN SULFIDE						PROPANE							
	P_r	Vapor Phase			Liquid Phase		P_r	Vapor Phase			Liquid Phase			
		y_1	ϕ_1	(f_1^V/P)	γ_1^V	x_1		$(\gamma_1^L)_{SH}$	ϕ_2	$(f_2^V/P)_h$	γ_2^V	(f_2^L/P)	$(\gamma_2^L)_{SH}$	$(\gamma_2^L)_d$
307.6	0.236	0.0000				0.000								
320.5	0.245	0.050	0.9268	0.8856	1.047	0.020	1.395	0.519	0.7654	0.7653	1.000	0.696	1.000	1.066
336	0.257	0.100	0.9194	0.8801	1.045	0.045	1.383	0.544	0.7541	0.7538	1.000	0.667	1.000	1.065
357	0.273	0.1633	0.9094	0.8727	1.042	0.078	1.368	0.578	0.7392	0.7387	1.001	0.631	1.001	1.063
411	0.315	0.2986	0.8851	0.8536	1.037	0.170	1.325	0.666	0.7021	0.7006	1.002	0.555	1.006	1.069
475	0.364	0.4342	0.8565	0.8310	1.031	0.289	1.267	0.769	0.6600	0.6561	1.006	0.489	1.019	1.074
539	0.413	0.5641	0.8267	0.8083	1.023	0.437	1.197	0.873	0.6213	0.6129	1.014	0.438	1.054	1.098
591	0.453	0.6755	0.8013	0.7897	1.015	0.592	1.124	0.957	0.5943	0.5749	1.034	0.405	1.127	1.167
624	0.478	0.7817	0.7830	0.7778	1.007	0.684	1.084	1.011	0.5848	0.5575	1.049	0.387	1.201	1.044
638	0.489	0.8984	0.7738	0.7728	1.001	0.926	1.007	1.033	0.5922	0.5482	1.080	0.380	1.677	2.140
631.6	0.484	1.0000				1.000								

x-y Data Source: Kay & Rambosek, Ind. Eng. Chem. 45, 221(1953)

TABLE XVI

SYSTEM: PROPANE - HYDROGEN SULFIDE

Temperature: 160°F, Reduced Temperatures: Propane, 0.931; Hydrogen Sulfide, 0.921

Pressure psia	HYDROGEN SULFIDE							PROPANE							
	P_r	Vapor Phase				Liquid Phase		P_r	Vapor Phase			Liquid Phase			
		y_1	ϕ_1	$(f_1^{V/P})$	γ_1^V	x_1	$(\gamma_1^L)_{SH}$		ϕ_2	$(f_2^{V/P})_h$	γ_2^V	$(f_2^{L/P})$	$(\gamma_2^L)_{SH}$	$(\gamma_2^L)_d$	
384.5	0.294	0.0000				0.000									
400	0.306	0.050	0.9244	0.8702	1.062	0.023	1.384	0.648	0.7334	0.7334	1.000	0.712	1.000	1.001	
419	0.321	0.100	0.9160	0.8642	1.060	0.050	1.371	0.679	0.7207	0.7204	1.000	0.683	1.000	0.999	
447	0.342	0.1633	0.9047	0.8552	1.058	0.089	1.354	0.724	0.7022	0.7027	0.999	0.644	1.001	1.001	
519	0.397	0.2986	0.8780	0.8321	1.055	0.198	1.305	0.841	0.6551	0.6538	1.002	0.563	1.008	1.018	
596.5	0.457	0.4342	0.8475	0.8072	1.050	0.326	1.244	0.966	0.6059	0.6032	1.004	0.513	1.025	0.991	
671	0.514	0.5641	0.8150	0.7831	1.041	0.470	1.177	1.087	0.5612	0.5538	1.013	0.461	1.064	1.001	
734	0.562	0.6755	0.7846	0.7625	1.029	0.623	1.108	1.189	0.5282	0.5110	1.034	0.428	1.145	1.063	
773	0.592	0.7817	0.7581	0.7496	1.011	0.759	1.053	1.252	0.5259	0.4863	1.081	0.400	1.284	1.191	
790	0.605	0.8984	0.7453	0.7439	1.002	0.925	1.007	1.280	0.5406	0.4765	1.135	0.393	1.654	1.864	
781.6	0.598	1.0000				1.000									

x-y Data Source: Kay & Rambosek, Ind. Eng. Chem. 45, 221(1953)

TABLE XVII.

SYSTEM: PROPANE - HYDROGEN SULFIDE

Temperature: 180°F, Reduced Temperatures: Propane, 0.961; Hydrogen Sulfide, 0.951

Pressure psia	HYDROGEN SULFIDE							PROPANE						
	P_r	Vapor Phase				Liquid Phase		P_r	Vapor Phase			Liquid Phase		
		y_1	ϕ_1	(f_1^V/P)	γ_1^V	x_1	$(\gamma_1^L)_{SH}$		ϕ_2	$(f_2^V/P)_h$	γ_2^V	(f_2^L/P)	$(\gamma_2^L)_{SH}$	$(\gamma_2^L)_d$
474.8	0.364	0.0000				0.000								
496	0.380	0.050	0.9295	0.8535	1.089	0.026	1.373	0.803	0.6979	0.6979	1.000	0.684	1.000	0.995
521	0.399	0.100	0.9212	0.8462	1.089	0.057	1.359	0.844	0.6820	0.6818	1.000	0.654	1.000	0.995
558	0.427	0.1633	0.9120	0.8355	1.092	0.105	1.338	0.904	0.6580	0.6581	1.000	0.615	1.002	1.000
651	0.498	0.2986	0.9970	0.8083	1.233	0.230	1.281	1.055	0.5576	0.5806	0.960	0.536	1.011	0.948
748	0.573	0.4342	0.8908	0.7799	1.142	0.369	1.218	1.212	0.4999	0.4984	1.003	0.476	1.055	0.942
838.5	0.642	0.5641	0.8116	0.7531	1.078	0.522	1.149	1.358	0.4581	0.4302	1.065	0.432	1.084	0.967
904	0.692	0.6755	0.7627	0.7334	1.040	0.652	1.093	1.464	0.4336	0.3812	1.137	0.406	1.164	0.995
945	0.724	0.7817	0.7342	0.7207	1.019	0.755	1.054	1.531	0.4214	0.3542	1.190	0.391	1.272	0.960
964.2	0.738	0.8984	0.7173	0.7147	1.004	0.841	1.026	1.567	0.4824	0.3759	1.283	0.384	1.861	0.803
956.4	0.732	1.0000				1.000								

x-y Data Source: Kay & Rambosek, Ind. Eng. Chem. 45, 221(1953)

TABLE XVIII

SYSTEM: PENTANE - HYDROGEN SULFIDE

Temperature: 40°F, Reduced Temperatures: Pentane, 0.591; Hydrogen Sulfide, 0.743

Pressure psia	HYDROGEN SULFIDE						n-PENTANE							
	P _r	Vapor Phase			Liquid Phase		P _r	Vapor Phase			Liquid Phase			
		y ₁	φ ₁	(f ₁ ^V /P)	γ ₁ ^V	x ₁		(γ ₁ ^L) _{SH}	φ ₂	(f ₂ ^V /P) _h	γ ₂ ^V	(f ₂ ^L /P)	(γ ₂ ^L) _{SH}	(γ ₂ ^L) _d
4.4*		0.0000				0.0000								
4.5	0.0034	0.0300	1.0014	0.9974	1.004			0.0092	0.9867	0.9940	0.993			
4.8	0.0037	0.1000	1.0010	0.9973	1.004			0.0098	0.9862	0.9861	1.000			
5.3	0.0040	0.2000	1.0001	0.9969	1.003			0.0107	0.9848	0.9847	1.000			
8.1	0.0062	0.5000	0.9972	0.9953	1.002			0.0166	0.9781	0.9773	1.001			
20	0.0153	0.7842	0.9889	0.9880	1.001	0.0617	1.126	0.0409	0.9531	0.9502	1.003	0.220	1.000	0.996
40	0.0306	0.8950	0.9765	0.9761	1.000	0.1425	1.118	0.0817	0.9142	0.9088	1.006	0.114	1.001	0.978
60	0.0459	0.9304	0.9645	0.9642	1.000	0.2260	1.109	0.1226	0.8764	0.8696	1.008	0.075	1.003	1.051
80	0.0613	0.9534	0.9525	0.9523	1.000	0.3232	1.097	0.1634	0.8402	0.8324	1.009	0.057	1.007	1.016
100	0.0766	0.9685	0.9405	0.9404	1.000	0.4372	1.082	0.2043	0.8051	0.7963	1.011	0.046	1.016	0.980
125	0.0957	0.9820	0.9256	0.9255	1.000	0.6106	1.055	0.2554	0.7628	0.7526	1.014	0.037	1.045	0.952
150	0.1149	0.993	0.9107	0.9107	1.000	0.821	1.020	0.3064	0.7222	0.7099	1.017	0.031	1.146	0.955
169**	0.1294	1.000				1.000								

* Vapor Pressure of n-Pentane ** Vapor Pressure of Hydrogen Sulfide

x-y Data Source: Reamer, Sage & Lacey, Ind. Eng. Chem. 45, 1805(1953)

TABLE XIX

SYSTEM: n-PENTANE - HYDROGEN SULFIDE

Temperature: 100°F, Reduced Temperatures: n-Pentane, 0.662; Hydrogen Sulfide, 0.832

Pressure psia	HYDROGEN SULFIDE							n-PENTANE							
	P_r	Vapor Phase				Liquid Phase		P_r	Vapor Phase			Liquid Phase			
		y_1	ϕ_1	(f_1^V/P)	γ_1^V	x_1	$(\gamma_1^L)_{SH}$		ϕ_2	$(f_2^V/P)_h$	γ_2^V	(f_2^L/P)	$(\gamma_2^L)_{SH}$	$(\gamma_2^L)_d$	
15.7*		0.0000				0.0000									
16.2	0.012	0.0300	1.0045	0.9930	1.012			0.033	0.9646	0.9646	1.000				
17.3	0.013	0.1000	1.0031	0.9926	1.011			0.035	0.9625	0.9624	1.000				
19.4	0.015	0.2000	1.0010	0.9915	1.010			0.040	0.9584	0.9582	1.000				
26	0.020	0.4000	0.9957	0.9886	1.007			0.053	0.9465	0.9452	1.001				
50	0.038	0.6684	0.9824	0.9781	1.004	0.0788	1.115	0.102	0.9086	0.9043	1.005	0.297	1.000	1.101	
100	0.076	0.8310	0.9586	0.9564	1.002	0.1951	1.103	0.204	0.8381	0.8290	1.011	0.153	1.002	1.150	
150	0.114	0.8970	0.9360	0.9347	1.001	0.3151	1.090	0.306	0.7740	0.7606	1.018	0.105	1.006	1.109	
200	0.153	0.9280	0.9139	0.9131	1.001	0.4380	1.075	0.409	0.7127	0.6968	1.023	0.080	1.015	1.141	
250	0.191	0.9491	0.8920	0.8915	1.001	0.5662	1.057	0.511	0.6547	0.6370	1.028	0.066	1.032	1.164	
300	0.230	0.9675	0.8702	0.8699	1.000	0.7080	1.036	0.613	0.6009	0.5807	1.035	0.056	1.071	1.194	
350	0.268	0.9850	0.8484	0.8483	1.000	0.860	1.012	0.715	0.5512	0.5276	1.045	0.049	1.168	1.215	
394**	0.302	1.0000				1.000									

* Vapor Pressure of n-Pentane ** Vapor Pressure of Hydrogen Sulfide

x-y Data Source: Reamer, Sage & Lacey, Ind. Eng. Chem. 45, 1805(1953)

TABLE XX

SYSTEM: n-PENTANE - HYDROGEN SULFIDE

Temperature: 160°F, Reduced Temperatures: n-Pentane, 0.734; Hydrogen Sulfide, 0.921

Pressure psia	HYDROGEN SULFIDE						n-PENTANE							
	P _r	Vapor Phase			Liquid Phase		P _r	Vapor Phase			Liquid Phase			
		y ₁	φ ₁	(f ₁ ^{V/P})	γ ₁ ^V	x ₁		(γ ₁ ^L) _{SH}	φ ₂	(f ₂ ^{V/P}) _h	γ ₂ ^V	(f ₂ ^{L/P})	(γ ₂ ^L) _{SH}	(γ ₂ ^L) _d
42.5*		0.0000				0.0000								
44.0	0.034	0.0300	1.0118	0.9856	1.027		0.090	0.9274	0.9274	1.000				
48.3	0.037	0.1000	1.0090	0.9842	1.025		0.099	0.9206	0.9205	1.000				
55.7	0.043	0.2000	1.0044	0.9817	1.023		0.114	0.9096	0.9092	1.000				
71.4	0.055	0.3500	0.9958	0.9766	1.020		0.146	0.8880	0.8864	1.002				
100	0.077	0.5124	0.9825	0.9671	1.016	0.0799	1.106	0.204	0.8525	0.8485	1.005	0.392	1.000	1.152
200	0.153	0.7355	0.9441	0.9347	1.010	0.2218	1.093	0.409	0.7451	0.7341	1.015	0.205	1.003	1.235
300	0.230	0.8279	0.9088	0.9024	1.007	0.3626	1.078	0.613	0.6529	0.6359	1.028	0.143	1.008	1.233
400	0.306	0.8840	0.8744	0.8702	1.005	0.4995	1.062	0.817	0.5714	0.5492	1.040	0.113	1.020	1.172
500	0.383	0.9277	0.8403	0.8382	1.003	0.6372	1.043	1.021	0.5004	0.4711	1.062	0.094	1.045	1.061
600	0.459	0.9553	0.8072	0.8061	1.001	0.7687	1.024	1.226	0.4330	0.3978	1.088	0.082	1.093	1.021
700	0.536	0.981	0.7739	0.7736	1.000	0.900	1.007	1.430	0.3732	0.3333	1.120	0.073	1.197	0.951
778.9**		1.000				1.000								

* Vapor Pressure of n-Pentane ** Vapor Pressure of Hydrogen Sulfide

x-y Data Source: Reamer, Sage & Lacey, Ind. Eng. Chem. 45, 1805(1953)

TABLE XXI

SYSTEM: n-PENTANE - HYDROGEN SULFIDE

Temperature: 220°F, Reduced Temperatures: n-Pentane, 0.804; Hydrogen Sulfide, 1.011

Pressure psia	HYDROGEN SULFIDE							n-PENTANE								
	P _r	Vapor Phase				Liquid Phase			P _r	Vapor Phase			Liquid Phase			
		y ₁	φ ₁	(f ₁ ^{V/P})	γ ₁ ^V	x ₁	(γ ₁ ^L) _{SH}	φ ₂		(f ₂ ^{V/P}) _h	γ ₂ ^V	(f ₂ ^{L/P})	(γ ₂ ^L) _{SH}	(γ ₂ ^L) _d		
94.9*	0.073	0.0000				0.0000										
100	0.077	0.0559	1.0249	0.9748	1.051	0.0062	1.105	0.204	0.8726	0.8725	1.000	0.808	1.000	1.026		
200	0.153	0.4698	0.9820	0.9498	1.034	0.1014	1.098	0.409	0.7710	0.7658	1.007	0.420	1.000	1.083		
300	0.230	0.6251	0.9502	0.9251	1.027	0.1965	1.090	0.613	0.6881	0.6782	1.015	0.292	1.002	1.100		
400	0.306	0.7147	0.9208	0.9005	1.022	0.2912	1.081	0.817	0.6159	0.6013	1.024	0.228	1.004	1.087		
500	0.383	0.7745	0.8928	0.8761	1.019	0.3838	1.071	1.021	0.5509	0.5324	1.035	0.190	1.009	1.044		
600	0.459	0.8185	0.8656	0.8519	1.016	0.4740	1.061	1.226	0.4919	0.4701	1.046	0.165	1.016	1.029		
700	0.536	0.8518	0.8392	0.8277	1.014	0.5604	1.051	1.430	0.4372	0.4133	1.058	0.147	1.027	1.003		
800	0.613	0.8769	0.8136	0.8036	1.012	0.6421	1.040	1.634	0.3851	0.3608	1.067	0.133	1.043	0.996		
900	0.689	0.8963	0.7886	0.7796	1.012	0.7165	1.030	1.839	0.3345	0.3111	1.075	0.123	1.065	0.995		
1000	0.766	0.9125	0.7639	0.7554	1.011	0.7859	1.020	2.043	0.2848	0.2642	1.078	0.115	1.096	1.012		
1100	0.842	0.9289	0.7391	0.7309	1.011	0.8506	1.012	2.247	0.2362	0.2187	1.080	0.108	1.138	1.041		
1200	0.919	0.9474	0.7138	0.7060	1.011	0.9110	1.005	2.451	0.1855	0.1714	1.082	0.102	1.196	1.075		
1300	0.995	0.968	0.6856	0.6802	1.008	0.966	1.001	2.656	0.1372			0.098	1.277	1.277		
1302**	0.997	0.966	0.6853	0.6797	1.008	0.966	1.001	2.660	0.1344			0.098	1.277			

* Vapor Pressure of n-Pentane ** Critical State

x-y Data Source: Reamer, Sage & Lacey, Ind. Eng. Chem. 45, 1805(1953)

TABLE XIII

SYSTEM: n-PENTANE - HYDROGEN SULFIDE

Temperature: 280°F, Reduced Temperatures: n-Pentane, 0.875; Hydrogen Sulfide, 1.100

Pressure psia	HYDROGEN SULFIDE							n-PENTANE							
	P_r	Vapor Phase				Liquid Phase			P_r	Vapor Phase			Liquid Phase		
		y_1	ϕ_1	(f_1^V/P)	γ_1^V	x_1	$(\gamma_1^L)_{SH}$	ϕ_2		$(f_2^V/P)_h$	γ_2^V	(f_2^L/P)	$(\gamma_2^L)_{SH}$	$(\gamma_2^L)_d$	
185.6*	0.142	0.0000			0.0000										
200	0.153	0.0662	1.0557	0.9608	1.099	0.0118	1.054	0.409	0.7999	0.7997	1.000	0.749	1.000	1.009	
300	0.230	0.3452	1.0107	0.9415	1.073	0.0897	1.051	0.613	0.7185	0.7139	1.006	0.517	1.000	1.000	
400	0.306	0.4850	0.9807	0.9223	1.063	0.1630	1.048	0.817	0.6502	0.6418	1.013	0.401	1.001	0.998	
500	0.383	0.5698	0.9564	0.9034	1.059	0.2326	1.044	1.021	0.5885	0.5780	1.018	0.332	1.001	0.994	
600	0.459	0.6292	0.9341	0.8846	1.056	0.3003	1.041	1.226	0.5321	0.5208	1.022	0.286	1.003	0.986	
700	0.536	0.6709	0.9144	0.8659	1.056	0.3655	1.038	1.430	0.4786	0.4683	1.022	0.253	1.004	0.981	
800	0.613	0.7018	0.8965	0.8474	1.058	0.4294	1.034	1.634	0.4274	0.4196	1.019	0.229	1.006	0.975	
900	0.689	0.7230	0.8818	0.8290	1.064	0.4910	1.031	1.839	0.3763	0.3750	1.003	0.210	1.010	0.975	
1000	0.766	0.7356	0.8724	0.8107	1.076	0.5510	1.027	2.043	0.3233	0.3312	0.976	0.195	1.014	0.976	
1100	0.842	0.7420	0.8674	0.7926	1.094	0.6108	1.023	2.247	0.2708	0.2836	0.955	0.183	1.019	0.981	
1200	0.919	0.749	0.8504	0.7745	1.098	0.680	1.018	2.451	0.2346	0.2528	0.928	0.173	1.028	1.063	
1245**	0.953	0.726	0.8504	0.7664	1.110	0.726	1.015	2.543	0.2149	0.2412	0.891	0.169	1.036		

* Vapor Pressure of n-Pentane ** Critical State

x-y Data Source: Reamer, Sage & Lacey, Ind. Eng. Chem. 45, 1805(1953)

TABLE XXIII

SYSTEM: n-PENTANE - HYDROGEN SULFIDE

Temperature: 340°F, Reduced Temperatures: n-Pentane, 0.946; Hydrogen Sulfide, 1.189

Pressure psia	HYDROGEN SULFIDE						n-PENTANE							
	P _r	Vapor Phase			Liquid Phase			P _r	Vapor Phase			Liquid Phase		
		y ₁	φ ₁	(f ₁ ^V /P)	γ ₁ ^V	x ₁	(γ ₁ ^L) _{SH}		φ ₂	(f ₂ ^V /P) _h	γ ₂ ^V	(f ₂ ^L /P)	(γ ₂ ^L) _{SH}	(γ ₂ ^L) _d
329.2*	0.252	0.0000				0.0000								
400	0.306	0.1385	1.1213	0.9385	1.195	0.0402	1.092	0.817	0.6825	0.6817	1.001	0.623	1.000	0.983
500	0.383	0.2732	1.0874	0.9235	1.177	0.0983	1.088	1.021	0.6178	0.6144	1.006	0.511	1.000	0.974
600	0.459	0.3689	1.0589	0.9087	1.165	0.1585	1.083	1.226	0.5615	0.5559	1.010	0.437	1.001	0.964
700	0.536	0.4420	1.0321	0.8940	1.155	0.2217	1.078	1.430	0.5126	0.5044	1.016	0.384	1.002	0.957
800	0.613	0.4990	1.0074	0.8790	1.146	0.2880	1.073	1.634	0.4692	0.4584	1.024	0.344	1.004	0.960
900	0.689	0.5352	0.9929	0.8649	1.148	0.3547		1.839				0.314		
1000	0.766	0.566	0.9749	0.8506	1.146	0.428		2.043				0.290		
1100	0.842	0.575	0.9687	0.8365	1.158	0.515		2.247				0.271		
1120**	0.858	0.536	1.0005	0.8337	1.200	0.536						0.267		

* Vapor Pressure of n-Pentane ** Critical State

x-y Data Source: Reamer, Sage & Lacey, Ind. Eng. Chem. 45, 1805(1953)

APPENDIX B

DISCUSSION OF THE REDLICH-KWONG EQUATION OF STATE FOR THE CALCULATION OF VAPOR PHASE FUGACITY COEFFICIENTS

The Redlich-Kwong (41) equation of state, developed in 1949, is an empirical two coefficient equation designed to describe the P-V-T behaviour of gases at temperatures above the critical and at all pressures. This equation is applicable to both pure gases and mixtures of gases. Its utility lies upon the fact that with only two coefficients it is relatively simple and that these coefficients are derived from the readily attainable critical constants of the gases in question.

The equation is represented by

$$P = \frac{RT}{(\underline{V}_i - b)} - \frac{a}{T^{0.5} \underline{V}_i (\underline{V}_i + b)} \quad (\text{B-1})$$

Five auxiliary equations are presented to make equation B-1 usable

$$Z = \frac{1}{(1 - h)} - \frac{A^2}{B} \left[\frac{h}{(1 + h)} \right] \quad (\text{B-2})$$

$$Z = \frac{P \underline{V}_i}{RT} \quad (\text{B-3})$$

$$A^2 = \frac{a}{R^2 T^{2.5}} = \frac{0.4278 T_c^{2.5}}{P_c T^{2.5}} \quad (\text{B-4})$$

$$B = \frac{b}{RT} = \frac{0.0867 T_c}{P_c T} \quad (\text{B-5})$$

$$h = BP/Z = b/\bar{v}_i \quad (\text{B-6})$$

Since gases at high pressures approach a limiting volume equal to 0.26 of the critical volume (41), the coefficient b was chosen as

$$b = 0.26 \bar{v}_c \quad (\text{B-7})$$

in order to give good numbers at high pressures.

Since b represents the limiting volume at high pressures it is apparent that for gas mixtures b depends linearly upon the mole fractions. Thus

$$b = \sum_i y_i b_i, \quad B = \sum_i y_i B_i \quad (\text{B-8})$$

The coefficient a according to molecular theory and supported by experimental data (30) is a function of the second degree of the mole fractions. Thus

$$a = a_1 y_1^2 + a_2 y_2^2 + \text{-----} + 2a_{12} y_1 y_2 \quad (\text{B-9})$$

and computing the coefficient a_{12} of the cross terms by the normal arbitrary assumption that

$$a_{12} = (a_1 a_2)^{0.5} \quad (\text{B-10})$$

leads to

$$A = \sum_i y_i A_i \quad (\text{B-11})$$

The fugacity coefficient of component i in a mixture is by definition

$$\phi_i = \bar{f}_i / P y_i \quad (\text{B-12})$$

and is obtained from the equation of state by integrating the equation

$$\ln \phi_i = \ln \frac{\bar{f}_i}{P y_i} = \int_0^P (\bar{Z}_i - 1) \frac{dP}{P} \quad (\text{B-13})$$

from $P = 0$ to $P = P$.

Integration of this equation gives

$$\begin{aligned} \log \phi_i = & 0.4343(Z - 1) \frac{B_i}{B} - \log(Z - BP) \\ & - \frac{A^2}{B} \left[\frac{2A_i}{A} - \frac{B_i}{B} \right] \log \left[1 + \frac{BP}{Z} \right] \end{aligned} \quad (\text{B-14})$$

For the details of the integration the reader is referred to the original paper (41).

To simplify this equation in making hand calculations, it is rearranged by use of two additional terms,

$$U = \frac{2A^2}{B} \log \left[1 + \frac{BP}{Z} \right] \quad (\text{B-15})$$

$$W = 0.4343(Z - 1) + 0.5U \quad (\text{B-16})$$

Substitution of these terms reduces equation B-14 to

$$\log \phi_i = 0.4343(Z - 1) - \log(Z - BP) - \frac{A^2}{B} \log \left[1 + \frac{BP}{Z} \right] \quad (\text{B-17})$$

$$\log \phi_i = \log \phi - \frac{U}{A} (A_i - A) + \frac{W}{B} (B_i - B) \quad (\text{B-18})$$

This equation is used by first calculating the constants A_i , B_i , A , B , and A^2/B under the known conditions of pressure, temperature

and composition by means of equations B-4, B-5, B-8, and B-11. A value of Z is assumed from which a value of h is calculated by equation B-6. Z is then calculated by means of equation B-2. The correct value of Z is obtained when the calculated value checks the assumed value. It is then used in equations B-15 and B-16 to calculate U and W . These values are substituted into equation B-17 and B-18 and the fugacity coefficient of component i in the mixture is calculated. This equation is valid for calculation of the fugacity coefficient of pure components as the values of A_i and B_i become equal to A and B respectively, hence the last two terms of equation B-18 become zero and ϕ_i becomes the fugacity coefficient of the pure component.

The use of the Redlich-Kwong equation of state in a sample calculation is presented in Appendix H.

APPENDIX C

DISCUSSION OF THE CHAO-SEADER EQUATION FOR CALCULATION OF THE PURE LIQUID FUGACITY COEFFICIENTS

Chao and Seader developed an equation (9) for the pure liquid fugacity coefficient within the framework of the generalized correlation of Curl and Pitzer (11). This was done by developing an algebraic form of the equation and extending with the use of experimental data into the region of the hypothetical liquids, i. e., into the region where a component cannot exist in the pure state as when the system pressure is below the vapor pressure or the temperature is above the critical temperature. The extension was also made toward lower reduced temperatures.

The equation is given by

$$\log \mathcal{V}^{\circ} = \log \mathcal{V}^{(0)} + \omega \log \mathcal{V}^{(1)} \quad (\text{C-1})$$

where

$$\begin{aligned} \log \mathcal{V}^{(0)} = & A_0 + A_1/T_r + A_2 T_r + A_3 T_r^2 + A_4 T_r^3 \\ & + (A_5 + A_6 T_r + A_7 T_r^2) P_r \\ & + (A_8 + A_9 T_r) P_r^2 - \log P_r \end{aligned} \quad (\text{C-2})$$

$$\begin{aligned} \log \mathcal{V}^{(1)} = & - 4.23893 + 8.65808 T_r - 1.22060/T_r \\ & - 3.15224 T_r^3 - 0.025(P_r - 0.6) \end{aligned} \quad (\text{C-3})$$

The coefficients for equation C-2 are given in Table XXIV.

TABLE XXIV
COEFFICIENTS FOR EQUATION C-1

<u>Coefficient</u>	<u>Simple Fluid</u>	<u>Methane</u>	<u>Hydrogen</u>
A ₀	5.75748	2.43840	1.96718
A ₁	- 3.01761	- 2.24550	1.02972
A ₂	- 4.98500	- 0.34084	- 0.054009
A ₃	2.02299	0.00212	0.0005288
A ₄	0.00	- 0.00223	0.00
A ₅	0.08427	0.10486	0.008585
A ₆	0.26667	- 0.03691	0.00
A ₇	- 0.31138	0.00	0.00
A ₈	- 0.02655	0.00	0.00
A ₉	0.02883	0.00	0.00

The term $\mathcal{V}^{(0)}$ is the fugacity coefficient of the simple fluid which is characterized by an acentric factor, ω , of zero. The term $\omega\mathcal{V}^{(1)}$ is a correction applied to real fluids to account for their departure from simple fluids.

The terms $\mathcal{V}^{(0)}$ and $\mathcal{V}^{(1)}$ are functions only of the reduced temperature and pressure.

Special coefficients were devised when using this equation for hydrogen and methane since the normal temperature of interest with these compounds is far above their critical. The acentric factor for these compounds is taken as zero.

The acentric factor measuring the deviation of a given real fluid

from a simple fluid is defined by Pitzer (11) as

$$\omega = - (1.000 + \log P_r^\circ)_{T_r = 0.7}$$

where P_r° is the reduced vapor pressure at a reduced temperature of 0.7.

Chao and Seader, however, used an acentric factor, only slightly different, calculated in a manner to minimize the error between the experimental \mathcal{V}° and the calculated \mathcal{V}° .

In this work, however, the value of ω as calculated by the Pitzer equation is used.

APPENDIX D

VAN LAAR EQUATION AS MODIFIED BY THE SCATCHARD
AND HILDEBRAND REGULAR SOLUTION TREATMENT

Van Laar using the constants in van der Waals' equation of state developed expressions for the activity coefficients of components in solution with one another. These equations are stated as

$$\ln \gamma_1^L = \frac{B'/T}{(1 + A'x_1/x_2)^2} \quad (D-1)$$

$$\ln \gamma_2^L = \frac{A'B'/T}{(A' + x_2/x_1)^2} \quad (D-2)$$

where

$$A' = b_1/b_2 \quad (D-3)$$

$$B' = \frac{b_1}{R} \left[\frac{a_1^{0.5}}{b_1} - \frac{a_2^{0.5}}{b_2} \right]^2 \quad (D-4)$$

a and b are the van der Waals' constants.

If B' is made equal to A and A' equal to A/B then

$$\ln \gamma_1^L = \frac{A}{\left[1 + \frac{Ax_1}{Bx_2} \right]^2} \quad (D-5)$$

$$\ln \gamma_2^L = \frac{B}{\left[1 + \frac{Bx_2}{Ax_1}\right]^2} \quad (D-6)$$

where

$$A = B' = \frac{b_1}{R} \left[\frac{a_1^{0.5}}{b_1} - \frac{a_2^{0.5}}{b_2} \right]^2 \quad (D-7)$$

$$B = \frac{A}{A'} = \frac{b_2}{R} \left[\frac{a_1^{0.5}}{b_1} - \frac{a_2^{0.5}}{b_2} \right]^2 \quad (D-8)$$

For more complete details of the development of the Van Laar equation the reader is referred to the text of Robinson and Gilliland (42).

Scatchard (43) and Hildebrand (21) independently without the use of the inexact van der Waals fluid arrived at similar expressions. These developments were based on 'regular solutions'. A 'regular solution' may be defined as one having the properties:

1. The energy of a molecular pair is dependent only on their relative position in the solution and their orientation and is independent of all other molecules present and of the temperature.
2. The distribution and orientation of the molecules is random, i. e., other molecules and temperature have no effect.
3. The volume of a component in the mixture does not change upon mixing at constant pressure and temperature.

The development for a binary solution only will be described.

Using the above criteria for a 'regular solution' the cohesive energy of one mole of a mixture is

$$-\underline{E}_m = \frac{C_{11}V_1^2x_1^2 + 2C_{12}V_1V_2x_1x_2 + C_{22}V_2^2x_2^2}{x_1V_1 + x_2V_2} \quad (D-9)$$

In terms of the volume fraction, ϕ , equation D-9 may be rewritten as

$$-\underline{E}_m = (x_1V_1 + x_2V_2)(C_{11}\phi_1^2 + 2C_{12}\phi_1\phi_2 + C_{22}\phi_2^2) \quad (D-10)$$

From equation D-10 the energy of pure component i becomes

$$-\underline{E}_i = C_{ii}/V_i \quad (D-11)$$

The energy change upon mixing is by definition

$$\Delta\underline{E}^m = \underline{E}_m - (x_1\underline{E}_1 + x_2\underline{E}_2) \quad (D-12)$$

Substituting the energy of the mixture, \underline{E}_m , from equation D-9 and the pure component energies from equation D-11 into equation D-12 gives for the molar change in internal energy upon mixing

$$\Delta\underline{E}^m = (x_1V_1 + x_2V_2)(C_{11} + C_{22} - 2C_{12})\phi_1\phi_2 \quad (D-13)$$

and using the usual arbitrary assumption that

$$C_{12} = (C_{11}C_{22})^{0.5} \quad (D-14)$$

and substituting into equation D-13 gives

$$\Delta\underline{E}^m = (x_1V_1 + x_2V_2) \left[C_{11}^{0.5} + C_{22}^{0.5} \right]^2 \phi_1\phi_2 \quad (D-15)$$

Since the internal energy is measured from the reference state of a vapor at infinite volume to the saturated liquid, $-\underline{E}_i$ of equation D-11 becomes equal to $\Delta\underline{E}_i$, where $\Delta\underline{E}_i$ is defined as the

internal energy of vaporization to infinite volume. Hence from equation D-11

$$C_{11} = \left[\frac{\Delta \underline{E}_1}{V_1} \right]^{0.5} \quad \text{and} \quad C_{22} = \left[\frac{\Delta \underline{E}_2}{V_2} \right]^{0.5} \quad (\text{D-16})$$

The term $(\Delta \underline{E}_i / V_i)^{0.5}$ was named the "solubility parameter" with the units of $(\text{cal/cc})^{0.5}$ and given the symbol delta, δ , by Hildebrand.

Substituting the equivalents of C_{11} and C_{22} into equation D-15 gives

$$\Delta \underline{E}^m = (x_1 V_1 + x_2 V_2) \left[\left[\frac{\Delta \underline{E}_1}{V_1} \right]^{0.5} + \left[\frac{\Delta \underline{E}_2}{V_2} \right]^{0.5} \right]^2 \phi_1 \phi_2 \quad (\text{D-17})$$

or

$$\Delta \underline{E}^m = (x_1 V_1 + x_2 V_2) (\delta_1 - \delta_2)^2 \phi_1 \phi_2 \quad (\text{D-18})$$

From the definition of a 'regular solution' that $\Delta \underline{V}_i = 0$ on mixing

$$\Delta \underline{H}^m = \Delta \underline{E}^m \quad (\text{D-19})$$

Thus converting equation D-18 to

$$\Delta \underline{H}^m = (x_1 V_1 + x_2 V_2) (\delta_1 - \delta_2)^2 \phi_1 \phi_2 \quad (\text{D-20})$$

and going to a total mole basis

$$\Delta \underline{H}^m = (n_1 V_1 + n_2 V_2) (\delta_1 - \delta_2)^2 \phi_1 \phi_2 \quad (\text{D-21})$$

and taking the partial derivative with respect to n_1

$$\left[\frac{\partial \underline{H}^m}{\partial n_1} \right]_{n_2, P, T} = V_1 \phi_2^2 (\delta_1 - \delta_2)^2 \quad (\text{D-22})$$

By definition the change in free energy on mixing is

$$\Delta \bar{G}_1^m = \Delta \bar{H}_1^m - T \Delta \bar{S}_1^m \quad (\text{D-23})$$

and for a 'regular solution'

$$\Delta \bar{S}_1^m = -R \ln x_1 \quad (\text{D-24})$$

therefore

$$\Delta \bar{G}_1^m = \underline{V}_1 \phi_2^2 (\delta_1 - \delta_2)^2 + RT \ln x_1 \quad (\text{D-25})$$

From the definition of fugacity and activity

$$\bar{G}_1 = RT \ln \bar{f}_1 \quad (\text{D-26})$$

$$G^\circ = RT \ln f^\circ \quad (\text{D-27})$$

$$a_1 = \bar{f}_1 / f^\circ \quad (\text{D-28})$$

and since the pure liquid is used as the reference state

$$\Delta \bar{G}_1^m = \bar{G}_1 - G^\circ = RT [\ln \bar{f}_1 - \ln f^\circ] = RT \ln a_1 \quad (\text{D-29})$$

Substitution of this value of $\Delta \bar{G}_1^m$ into equation D-25 gives

$$RT \ln a_1 = \underline{V}_1 \phi_2^2 (\delta_1 - \delta_2)^2 + RT \ln x_1 \quad (\text{D-30})$$

or

$$RT \ln (a_1/x_1) = \underline{V}_1 \phi_2^2 (\delta_1 - \delta_2)^2 \quad (\text{D-31})$$

By definition

$$a_1/x_1 = \gamma_1 \quad (\text{D-32})$$

Substituting into equation D-31 gives

$$\ln \gamma_1 = \frac{V_1}{RT} (\delta_1 - \delta_2)^2 \phi_2^2 \quad (D-33)$$

and converting to mole fractions

$$\ln \gamma_1 = \frac{V_1}{RT} (\delta_1 - \delta_2)^2 \left[\frac{x_2 V_2}{x_1 V_1 + x_2 V_2} \right]^2 \quad (D-34)$$

and rearranging

$$\ln \gamma_1 = \frac{A}{\left[\frac{x_1 V_1}{x_2 V_2} + 1 \right]^2} \quad (D-35)$$

where

$$A = \frac{V_1}{RT} (\delta_1 - \delta_2)^2 \quad (D-36)$$

A quantity B may be defined as

$$B = \frac{V_2}{RT} (\delta_1 - \delta_2)^2 \quad (D-37)$$

Then since $A/B = V_1/V_2$ equation D-35 may be written thus

$$\ln \gamma_1 = \frac{A}{\left[\frac{Ax_1}{Bx_2} + 1 \right]^2} \quad (D-38)$$

where A and B are constants for given components at a fixed temperature. The expression for the activity coefficient of component 2 is

$$\ln \gamma_2 = \frac{B}{\left[\frac{Bx_2}{Ax_1} + 1 \right]^2} \quad (\text{D-39})$$

and is derived in a like manner.

Note that these are forms of the Van Laar equations D-7 and D-8, but do not depend upon the van der Waals fluid to calculate the constants A and B.

APPENDIX E

DISCUSSION OF THE WATSON VOLUME FACTOR

AS MODIFIED BY STUCKEY

Molar liquid volumes are necessary in the application of the Scatchard-Hildebrand equation for the liquid activity coefficient. An equation, E-1, first introduced by Gamson and Watson (17) permitted calculation of the molar volume for both real and hypothetical liquids.

$$\underline{V}^L = V_{11} W_{11} (5.7 + 3.0 T_r) \quad (\text{E-1})$$

where $V_{11} W_{11}$ is a reference volume expansion factor

Watson initially applied to the liquid phase the gas phase relationship that

$$PV = ZRT \quad (\text{E-2})$$

where Z is a generalized function of the reduced temperature and pressure only. The expression for the liquid density obtained from equation E-2 is

$$\rho = \frac{M}{V} = \frac{MP}{ZRT} = \frac{P_r}{ZRT_r} \frac{P_c M}{T_c} = \frac{WP_c M}{T_c} \quad (\text{E-3})$$

where W, the expansion factor, is defined as

$$W = \frac{P_r}{ZRT_r} \quad (\text{E-4})$$

W has the units of R^{-1} and is a function of the reduced pressure and temperature only.

The expansion factor, W , can be made dimensionless by redefining it as the ratio of the ideal critical volume to the actual volume thus

$$W = \frac{V_{c_i}/V}{\rho_{c_i}/\rho} = \frac{RT_c/P}{ZRT/P} = \frac{P}{ZT_r} \quad (\text{E-5})$$

where

$$\begin{aligned} V_{c_i} &= \text{ideal critical volume} \\ \rho_{c_i} &= \text{ideal critical density} \end{aligned}$$

Watson found that equation E-4 defining the expansion factor did not give satisfactory results but that by applying the value of W obtained for just one compound to all compounds gave a greatly improved correlation. He used iso-pentane to obtain his initial plot of the expansion factor. This was then applied to all compounds through the equation

$$V = V_1 W_1 / W \quad (\text{E-6})$$

To apply this equation a single density at some convenient temperature must be known. W_1 is read from Watson's plot at the same temperature, then V at any other temperature is found by obtaining W from the plot at this new temperature and applying equation E-4.

Equation E-4 was further simplified by Watson without a great loss in accuracy by making

$$1/W = 5.7 + 3.0 T_r \quad (\text{E-7})$$

W was selected at a sufficiently high pressure to make the liquid phase essentially incompressible. The expansion factor then

becomes a function of only the reduced temperature.

Stuckey (46) because of the difficulty in locating values of V_1W_1 and for ease of use on a digital computer defined a 'reduced expansion factor' as

$$v' = V_1W_1/V_{c_i} = P_c V_1W_1/RT_c \quad (E-8)$$

which he correlated with established values of V_1W_1 using the acentric factor, ω , as a third identifying parameter. The resulting equation

$$v' = 0.01361 - 0.00328\omega - 0.0244\omega^2 + 0.0599\omega^3 - 0.0308\omega^4 \quad (E-9)$$

was further simplified to increase its usefulness without appreciable loss in accuracy to

$$v' = 0.01361 - 0.00436\omega \quad (E-10)$$

The reduced volume, V_r , is calculated using the Watson form of the equation as

$$V_r = v'(5.7 + 3.0 T_r) \quad (E-11)$$

The reduced volume was separated into that of a simple fluid ($\omega = 0$) plus a correction for a real fluid by the equation

$$V_r = V_r^o + \omega V_r' \quad (E-12)$$

where

$$V_r = \text{reduced volume for the simple fluid}$$

$$V_r' = \text{correction for the acentric factor}$$

V_r^0 and V_r^1 are linear functions of reduced temperature and as such are easily calculated. The molar liquid volume is calculated from the reduced volume by

$$\underline{V}^L = RT_c V_r^L / P_c \quad (\text{E-13})$$

Stuckey (46) has tabulated the values of V_r^0 and V_r^1 over the range of reduced temperatures normally encountered.

Stuckey found excellent agreement between the volumes calculated by equation E-13 and those calculated by equation E-1.

APPENDIX F

CALCULATION OF THE SOLUBILITY PARAMETER
FOR HYDROGEN SULFIDE

The solubility parameter as listed by Hildebrand and Scott (21) was used for all components except hydrogen sulfide, for which they did not tabulate a value. This value was calculated from equation D-16.

$$\delta_i = \left[\frac{\Delta \underline{E}_i}{\underline{V}_i} \right]^{0.5} \quad (D-16)$$

where

\underline{E}_i = energy of vaporization to infinite volume, cal/gm-mole

\underline{V}_i = molar volume, cc/gm-mole

The thermodynamic relationship

$$\Delta \underline{H}_i = \Delta \underline{E}_i + \Delta PV_i \quad (F-1)$$

gives

$$\Delta \underline{E}_i = (\underline{H}_i - PV_i)^* - (\underline{H}_i - PV_i)^{sl} \quad (F-2)$$

or

$$\begin{aligned} \Delta \underline{E}_i &= (\underline{H}_i - PV_i)^{sv} - (\underline{H}_i - PV_i)^{sl} + (\underline{H}_i - PV_i)^* \\ &\quad - (\underline{H}_i - PV_i)^{sv} \end{aligned} \quad (F-3)$$

or

$$\Delta \underline{E}_i = \underline{H}_{\text{vaporization}_i} + \underline{H}_i^* - \underline{H}_i^{\text{sv}} + RT(Z^{\text{sl}} - 1) \quad (\text{F-4})$$

where sv, sl, and * refer to the saturated vapor state, saturated liquid state and ideal gas state respectively.

For hydrogen sulfide at saturation and 25°C.

$$P_r = 0.224 \quad (49)$$

$$T_r = 0.798 \quad (49)$$

$$Z_c = 0.278 \quad (2)$$

$$Z^{\text{sl}} = 0.034 \quad (24)$$

$$\underline{V}^{\text{L}} = 0.02091 \text{ ft}^3/\# \quad (49)$$

$$\underline{H}_{\text{vap}} = 183.2 \text{ BTU}/\# \quad (49)$$

$$(\underline{H}^* - \underline{H}^{\text{sv}})/T_c = 0.711 \text{ cal/gm-mole}/^\circ\text{K} \quad (24)$$

$$(\underline{H}^* - \underline{H}^{\text{sv}}) = (0.711)(373.61^\circ\text{K}) = 266 \text{ cal/gm-mole}$$

$$\underline{V}^{\text{L}} = (0.02091 \text{ ft}^3/\#)(34.08 \text{ \#/}\#\text{-mole})(62.422 \text{ cc/gm}/\text{ft}^3/\#)$$

$$\underline{V}^{\text{L}} = 44.48 \text{ cc/gm-mole}$$

$$\underline{H}_{\text{vap}} = (183.2 \text{ BTU}/\#)(34.08 \text{ \#/}\#\text{-mole})/(1.8 \text{ BTU}/\#\text{-mole}/\text{cal/gm-mole})$$

$$\underline{H}_{\text{vap}} = 3469 \text{ cal/gm-mole}$$

Substituting these values into equation F-4 gives

$$\begin{aligned} \Delta \underline{E} &= (3469 \text{ cal/gm-mole}) + (266 \text{ cal/gm-mole}) \\ &\quad + (1.987 \text{ cal/gm-mole}/^\circ\text{K})(373.61^\circ\text{K})(0.034 - 1) \end{aligned}$$

$$\Delta \underline{E} = 3163 \text{ cal/gm-mole}$$

Then substituting into equation F-1 gives for the solubility parameter

$$\delta_{25^\circ\text{C}} = \left[\frac{3163 \text{ cal/gm-mole}}{44.48 \text{ cc/gm-mole}} \right]^{0.5} = 8.43 \text{ (cal/cc)}^{0.5}$$

APPENDIX G

PHYSICAL CONSTANTS

<u>Component</u>	<u>T_c - °R</u>	<u>P_c - Atm</u>	<u>ω</u>	<u>(cal/cc)^{0.5}</u>
Methane	343.91	45.80	0.013	5.45
Ethane	550.01	48.30	0.105	5.88
Propane	665.95	42.01	0.152	6.00
n-Pentane	845.60	33.31	0.252	7.05
Hydrogen Sulfide	672.5	88.87	0.100	8.43

The critical temperatures and pressures were taken from the API Project 44 compilations (2).

The acentric factors are those tabulated by Pitzer (11).

The solubility parameters with the exception of hydrogen sulfide which was calculated in Appendix F were taken from Hildebrand and Scott (21).

APPENDIX H

SAMPLE CALCULATION

This sample calculation illustrates the method used to obtain the hypothetical vapor phase fugacity coefficient of the heavy component in a binary solution.

The methane-hydrogen sulfide system at 40°F. is used here for illustrative purposes. The x-y data selected are those of Reamer, Sage and Lacey tabulated in Table V.

Step 1

Calculate the vapor phase fugacity coefficient via the Redlich-Kwong equation of state for both components in the mixture at each data point and the fugacity coefficient of the pure light component (methane).

The data point at 600 psia is selected to illustrate the calculation of fugacity coefficients by the Redlich-Kwong equation. The Redlich-Kwong equation is further discussed in Appendix B.

The Redlich-Kwong equation is

$$\log \varphi = 0.4343(Z - 1) - \log (Z - BP) - \frac{A^2}{B} \log \left[1 + \frac{BP}{Z} \right] \quad (\text{B-17})$$

$$\log \phi_i = \log \varphi - \frac{U}{A}(A_i - A) + \frac{W}{B}(B_i - B) \quad (\text{B-18})$$

Experimental data:

System: methane-hydrogen sulfide binary

Pressure: 600 psia - 40.827 atm.

Temperature: 40°F.

Mole fraction methane:

Liquid (x): 0.0636

Vapor (y): 0.6394

Critical constants:

Methane:

$$P_c = 45.80 \text{ atm.}$$

$$T_c = 343.91^\circ\text{R.}$$

Hydrogen sulfide:

$$P_c = 88.87 \text{ atm.}$$

$$T_c = 672.5^\circ\text{R.}$$

Calculate P_r and T_r :

Methane:

$$P_{r1} = P/P_c = 40.827/45.80 = 0.891$$

$$T_{r1} = T/T_c = 499.69/343.91 = 1.453$$

Hydrogen sulfide:

$$P_{r2} = P/P_c = 40.827/88.87 = 0.459$$

$$T_{r2} = T/T_c = 499.69/672.5 = 0.743$$

Calculate A_i and B_i :

Methane:

$$A_1 = \left[\frac{0.4278}{P_c T_r^{2.5}} \right]^{0.5} = \left[\frac{0.4278}{(45.80)(1.453)^{2.5}} \right]^{0.5} = 0.06059$$

$$B_1 = \frac{0.0867}{P_c T_r} = \frac{0.0867}{(45.80)(1.453)} = 0.0013029$$

Hydrogen sulfide:

$$A_2 = \left[\frac{0.4278}{P_c T_r^{2.5}} \right]^{0.5} = \left[\frac{0.4278}{(88.87)(0.743)^{2.5}} \right]^{0.5} = 0.10057$$

$$B_2 = \frac{0.0867}{P_c T_r} = \frac{0.0867}{(88.87)(0.743)} = 0.0013130$$

Calculate A, B, and A²/B:

For the mixture:

$$A = \sum y_i A_i = y_1 A_1 + y_2 A_2$$

$$A = (0.6394)(0.06059) + (0.3606)(0.10057) = 0.07501$$

$$B = \sum y_i B_i = y_1 B_1 + y_2 B_2$$

$$B = (0.6394)(0.0013029) + (0.3606)(0.0013130) = 0.0013065$$

$$A^2/B = (0.07501)^2 / (0.0013065) = 4.30654$$

Calculate Z

$$\text{Assume } Z = 0.80288$$

$$h = BP/Z = (0.0013065)(40.827) / (0.80288) = 0.06644$$

$$Z = \left[\frac{1}{1-h} \right] - \frac{A^2}{B} \left[\frac{h}{1+h} \right]$$

$$Z = \left[\frac{1}{1.00000 - 0.06644} \right] - \left[\frac{(4.30654)(0.06644)}{1.06644} \right] = 0.80288$$

Z calculated equals Z assumed so is considered correct

Calculate log φ

$$0.4343(Z - 1) = 0.4343(0.80288 - 1) = -0.08561$$

$$- \log (Z - BP) = - \log [0.80288 - (0.0013065)(40.827)]$$

$$- \log (Z - BP) = - 9.87480 + 10$$

$$- \frac{A^2}{B} \log \left[1 + \frac{BP}{Z} \right] = 4.30654 \log \left[1 + \frac{(0.0013065)(40.827)}{0.80288} \right]$$

$$- \frac{A^2}{B} \log \left[1 + \frac{BP}{Z} \right] = - 0.12032$$

$$\log \psi = 0.4343 (Z - 1) - \log (Z - BP) - \frac{A^2}{B} \log \left[1 + \frac{BP}{Z} \right]$$

$$\log \psi = - 0.08561 - 9.87480 + 10 - 0.12032$$

$$\log \psi = 9.91927 - 10$$

Calculate ϕ_1 and ϕ_2

$$U = \frac{2A^2}{B} \log \left(1 + \frac{BP}{Z} \right)$$

$$U = (2)(0.12032) = 0.24064$$

$$W = 0.4343 (Z - 1) + 0.5 U$$

$$W = - 0.08561 + 0.12032 = 0.03471$$

For methane

$$- (U/A)(A_1 - A) = (0.24064/0.07501)(0.06059 - 0.07501)$$

$$- (U/A)(A_1 - A) = 0.04626$$

$$(W/B)(B_1 - B) = (0.03471/0.0013065)(0.0013029 - 0.0013065)$$

$$\log \phi_1 = \log \psi - (U/A)(A_1 - A) + (W/B)(B_1 - B)$$

$$\log \phi_1 = 9.91927 - 10 + 0.04626 - 0.00009$$

$$\log \phi_1 = 9.96562 - 10$$

$$\phi_1 = 0.9235$$

For hydrogen sulfide

$$- (U/A)(A_2 - A) = (0.24064/0.07501)(0.10057 - 0.07501)$$

$$- (U/A)(A_2 - A) = - 0.08199$$

$$(W/B)(B_2 - B) = (0.03471/0.0013065)(0.0013130 - 0.0013065)$$

$$(W/B)(B_2 - B) = 0.00017$$

$$\log \phi_2 = \log \varphi - (U/A)(A_2 - A) + (W/B)(B_2 - B)$$

$$\log \phi_2 = 9.91927 - 10 - 0.08199 + 0.00017$$

$$\log \phi_2 = 9.83749 - 10$$

$$\phi_2 = 0.6878$$

Repeating the above calculation for pure methane and remembering that $A = A_1$ and $B = B_1$ makes $\log \varphi = \log \phi_1^{\circ}$. This calculation gives

$$\log \phi_1^{\circ} = 9.95852 - 10$$

$$\phi_1^{\circ} = 0.9089$$

Step 2

Calculate the vapor activity coefficient (γ_1^V) for the light component (methane).

$$\gamma_1^V = \phi_1 / \phi_1^{\circ} = \phi_1 / (f_1^V / P) = 0.9235 / 0.9089 = 1.016$$

Step 3

Plot the mole fraction of the light component in the vapor phase (methane) versus the logarithm of the vapor phase activity coefficient (γ_1^V). The data for the methane-hydrogen sulfide system at 40°F. from Table V is retabulated in Table XXV and plotted in Figure 11.

Step 4

Calculate the logarithm of the hydrogen sulfide activity coefficient by numerically integrating equation III-1. Use Figure 11 to obtain the relationship between y_1 and $\log \gamma_1^V$. The integrating equation is

$$\Delta \log \gamma_2^V = - \frac{\Delta \log \gamma_1^V}{2} \left[\left[\frac{y_1}{1 - y_1} \right]_{\text{①}} + \left[\frac{y_1}{1 - y_1} \right]_{\text{②}} \right] \quad (\text{H-1})$$

The subscripts ①, and ② refer to the initial and the terminal values of the $\log \gamma_1^V$ increment. $\log \gamma_2^V$ at any value of y_1 is calculated by the summation of all increments of $\log \gamma_2^V$ from $y_1 = 0$ to $y_1 = y_1$ as indicated by the equation

$$\Delta \log \gamma_2^V = \sum_0^{y_1} \Delta \log \gamma_2^V \quad (\text{H-2})$$

TABLE XXV

ACTIVITY COEFFICIENTS FOR METHANE IN EQUILIBRIUM
WITH HYDROGEN SULFIDE AT 40°F.

Pressure psia	Mole Fraction in Vapor	γ_1^V	$\log \gamma_1^V$
169	0.0000		
178	0.053	1.023	0.00990
200	0.1371	1.022	0.00941
250	0.2783	1.020	0.00865
300	0.3896	1.018	0.00768
350	0.4604	1.017	0.00729
400	0.5126	1.016	0.00710
450	0.5551	1.016	0.00694
500	0.5879	1.016	0.00691
600	0.6394	1.016	0.00694
700	0.6755	1.017	0.00718
800	0.6989	1.018	0.00779
900	0.7141	1.020	0.00877
1000	0.7242	1.024	0.01009
1100	0.7299	1.028	0.01191
1200	0.7321	1.034	0.01436
1250	0.7319	1.037	0.01589
1300	0.7306	1.042	0.01773
1400	0.7262	1.052	0.02219
1500	0.7185	1.067	0.02809
1600	0.7075	1.085	0.03557
1700	0.6931	1.108	0.04452
1750	0.6828	1.123	0.05034
1800	0.6686	1.143	0.05804
1900	0.6130	1.226	0.08856
1949	0.5500	1.337	0.12602

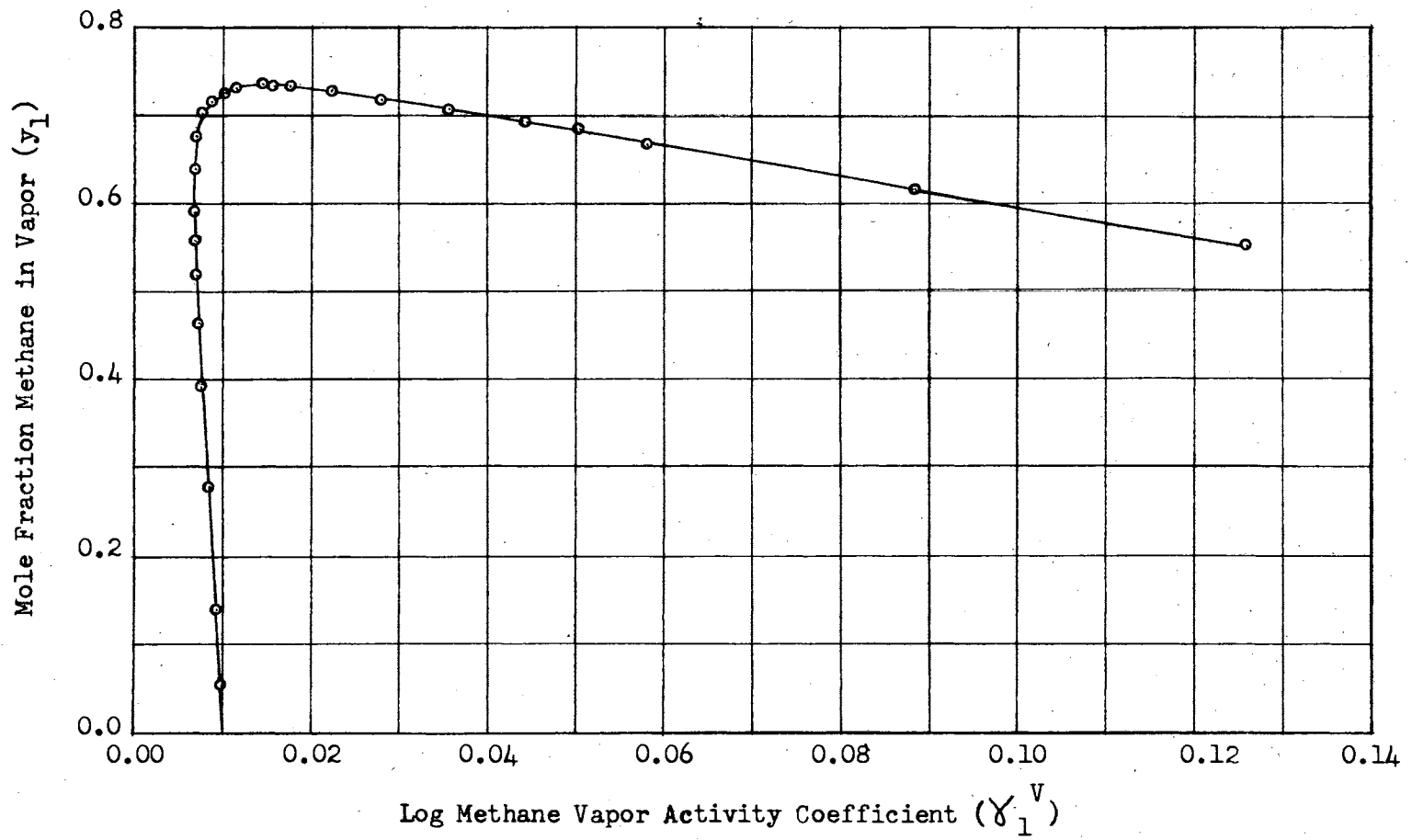


Figure 11

Log Methane Vapor Activity Coefficient versus Mole Fraction in Vapor.
Methane in Equilibrium with Hydrogen Sulfide at 40°F.

The integration was performed by dividing the $\log \gamma_1^V$ scale of Figure 11 into sufficiently small increments so that the area bounded by the limits of the increment, the abscissa and the curve approximated a trapezoid. The application of the integrating equation is demonstrated in Table XXVI.

TABLE XXVI
NUMERICAL INTEGRATION OF EQUATION III-1

$\log \gamma_1^V$	$\Delta \log \gamma_1^V$	y_1	$\frac{y_1}{1-y_1}$	$\Delta \log \gamma_2^V$	$\log \gamma_2^V$
0.0103		0.000	0.00000		
0.0100	-0.0003	0.050	0.05263	0.00001	0.00001
0.0095	-0.0005	0.150	0.17647	0.00006	0.00007
0.0090	-0.0005	0.225	0.29032	0.00012	0.00019
0.0085	-0.0005	0.300	0.42857	0.00018	0.00037
0.0080	-0.0005	0.368	0.58227	0.00025	0.00062
0.0075	-0.0005	0.425	0.73913	0.00033	0.00095
0.0070	-0.0005	0.545	1.19780	0.00048	0.00143
0.0068	-0.0002	0.615	1.59740	0.00028	0.00171
0.0070	0.0002	0.652	1.87356	-0.00035	0.00136
0.0075	0.0005	0.689	2.21543	-0.00102	0.00034
0.0080	0.0005	0.701	2.34448	-0.00114	-0.00080
0.0085	0.0005	0.710	2.44827	-0.00120	-0.00200
0.0090	0.0005	0.716	2.52112	-0.00124	-0.00324
0.0095	0.0005	0.720	2.57142	-0.00127	-0.00451
0.0100	0.0005	0.723	2.61010	-0.00130	-0.00581
0.0105	0.0005	0.726	2.64963	-0.00131	-0.00712
0.0110	0.0005	0.727	2.66300	-0.00133	-0.00845
0.0115	0.0005	0.728	2.67647	-0.00133	-0.00978
0.0120	0.0005	0.731	2.71747	-0.00135	-0.01113
0.0125	0.0005	0.731	2.71747	-0.00136	-0.01249
0.0130	0.0005	0.732	2.73134	-0.00136	-0.01385
0.0135	0.0005	0.733	2.74531	-0.00137	-0.01522
0.0140	0.0005	0.733	2.74531	-0.00137	-0.01659
0.0145	0.0005	0.733	2.74531	-0.00137	-0.01796
0.0150	0.0005	0.733	2.74531	-0.00137	-0.01933
0.0200	0.0050	0.729	2.69003	-0.01359	-0.03292
0.0250	0.0050	0.724	2.62318	-0.01328	-0.04620
0.0300	0.0050	0.717	2.53356	-0.01289	-0.05909
0.0350	0.0050	0.709	2.43642	-0.01242	-0.07151
0.0400	0.0050	0.701	2.34448	-0.01195	-0.08346

TABLE XXVI (Continued)

$\text{Log } \gamma_1^V$	$\Delta \text{Log } \gamma_1^V$	y_1	$\frac{y_1}{1 - y_1}$	$\Delta \text{Log } \gamma_2^V$	$\text{Log } \gamma_2^V$
0.0450	0.0050	0.692	2.24675	-0.01148	-0.09494
0.0500	0.0050	0.683	2.15457	-0.01100	-0.10594
0.0550	0.0050	0.675	2.07692	-0.01058	-0.11652
0.0600	0.0050	0.666	1.99401	-0.01018	-0.12670
0.0650	0.0050	0.657	1.91545	-0.00977	-0.13647
0.0700	0.0050	0.648	1.84090	-0.00939	-0.14586
0.0750	0.0050	0.639	1.77008	-0.00903	-0.15489
0.0800	0.0050	0.630	1.70270	-0.00868	-0.16357
0.0850	0.0050	0.620	1.63157	-0.00834	-0.17191
0.0900	0.0050	0.611	1.57069	-0.00801	-0.17992
0.0950	0.0050	0.601	1.50626	-0.00769	-0.18761
0.1000	0.0050	0.593	1.45700	-0.00741	-0.19502
0.1050	0.0050	0.584	1.40384	-0.00715	-0.20217
0.1100	0.0050	0.576	1.35849	-0.00691	-0.20908
0.1150	0.0050	0.568	1.31481	-0.00668	-0.21576
0.1200	0.0050	0.560	1.27272	-0.00647	-0.22223
0.1250	0.0050	0.552	1.23214	-0.00626	-0.22849
0.1260	0.0010	0.550	1.22222	-0.00123	-0.22972

Step 5

Plot the logarithm of the vapor activity coefficient of hydrogen sulfide versus the mole fraction of methane in the vapor. This plot is shown in Figure 12.

Step 6

The values for the logarithms of the vapor activity coefficients of hydrogen sulfide are read from the curve in Figure 12 at values of the mole fractions of methane corresponding to the data points. At these data points the fugacity coefficient of hydrogen sulfide in the mixture was calculated as illustrated in step 1. Then the fugacity coefficient for the hypothetical vapor of hydrogen sulfide was calculated from its activity coefficient and its mixture fugacity coefficient by equation III-2.

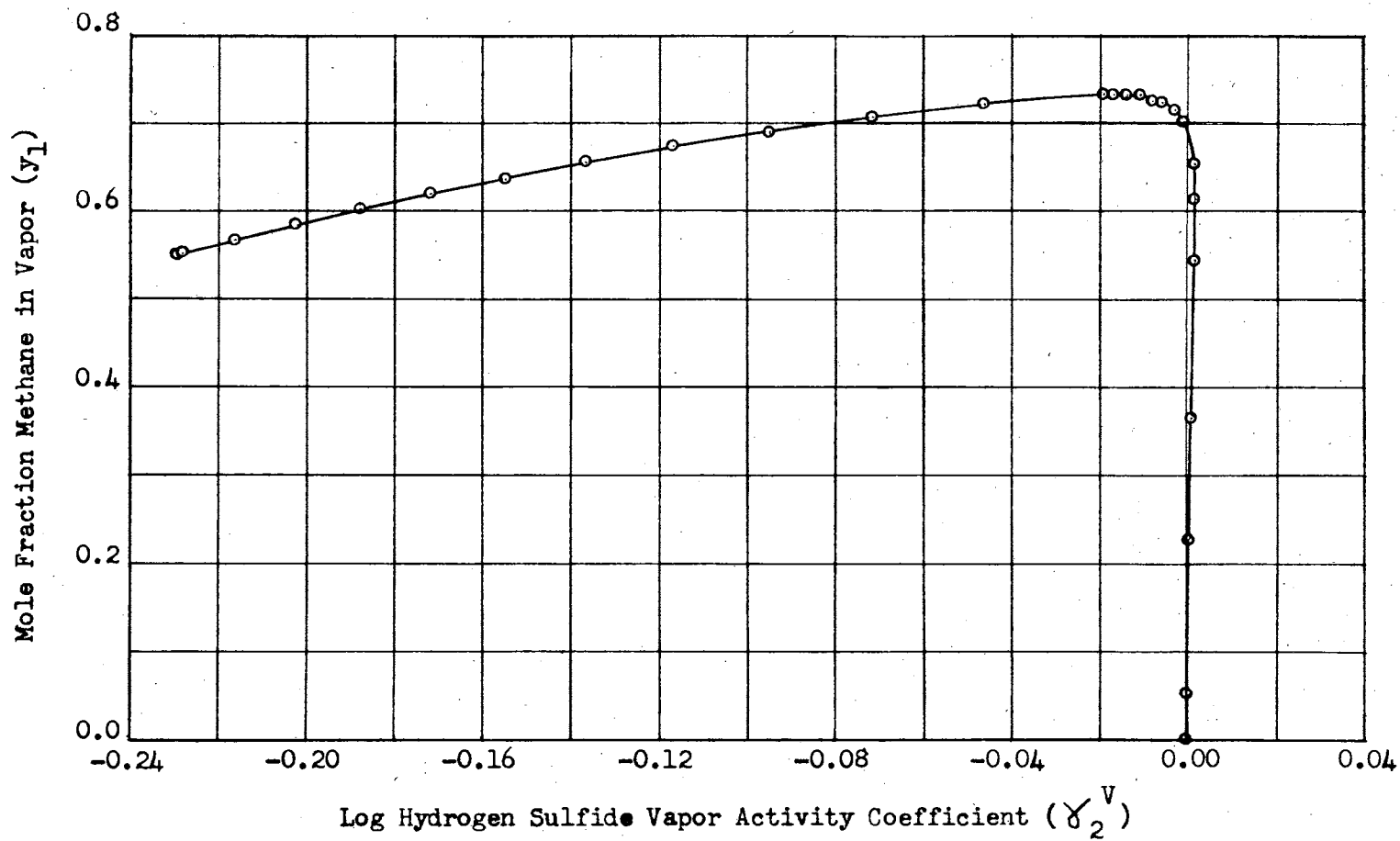


Figure 12

Log Vapor Activity Coefficient of Hydrogen Sulfide versus Mole Fraction Methane in Vapor.
Methane in Equilibrium with Hydrogen Sulfide at 40°F.

$$(f_2^V/P)_h = (\bar{f}_2^V/Py_2)/\gamma_2^V \quad (\text{III-2})$$

$$\log \phi_2 = \log (\bar{f}_2^V/Py_2) = 9.83749 - 10 \quad (\text{at } 600 \text{ psia})$$

$$\log \gamma_2^V = 0.0016 \quad (\text{at } 600 \text{ psia})$$

hence

$$\log (f_2^V/P)_h = \log \phi_2 - \log \gamma_2^V = 9.83749 - 10 - 0.0016$$

$$\log (f_2^V/P)_h = 9.83589 - 10$$

$$(f_2^V/P)_h = 0.6853$$

Calculation of the Liquid Activity Coefficient

The activity coefficient of the heavy component in the liquid was calculated from the activity coefficient of the light component in the vapor by bridging to the activity coefficient of the heavy component in the vapor and then to the heavy component in the liquid. This is done by means of equation III-3 as will be demonstrated for hydrogen sulfide in the methane-hydrogen sulfide system at 40°F. and 600 psia.

Step 1

The vapor fugacity coefficient of hydrogen sulfide in the mixture (ϕ_2) is calculated by the Redlich-Kwong equation of state as previously demonstrated.

Step 2

The K-value (y_2/x_2) is from the experimental data using the same point as used in determining the fugacity coefficient previously.

Step 3

The fugacity coefficient of the pure liquid (f_2^L/P) is calculated by the Chao-Seader equation which is stated as

$$\log (f_i^L/P) = \log \mathcal{V}^o = \log \mathcal{V}^{(o)} + \log \mathcal{V}^{(1)} \quad (C-1)$$

where using the coefficients for a simple fluid

$$\begin{aligned} \log \mathcal{V}_2^{(o)} = & 5.75748 - 3.01761/T_r - 4.98500 T_r + 2.02299 T_r^2 \\ & + (0.08427 + 0.26667 T_r - 0.31138 T_r^2) P_r \\ & + (- 0.02655 + 0.02883 T_r) P_r^2 - \log P_r \end{aligned}$$

$$\begin{aligned} \log \mathcal{V}_2^{(1)} = & - 4.23892 + 8.65808 T_r - 1.22060/T_r \\ & - 3.15224 T_r^3 - 0.025 (P_r - 0.6) \end{aligned}$$

For hydrogen sulfide $\omega = 0.100$ and as previously determined at 600 psia and 40° F., $T_r = 0.743$ and $P_r = 0.459$.

Therefore, the substitution of these numbers into the above equations gives

$$\begin{aligned} \log \mathcal{V}_2^{(o)} = & 5.75748 - 3.01761/0.743 - 4.98500 (0.743) \\ & + 2.02299 (0.743)^2 + [0.08427 + 0.26667 (0.743) \\ & - 0.31138 (0.743)^2] 0.459 + [- 0.02655 \\ & + 0.02883 (0.743)] (0.459)^2 - \log 0.459 \end{aligned}$$

$$\log \mathcal{V}_2^{(o)} = 9.49688 - 10$$

$$\begin{aligned} \log \mathcal{V}_2^{(1)} = & - 4.23893 + 8.65808 (0.743) - 1.22060/(0.743) \\ & - 3.15224 (0.743)^3 - 0.025 (0.459 - 0.6) \end{aligned}$$

$$\log \mathcal{V}_2^{(1)} = - 0.73765$$

$$\log \mathcal{V}_2^{\circ} = 0.49688 - 10 + 0.100 (-0.73765) = 9.42311 - 10$$

$$\mathcal{V}_2^{\circ} = f_2^{\text{L}}/P = 0.265$$

Step 4

Calculate the liquid activity coefficient for pure hydrogen sulfide

$$\gamma_2^{\text{L}} = \frac{(\phi_2)(y_2/x_2)}{(f_2^{\text{L}}/P)}$$

$$\gamma_2^{\text{L}} = (0.6878)(0.3851)/(0.265) = 1.000$$

Calculation of the Liquid Activity Coefficient

by the Modified Van Laar Equation

The modified Van Laar equation is

$$\log \gamma_1^{\text{L}} = \frac{0.43429 A}{[(A/B)(x_1/x_2) + 1]^2} \quad (\text{D-38})$$

and

$$\log \gamma_2^{\text{L}} = \frac{0.43429 B}{[(B/A)(x_2/x_1) + 1]^2} \quad (\text{D-39})$$

where

$$A = (\underline{V}_1^{\text{L}}/RT)(\delta_1 - \delta_2)^2 \quad (\text{D-36})$$

$$B = (\underline{V}_2^{\text{L}}/RT)(\delta_1 - \delta_2)^2 \quad (\text{D-37})$$

Step 1

The volumes used are the generalized volumes of Watson as modified by Stuckey.

$$\underline{V}_i^L = (RT_c V_{r_i}^L) / P_c \quad (\text{E-11})$$

$$V_{r_i} = V_{r_i}^{\circ} + \omega V_{r_i}' \quad (\text{E-12})$$

$V_{r_i}^{\circ}$ and V_{r_i}' are from the tabulated data of Stuckey (46).
For methane at 600 psia and 40°F.

$$T_r = 1.453; P_r = 0.891; \omega = 0.013$$

$$V_{r_1}^{\circ} = 0.13690$$

$$V_{r_1}' = -0.04390$$

$$V_{r_1}^L = 0.13690 - (0.013)(0.04390) = 0.13632$$

$$\underline{V}_1^L = RT_{c_1} V_{r_1}^L / P_{c_1} = (45.587)(343.91)(0.13632) / (45.80)$$

$$\underline{V}_1^L = 46.66 \text{ cc/gm-mole}$$

For hydrogen sulfide at 600 psia and 40°F.

$$T_r = 0.743; P_r = 0.459; \omega = 0.100$$

$$V_{r_2}^L = 0.10444$$

$$\underline{V}_2^L = RT_{c_2} V_{r_2}^L / P_{c_2} = (45.587)(672.5)(0.10444) / (88.87)$$

$$\underline{V}_2^L = 36.03 \text{ cc/gm-mole}$$

Step 2

Calculation of the A and B constants

$$A = (\underline{V}_1^L / RT)(\delta_1 - \delta_2)^2$$

$$A = [(46.66) / (1.987)(277.61)] (8.43 - 5.45)^2 = 0.7512$$

$$B = (V_2^L/RT)(\delta_1 - \delta_2)^2$$

$$B = [(36.03)/(1.987)(277.61)](8.43 - 5.45)^2 = 0.5800$$

Step 3

Calculation of γ_1^L and γ_2^L

$$x_1 = 0.0636; x_2 = 0.9364$$

$$\log \gamma_1^L = \frac{0.43429 A}{[(x_1/x_2)(A/B) + 1]^2} = \frac{(0.43429)(0.7512)}{\left[\frac{0.0636}{0.9364} \left[\frac{0.7512}{0.5800}\right] + 1\right]^2}$$

$$\log \gamma_1^L = 0.2756$$

$$\gamma_1^L = 1.886$$

$$\log \gamma_2^L = \frac{0.43429 B}{[(x/x)(B/A) + 1]^2} = \frac{(0.43429)(0.5800)}{\left[\frac{0.9364}{0.0636} \left[\frac{0.5800}{0.7512}\right] + 1\right]^2}$$

$$\log \gamma_2^L = 0.0016$$

$$\gamma_2^L = 1.004$$

APPENDIX I

NOMENCLATURE

- A
 - parameter in the Redlich-Kwong equation of state
 - parameter in the Scatchard-Hildebrand liquid activity coefficient equation
 - parameter in the Chao-Seader equation
 - thermodynamic work function
- A'
 - parameter in the Van Laar liquid activity coefficient equation
- a
 - parameter in the Van Laar liquid activity coefficient equation
 - parameter in the Redlich-Kwong equation of state
 - activity
- B
 - parameter in the Redlich-Kwong equation of state
 - parameter in the Scatchard-Hildebrand liquid activity coefficient equation
- B'
 - parameter in the Van Laar liquid activity coefficient equation
- b
 - parameter in the Van Laar liquid activity coefficient equation
 - parameter in the Redlich-Kwong equation of state
- C
 - Scatchard's cohesive energy density
- E
 - internal energy
- f
 - fugacity
- G
 - Gibbs' free energy
- H
 - enthalpy

- h - auxiliary constant in Redlich-Kwong equation of state
- K - vapor-liquid equilibrium distribution ratio
- M - molecular weight
- n - number of moles
- P - system pressure
- P° - vapor pressure
- p - partial pressure
- R - universal gas constant
- S - entropy
- T - temperature
- U - term of Redlich-Kwong equation of state defined by equation B-16
- V - volume
- v' - Stuckey's reduced expansion factor
- W - term of Redlich-Kwong equation of state defined by equation B-17
- Watson's expansion factor
- x - mole fraction of component in liquid
- y - mole fraction of component in vapor
- Z - compressibility factor

Greek Symbols

- γ - activity coefficient
- Δ - difference
- δ - Hildebrand's solubility parameter
- μ - chemical potential
- ν - fugacity coefficient of pure liquid
- ν° - fugacity coefficient of pure real or hypothetical liquid by Chao-Seader equation

- $\mathcal{V}^{(0)}$ - fugacity coefficient of the simple fluid by Chao-Seader equation
- $\mathcal{V}^{(1)}$ - correction for acentric factor in the Chao-Seader equation
- ρ - density
- ϕ - fugacity coefficient of component in gaseous solution
- volume fraction
- ϕ - fugacity coefficient of gaseous mixture
- ω - acentric factor

Subscripts

- c - property at critical conditions
- d - liquid activity coefficient calculated from equation III-3
- h - property of the hypothetical vapor or liquid
- i - component i
- j - component j
- m - property of the mixture
- N - number of components
- r - reduced property
- SH - liquid activity coefficient calculated from the Scatchard-Hildebrand equation

Superscripts

- L - liquid phase
- m - property change on mixing
- o - degree
- property of the simple fluid
- standard reference state
- sl - saturated liquid

- sv - saturated vapor
- V - vapor phase
- * - ideal gas state
- ' - correction applied to the simple fluid property for acentric factor

Miscellaneous

- Superbar - partial molar property
- Subbar - molar property
- 1 & 2 - light and heavy component in the mixture respectively

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Master of Science

Thesis: STANDARD STATE FUGACITY COEFFICIENTS FOR THE HYPOTHETICAL VAPOR BY BRIDGING FROM THE REAL GAS FUGACITY COEFFICIENTS THROUGH THE GIBBS-DUHEM EQUATION

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