VAPOR-LIQUID EQUILIBRIUM STUDY OF

THE METHANE-HYDROGEN SULFIDE-

N-DECANE TERNARY SYSTEM

By

ANTHONY LORING HINES

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University of Oklahoma

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Thesis Approved:

Robert L Robinson Jr
Thesis Adviser

B. L. Crynes

O. D. Durham
Dean of the Graduate College

824787

PREFACE

Gas-liquid chromatography was used in this work to obtain equilibrium K-values of hydrogen sulfide and propane at infinite dilution in the methane-n-decane system. Measurements were made over a temperature range of 15 to 130°F and a pressure range of 100 to 1000 psia.

Equilibrium K-values for hydrogen sulfide were calculated from combined Scatchard-Hildebrand and Flory-Huggins equations utilizing cohesive energy densities obtained by fitting binary data to the above-mentioned equations.

I wish to express my sincere appreciation to my adviser, Dr. R. L. Robinson, Jr., for his guidance, encouragement, and interest throughout the course of this study.

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CHAPTER I

INTRODUCTION

Gas-liquid chromatography has recently been used extensively by several investigators to study the thermodynamic properties of solutions. One of the primary advantages in making infinite dilution studies by chromatographic techniques is in the elimination of composition as a system variable thus resulting in a simplification of the thermodynamic equations that describe the system.

The purpose of this work was to study the methane-hydrogen sulfide-n-decane system and determine equilibrium K-values for hydrogen sulfide. This system is of interest to the petroleum industry because all three of the above components appear naturally in petroleum. Since hydrogen sulfide must be removed from petroleum, the equilibrium relationships between hydrogen sulfide and the hydrocarbon system should be known.

Another purpose for studying this particular system was to determine how accurately equilibrium K-values could be predicted in the ternary system from available binary data when fitted to the combined Scatchard-Hildebrand and Flory-Huggins equations.

CHAPTER II

LITERATURE SURVEY

History of Chromatography

According to Dal Nogare and Juvet (1) chromatography had its

beginning in 1850 in the work of F. F. Runge, a German dye chemist.

His separation process is today known as paper chromatography. In 1893

Reed (2) became the first to separate mixtures over a powdered bed. It

was not until 1906 that Tswelt (3), a Russian botanist, published the

first account of column chromatography in which he separated the color

pigments from plants by percolating a liquid phase through a column

packed with a solid adsorbent. He observed that the different pigments

separated into colored layers, which he called a chromatogram, thus

giving rise to the term chromatography, which is interpreted as color

writing. Chromatography was later defined by Keulemans (4) as being a

physical method of separation, in which the components to be separated

are distributed between two phases, one of these phases constituting a

stationary bed of large surface area, the other being a fluid that

percolates through the stationary bed.

Little progress occurred in chromatography until the mid 1940's

when Turner (5) and Classen (6) used gas rather than a liquid as the

mobile phase to demonstrate the separation of homologous mixtures in

sequence by adsorption and displacement from a solid adsorbent.

Phillips (7), Cremer (8) and their co-workers further developed the

separation of gases by the gas solid technique.

In 1942 Martin and Synge (9) discovered and developed liquid-liquid partition chromatography, in which an immobile, usually non-volatile, liquid phase fixed on an inert solid support held within the column served as a stationary bed while a mobile liquid phase moving through the column served as the carrier phase. In this process the carrier phase is broken into its individual constituents. During this same period of time Martin and Synge also suggested the utilization of an inert gas as the phase moving through the column instead of a liquid. However, this technique, known as gas-liquid partition chromatography, was not developed until 1952 by Martin and James (10). The above technique developed by Martin and Synge depended upon the different constituents being partitioned as the mobile phase percolated through the column. The theory set forth by Martin and Synge assumed that the column was composed of several equilibrium stages. A more detailed discussion of the theory and equations involved will be presented later in the thesis.

The two existing theories of chromatography are the plate theory and the rate theory. The development of the plate theory was attributed to Martin and Synge (10). Wilson (11) was the first to have developed a completely continuous column rate theory. For a detailed analysis of the theoretical development, the reader is referred to the work of Martin and Synge (10), Glueckauf (12), Van Deemter, Zuiderweg, and Klinkenberg (13), Wilson (11) and the theoretical review by Purnell (14).

Gas-Liquid Chromatography

Gas-liquid chromatography, as recognized by Martin (15) in 1956, may be one of the easiest methods for determining the thermodynamic properties of a volatile solute with a non-volatile solvent. Since that time the number of publications in the field of chromatography has increased considerably.

Chromatographic techniques have recently been applied to vapor-liquid studies in the determination of activity coefficients and equilibrium K-values, which is the ratio of the mole fraction of the solute in gas phase to its mole fraction in the liquid phase. This has been accomplished by relating the activity coefficient or equilibrium K-value of the solute to its retention time in a packed column, containing a relatively non-volatile solvent. This method of performing vapor-liquid equilibrium studies has the advantage over other methods in that it is more rapid than the conventional static and vapor recycle methods, yet it is still relatively accurate, as found by several authors. These authors and their work will be listed below.

For vapor-liquid properties calculated by chromatographic techniques to be valid, they must be independent of the parameters of the experimental system. Porter, Deal, and Stross (16) found in their work in this area that the experimental parameters such as column efficiency, length, and diameter, support size and nature, carrier gas flow rate, and the amount of stationary liquid had no appreciable effect on their measurements. Kwantes and Rijnders (17) also confirmed this conclusion with the restriction that the amount of stationary liquid fixed on the solid support must be greater than 15 percent by weight of the solid phase due to the adsorptive properties shown by the

solid material upon the liquid coatings. A further restriction of an upper limit on the carrier gas flow rate was found by Stalkup (18). However, he found the range of flow rates to be quite large. Kurkchi and Iogansen (19) also found that changes in the column length, amount of stationary phase, velocity of the carrier gas and nature of the solid support did not have any appreciable effect on the partition coefficient.

The history of gas-liquid chromatography can be traced by giving a chronological account of the work done in the field and the investigators carrying out this work.

In 1956 Porter, Deal and Stross (16) obtained partition coefficients and calculated partial excess heats of solution for the system n-heptane and n-propanol in diisodecycle phthalate. Also in 1956 Pierotti, Deal, Derr, Porter (20) extended the work of Porter, Deal and Stross to include solutes in polar solvents in order to obtain enough information to evaluate solvent effects in gas-liquid chromatography. In 1957 Anderson and Napier (21) studied the systems benzene and cyclohexane in polyethylene glycol for which they obtained partition coefficients, heats, and entropies of solution. During this same year Wilzbach and Riez (22) used radioactively tagged samples in their chromatographic experiments.

Kwantes and Rijnders (17) in 1958 worked with several non-polar solutes in polar and non-polar solvents and polar solutes in polar solvents with which they used partition coefficients to calculate activity coefficients.

Hardy (23) in 1959 calculated activity coefficients from GLC partition coefficients for several halogenated hydrocarbons compounds.

This data was later compared to data taken from static experiments, but was found to agree only relatively well. During this same year Preston (24) used the partition coefficients, obtained by Kwantes and Rijnders (17), to obtain equilibrium K-values for light hydrocarbons in heavier hydrocarbons. Lopez, according to Koonce, determined equilibrium K-values for methane, ethane, ethylene, propane, and butane in n-dodecane. He found that the lighter hydrocarbon K-values did not agree well with NGAA (25) K-values, but the K-values for the heavier hydro-carbons showed good agreement.

Lopez and Kobayashi (26) in 1960 determined activity coefficients, differential heats of solution, and differential entropies of solution for the C_4 hydrocarbons in furfural by GLC experiments. Their data were found to agree with published data. Adlard, Khan, and Whitman (27), working with benzene and cyclohexane in dinonyl phthalate, determined activity coefficients and heats of solutions for several normal alkanes, nitroalkanes, alkyl nitrates, and alcohols in squalane, dinonyl phthalate and diglycerol by GLC methods. Everett and Stoddart (28) determined activity coefficients for several paraffins and aromatic hydrocarbons in dinonyl phthalate by GLC measurements. Favorable agreement was found with values obtained by static methods.

Stalkup (18) and Stalkup and Kobayashi (29) determined equilibrium K-values from GLC data for ethane, propane, and n-butane at infinite dilution in the methane-n-decane systems over a temperature of $-20^{\circ}F$ to $70^{\circ}F$ and a pressure range of 20 to 2000 psia. These values compared favorably with NGAA (25) K-values. The K-values for n-butane in the methane-n-decane system at 40 and $160^{\circ}F$ were found to be in good agree-ment with static data of Sage and Lacy (30). In this same work

Stalkup and Kobayashi also investigated the use of GLC to measure freezing points in the methane-n-decane system. Experimental investigations were also extended to cover the case of an elution gas which showed appreciable solubility in the fixed liquid phase.

Koonce (31) and Koonce and Kobayashi (32) used GLC methods to determine equilibrium K-values for methane and propane in the ternary system methane-propane-n-decane at -20°, 0°, 40° and 70°F over at pressure range of 20 to 1000 psia at finite concentrations. Data were also taken for propane at infinite dilution and K-values determined over the same range of conditions as stated above. Koonce in his work modified the mathematical description of the elution process to include the case of an n-component elution gas from which equilibrium K-values of each component could be determined if retention data is known for each distinguishable component. For indistinguishable molecules the rate theory developed by Stalkup and Deans (33) was verified for a binary elution gas. In order to determine the identity of indistinguishable molecules, solute samples tagged with radioactive carbon-14 was used. K-values for propane at finite concentrations in the methane-propane-n-decane system at -20, 0, 40 and 70°F from 20 to 1000 psia and in the methane-propane-n-heptane system at -20 and -40°F from 100 to 1000 psia were found to be consistent. K-values obtained by elution data for methane at finite concentrations was found to scatter considerably at lower pressures. K-values for propane at infinite dilution in the methane-propane-n-decane system were found to be in excellent agreement with Stalkup (18) at low temperature in the lower pressure regions. However, at high pressures the deviation between Koonce and Stalkup was larger, in the range from 3 to 15 percent. The

data of Koonce at low pressure for propane in the system methane-propane-n-decane was shown to agree well with the data of Price and Kobayashi (34) taken by the vapor recirculation method. Discrepancies in the data of Koonce and Stalkup were attributed to two factors. One factor was the inability of Stalkup to determine the correct retention volume, V_G, of an unretained gas, which is required to calculate the K-values. It was demonstrated that the determination of V_G by direct calculation method as proposed by Stalkup was consistently low by 10 to 20 percent, thus giving a low K-value. The second factor was Stalkup's inability to determine the loss of liquid by evaporation from the fixed bed. It should be noted that the results of Stalkup were always quantitatively lower than those of Koonce.

Martire and Pollara (35) in 1965, using GLC methods, determined activity coefficients for a large number of solutes and solvents at three different temperatures. Cruickshank, Everett, and Westaway (36) presented a review of the work done by GLC methods in the determination of activity coefficients. They found, under good experimental conditions, accuracies ranging from 1 to 2 percent could be obtained. Chueh and Ziegler (37) studied the systems benzene in diethylene glycol at 50°, 70°, and 90°C and n-hexane at 30°C in 1, 2, 4-trichlorobenzene. They determined activity coefficients from infinite dilution to a finite concentration range. Partition coefficients and activity coefficients of the solute at finite concentrations were obtained based upon the mathematical analysis derived by Stalkup and Deans (33). Their data agreed with static measurements with $\pm$ 5 percent.

Van Horn (38) and Van Horn and Kobayashi (39) studied the phase behavior of light hydrocarbons in paraffin and aromatic hydrocarbon

solvents at low temperatures using GLC measurements. K-values of methane and ethane in the methane-ethane-n-heptane systems at -20°, -40°, and -60°F over a pressure range of 100 to 1000 psia were found. Retention data for methane and propane in the methane-propane-n-heptane system were taken over the same pressure range and a temperature range of 0° to -100°F. K-values at infinite dilution were found for methane at the above conditions. Solvent aromaticity was studied in the methane-propane-toluene system at -40°F and pressures up to 1000 psia. Van Horn used radioactively tagged solute samples in his experiment as well as untagged samples. The tagged samples were used mainly to obtain distinguishable solute molecules at finite concentrations, which was required by the equations used in this investigation. The data of this work were compared with that of Koonce and found to deviate from 5 percent at lower pressures to 19 percent at high pressure. Van Horn accounted for this discrepancy by the error in the calculation of V_G by Koonce. The data in this work were found to be internally consistent.

Kobayashi, Chappelear, and Deans (40) in 1967 gave a comprehensive review of chromatography, covering in detail the work done in the field of physicochemical measurements from 1952 up to 1967.

Masukawa and Kobayashi (41) and Masukawa, Alyea, and Kobayashi (42) successfully obtained the free gas volume of a chromatographic column as a function of pressure. This was accomplished by extrapolating several retention volumes to that of a hypothetical perfect gas.

Yudovich (43) and Yudovich, Robinson, and Chao (44) utilized chromatographical techniques to determine equilibrium K-values at infinite dilution for carbon dioxide, nitrogen, argon, ethylene and

propane in the methane-n-decane system at temperatures of 10°, 40°, 70°, 100°, 125°, and 150°F over a pressure range of 100 to 1750 psia. A correlation for liquid phase activity coefficients based on the combined Scatchard-Hildebrand and Flory-Huggins theories was developed, and found to represent accurately the experimental data by Yudovich. Free gas volumes were determined by an extrapolation of the solubility as a function of the polarizability to zero solubility. The data of Yudovich were found to be internally consistent.

Some of the conclusions drawn from the work in the field of GLC were summarized by Yudovich (43).

1. Equilibrium exists between the liquid and vapor phases in a properly operated GLC column.

2. Vapor-liquid equilibrium constants, activity coefficients, and heats of vaporization by GLC method can be determined for properly chosen systems; e.g., exclusion of highly polar solutes or solvents. However, if polar systems are studied, the solid support must have no adsorptive properties.

3. Thermodynamic properties calculated from GLC measurements agree with values obtained by classical methods.

4. GLC methods are particularly suited to infinite dilution studies.

5. The total packing material in a column should not contain less than 15 percent liquid by weight.

6. An accurate method of determining free gas volume must be used if reliable data is to be obtained from GLC measurements.

7. The loss of liquid in the stationary phase must be minimized by saturating the carrier with the solvent before it enters

the column.

The above-mentioned previous works in chromatography have clearly demonstrated its applicability to vapor-liquid equilibrium studies. Thus, the chromatographic technique was selected for the experimental work contained in the present study.

CHAPTER III

THEORY

Development of Equations Used in Calculations

Martin and Synge (9) presented a chromatographic equation based
upon their theoretical analogy. Their equation, which related the
retention of a solute in a column to the physical parameters of the
column, was based upon the following assumptions.

1. The packed bed consists of a large number of equilibrium
    stages arranged so that flow is continuous from plate to plate.

2. The liquid phase is stationary in the column.

3. Sample volume is negligibly small.

4. Pressure is constant throughout the column.

5. Instantaneous equilibrium exists between the sample in the
    carrier gas and the sample in the stationary liquid.

6. Diffusional effects can be neglected.

7. Solid support material in the column is inert.

8. The partition coefficient k is constant throughout the column.

A detailed discussion of the Martin and Synge equation is given by
Dal Nogare and Juvet (1) and Keulemans (4). A development similar to
that of the above authors is given here.

The partition function is defined as the ratio of the concentra-
tion of solute in the liquid phase to the concentration of solute in
mobile gas phase.

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$$k = \frac{\text{amount of solute/unit vol liquid phase}}{\text{amount of solute/unit vol gas phase}} \qquad (3\text{-}1)$$

The above relationship can be expressed mathematically as

$$k_i = \frac{n_{iL}/V_L}{n_{iG}/V_G} = \frac{n_{iL}V_G}{n_{iG}V_L} \qquad (3\text{-}2)$$

n_{iL} - number of moles of solute sample i in the stationary liquid phase

n_{iG} - number of moles of solute sample i in the mobile gas phase

V_L - volume of stationary liquid phase in column

V_G - volume of mobile gas phase equal to the void volume

The total number of moles of solute i in the column, n_i, is equal to the number of moles of i in the liquid phase, n_{iL}, plus the number of moles of i in the gas phase, n_{iG}.

$$n_i = n_{iL} + n_{iG} \qquad (3\text{-}3)$$

Division of the numerator and denominator of Equation (3-2) by Equation (3-3) given, upon rearrangement

$$k_i = \frac{x_i \rho_L}{y_i \rho_G} = \frac{1}{K_i} \frac{\rho_L}{\rho_G} \qquad (3\text{-}4)$$

Equation (3-4) does not present the parameters in the desired form. An equation for the equilibrium K-value written as a function of the experimental conditions of the system and the elution data is necessary for our purposes. We can define the retention volume V_{Ri} of solute i by:

$$V_{Ri} = t_{Ri} f \qquad (3\text{-}5)$$

where:

f - carrier gas flow rate

t_{Ri} - retention time of solute i in the column

An average linear velocity, u_i, of component i can now be expressed by,

$$u_i = \frac{L}{t_{Ri}} = \frac{L}{V_{Ri}/f} \qquad (3\text{-}6)$$

where L is the length of the GLC column. The velocity of the solute impulse through the column, u_i, can also be represented by a function of the solute velocity in the liquid phase and the solute velocity in the mobile gas phase.

$$u_i = \frac{n_{iG}u_{iG} + n_{iL}u_{iL}}{n_i} \qquad (3\text{-}7)$$

however

$$u_{iL} = 0 \qquad (3\text{-}8)$$

and

$$u_{iG} = u_G \qquad (3\text{-}9)$$

where u_G, the velocity of the carrier gas, or an unretained component, as it moves through the column is given by

$$u_G = \frac{L}{V_G/f} \qquad (3\text{-}10)$$

Upon substitution of Equations (3-8) and (3-9) into Equation (3-7)

$$\frac{u_i}{u_G} = \frac{n_{iG}}{n_i} \qquad (3\text{-}11)$$

Substituting Equation (3-6) and Equation (3-10) for u_i and u_G respectively into Equation (3-11) gives

$$\frac{V_G}{V_{Ri}} = \frac{n_{iG}}{n_i} = \frac{n_{iG}}{n_{iG} + n_{iL}} \qquad (3\text{-}12)$$

Upon substitution of Equation (3-1) into Equation (3-11)

$$\frac{V_G}{V_{Ri}} = \frac{n_{iG}}{n_{iG} + (\dfrac{k_i n_{iG} V_L}{V_G})} \qquad (3\text{-}13)$$

and rearranging

$$V_{Ri} = V_G + k_i V_L \qquad (3\text{-}14)$$

again rearranging and using the value $k_i = \dfrac{1}{K_i} \cdot \dfrac{\rho_L}{\rho_G}$

$$K_i = \frac{(\dfrac{\rho_L}{\rho_G}) V_L}{V_{Ri} - V_G} \qquad (3\text{-}15)$$

By using the relationship, $\rho_L V_L = W_L^o/(1 - x_1)$, for a binary system where W_L^o is defined as the number of moles of stationary liquid and x_1 is defined as the mole fraction of the carrier gas in the stationary liquid, Equation (3-14) becomes

$$K_i = \frac{W_L^o}{(1 - x_1)(\rho_G)(V_{Ri} - V_G)} \qquad (3\text{-}16)$$

where:

$\quad K_i \quad$ - vapor-liquid equilibrium constant for sample

$\quad W_L^o \quad$ - moles of stationary liquid in GLC column

$\quad x_1 \quad$ - mole fraction of carrier gas in the liquid phase at the system conditions

coefficient by the following expression:

$$\ln(\gamma_k)_{SH} = \frac{\overline{V}_k}{RT} \left[a_{kk} - 2\sum_j^n \phi_j a_{kj} + \sum_{ij}^{nn} \phi_i \phi_j a_{ij} \right] \qquad (3-18)$$

where:

γ_k - activity coefficient

$a_{ii} = \dfrac{\Delta E_i}{V_i}$ - cohesive energy density

$\overline{V}_k$ - molar volume

$\phi_i = \dfrac{x_i \overline{V}_i}{\sum x_j \overline{V}_j}$ - volume fraction of i

ΔE_i - isothermal molar change in energy of pure i in going from

the liquid to the ideal gas state

The following assumptions are involved in regular solution theory:

1. Orienting and chemical effects between molecules are absent.

2. Entropy change on mixing is zero.

3. Interaction energy between two unlike molecules is given by

the geometric mean of the energies of interaction for the

two species of like molecules.

4. The volume change on mixing at constant pressure and tempera-

ture is zero.

The athermal activity coefficient is independent of temperature
and is associated with the statistical effects due to a size differ-
ence between the solute and solvent molecules. The Flory-Huggins
theory is based on the following:

1. The heat of mixing is zero.

2. The volume change on mixing is zero.

For the general case of a solute in a multicomponent system, the Flory-

Huggins theory in terms of the activity coefficient, can be represented by the equation given below.

$$\ln(\gamma_k)_{FH} = \ln\left(\frac{\overline{V}_k}{\sum\limits_i x_i \overline{V}_i}\right) + \sum\limits_i^n \phi_i \left(1 - \frac{\overline{V}_k}{\overline{V}_i}\right) \qquad (3\text{-}19)$$

Combining the Scatchard-Hildebrand theory and the Flory-Huggins theory yields the relationship to be used in this work.

$$\ln \gamma_k = \ln(\gamma_k)_{SH} + \ln(\gamma_k)_{FH} \qquad (3\text{-}20)$$

It should be emphasized that combining the two theories gives an expression that is applicable only at constant temperature and pressure. The activity coefficient represented by Equation (3-20) is obtained by combining Equation (3-18) and Equation (3-19).

$$\ln \gamma_k = \frac{\overline{V}_k}{RT}\left[a_{kk} - 2\sum\limits_j^n \phi_j a_{kj} + \sum\limits_i^n \sum\limits_j^n \phi_j a_{ij} \right]$$

$$+ \ln\left(\frac{\overline{V}_k}{\sum\limits_i^n x_i \overline{V}_i}\right) + \sum\limits_i^n \phi_i \left(1 - \frac{\overline{V}_k}{\overline{V}_i}\right) \qquad (3\text{-}21)$$

At equilibrium in a vapor-liquid system, the fugacities of a component in the liquid phase and the vapor phase are equal.

$$f_{Li} = f_{Vi} \qquad (3\text{-}22)$$

By definition, the vapor-liquid equilibrium constant is expressed as the ratio of the mole fraction in the vapor and in the liquid.

$$K_i = y_i/x_i$$

Since the fugacities of component i are equal for a liquid and vapor at equilibrium

$$K_i = \frac{f_{Li}/x_i}{f_{Vi}/y_i} = \frac{f_{Li}/x_i \; P}{f_{Vi}/y_i \; P} = \frac{f_{Li}/x_i \; P}{\Psi_i} \tag{3-23}$$

where Ψ_i is defined as the vapor phase fugacity coefficient. Chao and Seader (48) separated the liquid phase fugacity coefficient, $(f_{Li}/x_i \, P)$, into two parts. One part was identified with the pure component and the other part with the liquid phase mixture non-ideality.

$$f_{Li}/x_i \; P = (f_{Li}^o/P)(f_{Li}/x_i f_{Li}^o) \tag{3-24}$$

where:

f_{Li}^o = the fugacity of the pure liquid at the temperature and pressure of the system

The first term in Equation (3-24) is defined as the pure component liquid fugacity coefficient,

$$\nu_i^o = f_{Li}^o/P \tag{3-25}$$

The second term which accounts for the non-ideality, is defined as the activity coefficient of component i in the liquid phase

$$\gamma_i = (f_{Li}/x_i f_{Li}^o) \tag{3-26}$$

Thus the K-value is expressed as

$$K_i = \frac{\gamma_i \nu_i^o}{\Psi_i} \tag{3-27}$$

Equation (3-27) arranged in terms of the activity coefficients, becomes

$$\gamma_i = \frac{K_i \Psi_i}{\nu_i^o} \tag{3-28}$$

For a solute "2" at infinite dilution, Equation (3-28) becomes

$$\gamma_2^\infty = \frac{K_2^\infty \Psi_2^\infty}{\nu_2^o} \qquad (3-29)$$

The measurements made in this study was for a solute at infinite dilution in a termany system. Thus, expressing the activity coefficient for a ternary system with component "2" present at infinite dilution, Equation (3-21) becomes

$$\ln \gamma_2^\infty = \frac{\overline{V}_2}{RT}\left[a_{22} - 2\phi_1 a_{21} - 2\phi_3 a_{23} + \phi_1^2 a_{11} + 2\phi_1\phi_3 a_{13} + \phi_3^2 a_{33} \right]$$
$$+ \ln\left(\frac{\overline{V}_2}{\overline{V}_m}\right) + \phi_1\left(1 - \frac{\overline{V}_2}{\overline{V}_1}\right) + \phi_3\left(1 - \frac{\overline{V}_2}{\overline{V}_3}\right) \qquad (3-30)$$

Infinite dilution activity coefficients of solute "2" can be obtained by knowing the pure component liquid volume and the cohesive energy parameters a_{12}, a_{13}, and a_{23}, which can be calculated from binary data available in the literature.

CHAPTER IV

EXPERIMENTAL EQUIPMENT

This equipment was designed to facilitate determination of

equilibrium K-values. A description of the experimental apparatus has

previously been given in the work of Yudovich (43). However, some

modifications were made to the equipment and will be discussed below.

General

The frame on which the equipment was mounted was constructed from

2" x 2" angle iron on which was mounted sections of plywood. Most of

the fixed components such as valves, tubing, pressure guages, flow and

temperature controllers, and stirrers were mounted on the platforms.

The refrigeration unit, temperature bath, coolant tank, circulation

pump and gas cylinders, were placed on the floor adjacent to the main

apparatus.

The tubing connecting the system was 1/8 inch OD, 304 stainless

steel tubing. This was used to replace some of the copper tubing used

by Yudovich (43) because of the corrosive action of hydrogen-sulfide on

copper. The presaturators and chromatographic columns were made from

1/4 inch OD, 0.049 inch wall thickness stainless steel tubing. The

lengths of the presaturator varied from 35 to 50 inches as in the work

of Yudovich. Both the chromatographic column and the presaturator

were packed with 30/60 mesh size firebrick. The firebrick used in the

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chromatographic column was impregnated with approximately 29% by weight
pure grade n-decane. The presaturator also contained approximately 29%
by weight n-decane. However, since the weight of the liquid on the
solid in the presaturator was not critical, the weight was not deter-
mined in the same manner as the weight of liquid in the column.

Sample Valve

The second change in the equipment described by Yudovich was not
a modification of the equipment, but the replacement of the sampling
valve, which was found to leak. This valve was fabricated by Pan
American Petroleum Corporation, Tulsa, Oklahoma. It has a 0.05 cc
volume sample cavity. The valve is connected so that the carrier
gas normally flows through a 1/8 inch tubing bypass. The sample can be
swept from the sample valve by proper manipulation of the valve as
described in the procedure.

Pressure Regulators

The pressure of the system was controlled by two pressure
regulators in series. The purpose for using two regulators was to
eliminate drift in pressure. The first regulator in the series was a
high precision Hoke, Model 521B20 ballast-loaded pressure regulator.
The second was an internally loaded Model 94 ballast-loaded Mity-Mite
pressure regulator manufactured by the Grove Regulator Company.

Electronic Components and Circuits

The last change made in the equipment described by Yudovich was a
modification in the F & M Wheatstone bridge. The changes made were in

the resistances of the two arms of the bridge. The resistance of each arm was changed from 14.7 K-ohms to 31.2 K-ohms with two 5,000 ohms potentiometers placed in the circuit to balance the bridge. The potentiometers were necessary due to the radical changes in the values of the fixed resistors as the conditions of the system changed. The balance of the Wheatstone bridge was found by using a Model 610B electrometer manufactured by Keithly Instruments.

Chemicals

The chemicals used in this work along with the suppliers are listed below.

MIN. PURITY

Material	Mole %	Grade	Supplier
Helium	99.995	High Purity	Airco
Argon	99.998	Purified	Matheson Company
Hydrogen Sulfide	99.6	Pure	Phillips Petroleum Co.
N-decane	99.0	Pure	Phillips Petroleum Co.
Methane	99.05	Instrument	Phillips Petroleum Co.

CHAPTER V

EXPERIMENTAL PROCEDURE

To make the procedure clear, the equation to be used in the calculation with a definition of the parameters must be given. The equilibrium K-values can be calculated via Equations (3-16) and (3-17).

$$K_i = \frac{W_L^o}{(1 - x_i)(\rho_G)(V_{Ri} - V_G)} \qquad (3\text{-}16)$$

and

$$V_{Ri} = t_{Ri} f_a \frac{P_a}{P} \frac{T}{T_a} Z_G \qquad (3\text{-}17)$$

The parameters x_1, ρ_G, and Z_G were found in the literature (30, 32, 49, 50, 51). The remaining parameters were obtained from the experiment.

The GLC column was prepared by using 13 inch sections of $\frac{1}{4}$ inch stainless steel tubing packed with 30/60 mesh firebrick impregnated with pure grade n-decane.

An unknown amount of firebrick was weighed on an analytical balance and its weight recorded. N-decane was then poured into the firebrick and stirred with a glass stirring rod until a slurry was formed which contained about 29 percent by weight of liquid on the solid. The slurry was reweighed, thus giving the exact amount of n-decane in the slurry. Care was taken not to lose any firebrick and also to insure that the n-decane was evenly distributed in the firebrick. The GLC column, which had already been fixed with $\frac{1}{4}$ inch Swagelok fittings,

was then weighed along with a small piece of glass wool for each end. The glass wool was used as plugs to retain the slurry inside of the column. After weighing the column and the glass wool and recording the weight, one end of the column was plugged with a piece of the glass wool and then packed with the slurry. The other end of the column was plugged with the remaining glass wool and total weight was recorded. The exact amount of n-decane in each column was then determined. Immediately after weighing, the columns were capped on each end with a rubber cap and placed in a refrigerator. Several small pre-weighed bottles were partially filled with a portion of the slurry during the packing of the columns. The amount of slurry in each weighing bottle was determined. All of the containers were then placed in a desiccator containing silica gel. A vacuum pump was connected to the desiccator and the n-decane on the firebricks was boiled off under a vacuum. The slurry was frequently stirred to insure that all of the liquid was removed from the firebrick. The dry firebrick was weighed and the weight percent of n-decane on the solid was determined. This was done as a check on the amount of n-decane on the firebricks determined by direct weighing as described above. Any error in determining W_L^o will result in an error in the calculated K-value; thus, the above check was necessary. After determining the K-values for each isotherm, the GLC column was removed from the system and weighed to determine if a loss of n-decane had occured.

Presaturator Preparation

The presaturator was placed in the system to saturate the carrier gas with n-decane before it entered the GLC column, thus reducing the

loss of stationary liquid from the solid support. Changes in the amount of liquid would result in an error in the K-value. The procedure used in the preparation of the GLC columns was also used in the preparation of the presaturator with the exception that the exact amount of n-decane on the firebrick was not determined.

Yudovich (43) in his work ran a preliminary experiment to determine the number of presaturators necessary for each isotherm to insure that no liquid would evaporate from the GLC column. Results of that experiment are shown below:

Isotherm - F°	Presaturator Length-Inch	Number of Presaturators Per Isotherm
150	50	4
125	50	3
100	45	3
70	45	3
40	40	3
10	40	2

Based upon the work of Yudovich, the above procedure was adopted in this work.

System Temperature

The system temperature was maintained at the desired operating value by a Hallikainen temperature controller within $\pm$ 0.04°F. The temperature was measured by a copper-constantan thermocouple.

Detector Cell Temperature

The temperature of the detector cell was maintained at a temperature from 2 to $5°F$ higher than the temperature of the system. It was also controlled by a Hallikainen controller with the temperature being measured by a copper-constantan thermocouple. The temperature of the detector cell was not used in the calculations, therefore; it was not necessary to know its exact value. Sufficient time was allowed for both the system temperature and detector cell temperature to come to a constant value. The temperature of the room was then determined by a mercury in glass thermometer with an accuracy of $\pm 0.1°F$.

Pressure and Flow Rate Control

The pressure of the carrier gas was set by using two pressure regulators in series. The pressure was set close to the desired value by the first of the pressure regulators and the exact system pressure was set by using the second regulator in the series. The pressure was measured at the inlet to the GLC column by a Heise gauge with an accuracy of ± 2.5 psi. After the carrier had passed through the column, it was reduced to approximately atmospheric pressure by expanding it through a needle valve at the column outlet. The pressure of the reference stream was set in a manner analogous to that of the carrier gas; it also was expanded through a needle valve to atmospheric pressure after having passed through a column designed to duplicate the same pressure drop as the GLC column. The atmospheric pressure was measured by a barometer to the nearest 0.1 mm Hg.

The flow rates of the carrier gas and the reference gas streams were then set by using a Ruska micrometer needle valve on each stream.

The flow rates were determined by measuring the time required for a soap film to travel between two reference marks on a bubble meter.

Only the carrier gas flow rate was accurately measured and recorded. The flow rate of the reference gas stream was kept as close as possible to that of the carrier gas, but was not recorded since its value did not enter into any of the calculations. The flow rates of both streams were kept constant for each pressure, their values being checked periodically during a run. Flows for both streams ranged from 30 ml/min at 100 psi to 120 ml/min at 1000 psi. Increasing the flows at higher pressures was necessary because of the greater retention times of the sample gas.

Upon establishing a constant rate of flow, the part of the system from the sampling valve to the sample manifold was evacuated by using a vacuum pump. The gas, which was stored under pressure in a cylinder, was connected to the system through a manifold. Sample gas was injected into the sample loop and the system was again evacuated. This procedure was followed after each run at a fixed temperature and pressure.

Sample Trapping and Injection

The steps used in trapping a sample and injecting it into the system are as follows:

1. Clean the sample loop and flush it twice by filling it with the sample gas at a pressure of about 60 psi and then evacuating the system.

2. Fill the sample loop with the solute at the desired pressure. The pressure used in filling the system was determined by the system pressure; the filling pressure being increased as the

system pressure was increased. Pressure in the sample loop varies from 2 to 32 inches of mercury as the system pressure changes from 100 to 1500 psi.

3. Trap the sample gas in the valve cavity at the desired pressure by manipulating the sample valve.

4. Inject the solute sample into the high pressure carrier gas stream by again manipulating the sample valve to connect the sample cavity with the carrier gas stream.

Each run was repeated twice under identical conditions. The values for retention times and flow rates averaged for all of the runs at each temperature and pressure are given in Appendix D.

Retention Time Measurement

After injecting the solute sample into the carrier gas stream, a stop-clock with divisions of 1/100 of a second was started. The time lapse between the sample injection into the carrier gas and the peak of the elution curve on the recorder chart was measured and recorded as the retention time.

CHAPTER VI

EXPERIMENTAL RESULTS

Equilibrium K-values for hydrogen sulfide at infinite dilution in the ternary system methane-hydrogen sulfide-n-decane were measured by the GLC elution method. Experimental data were taken at $15^{\circ}F$, $40^{\circ}F$, $70^{\circ}F$, $100^{\circ}F$, and $130^{\circ}F$ over a pressure interval of 100 to 1000 psia. Equilibrium K-values were calculated by using both the polarizability and molecular weight methods to determine the void volumes of the columns; results were essentially identical for the two methods. K-values calculated by using the polarizability method are given in Table I.

TABLE I

K-VALUES OF HYDROGEN SULFIDE AT INFINITE DILUTION
IN THE METHANE-N-DECANE SYSTEM

Pressure Psia	$15^{\circ}F$	$40^{\circ}F$	$70^{\circ}F$	$100^{\circ}F$	$130^{\circ}F$
100	1.467	1.951	2.781	3.434	4.716
200	0.836	1.140	1.644	2.164	2.798
400	0.499	0.685	1.013	1.384	1.857
600	0.373	0.520	0.793	1.098	1.504
800	0.306	0.434	0.687	0.982	1.350
1000	0.280	0.385	0.622	0.873	1.229

A preliminary investigation was performed to validate the reliability of the chromatographic apparatus used and the procedure followed during this work. This was done by measuring elution data for propane at infinite dilution in the methane-n-decane system over a pressure range of 100 to 1000 psia at isotherms of 15°F, 40°F, and 70°F. K-values for propane were also calculated by using both the polarizability and molecular weight to determine void volumes. The K-values were calculated from chromatographic elution data via Equation (3-16). Densities of methane gas and solubility of methane in n-decane were obtained from the literature (30, 32, 49, 50, 51).

The results of the preliminary work on propane are shown in Table II. The K-values tabulated in Tables I and II are plotted isothermally for each ternary system in Figures 1 and 2. Figure 4 shows a plot of hydrogen-sulfide K-values as a function of reciprocal temperature for each isobar.

TABLE II

K-VALUES OF PROPANE AT INFINITE DILUTION
IN THE METHANE-N-DECANE SYSTEM

Pressure Psia	15°F	40°F	70°F
100	0.532	0.793	1.180
200	0.292	0.428	0.626
400	0.187	0.259	0.372
600	0.161	0.209	0.293
800	0.159	0.195	0.257
1000	0.164	0.195	0.245
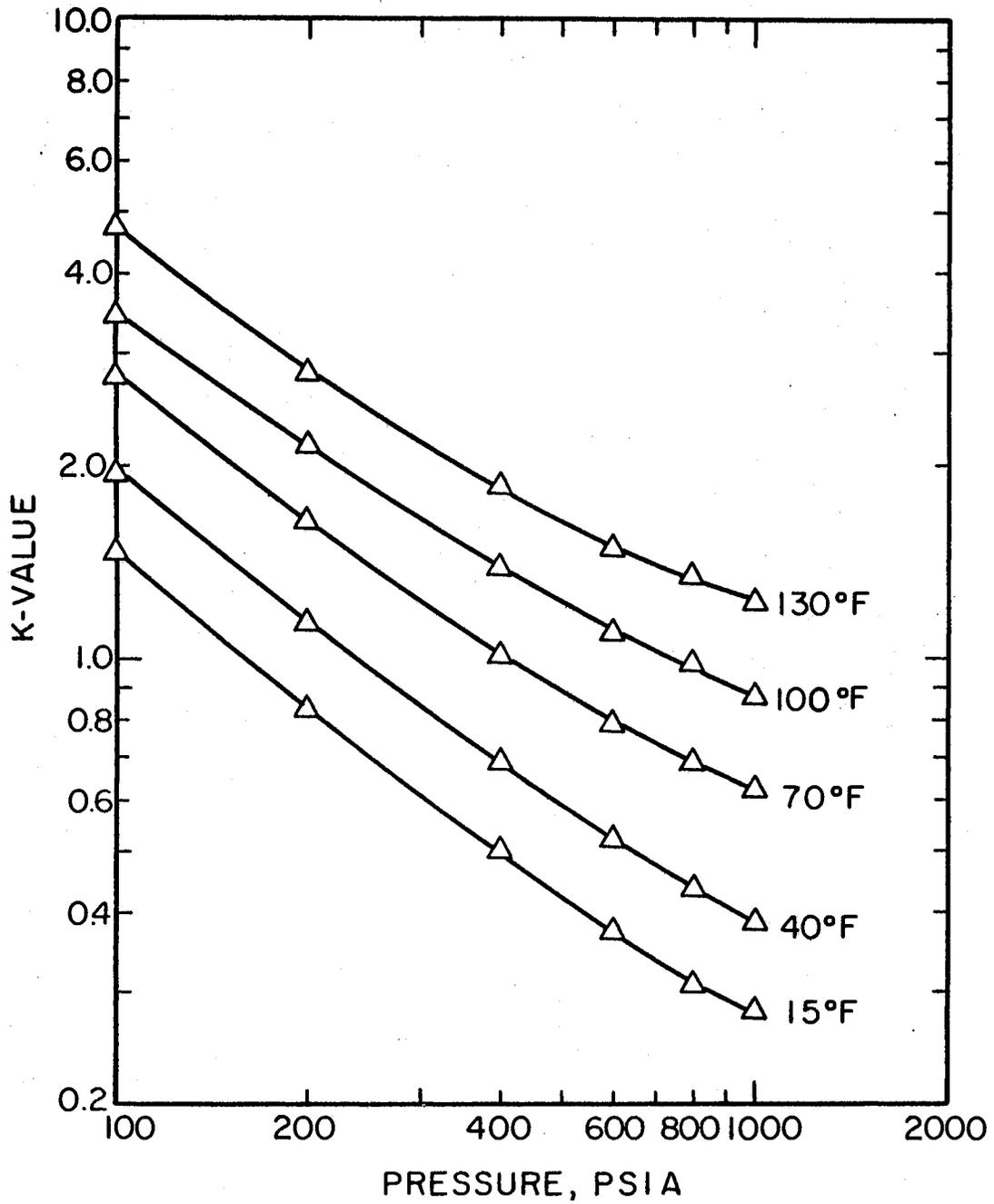
Figure 1. K-Values for Hydrogen Sulfide at Infinite
Dilution in the Methane-n-Decane System
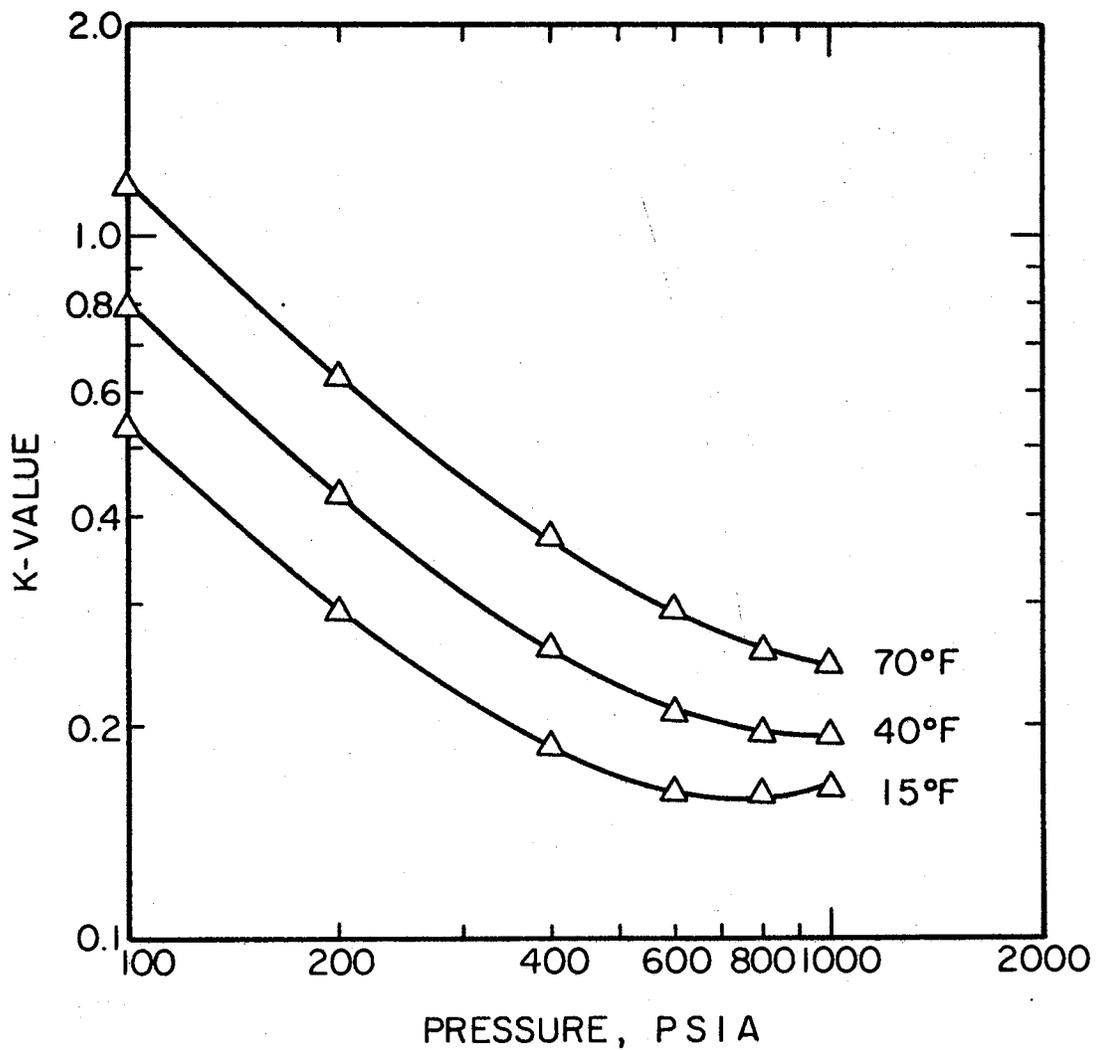
Figure 2. K-Values for Propane at Infinite Dilution in
the Methane-n-Decane System
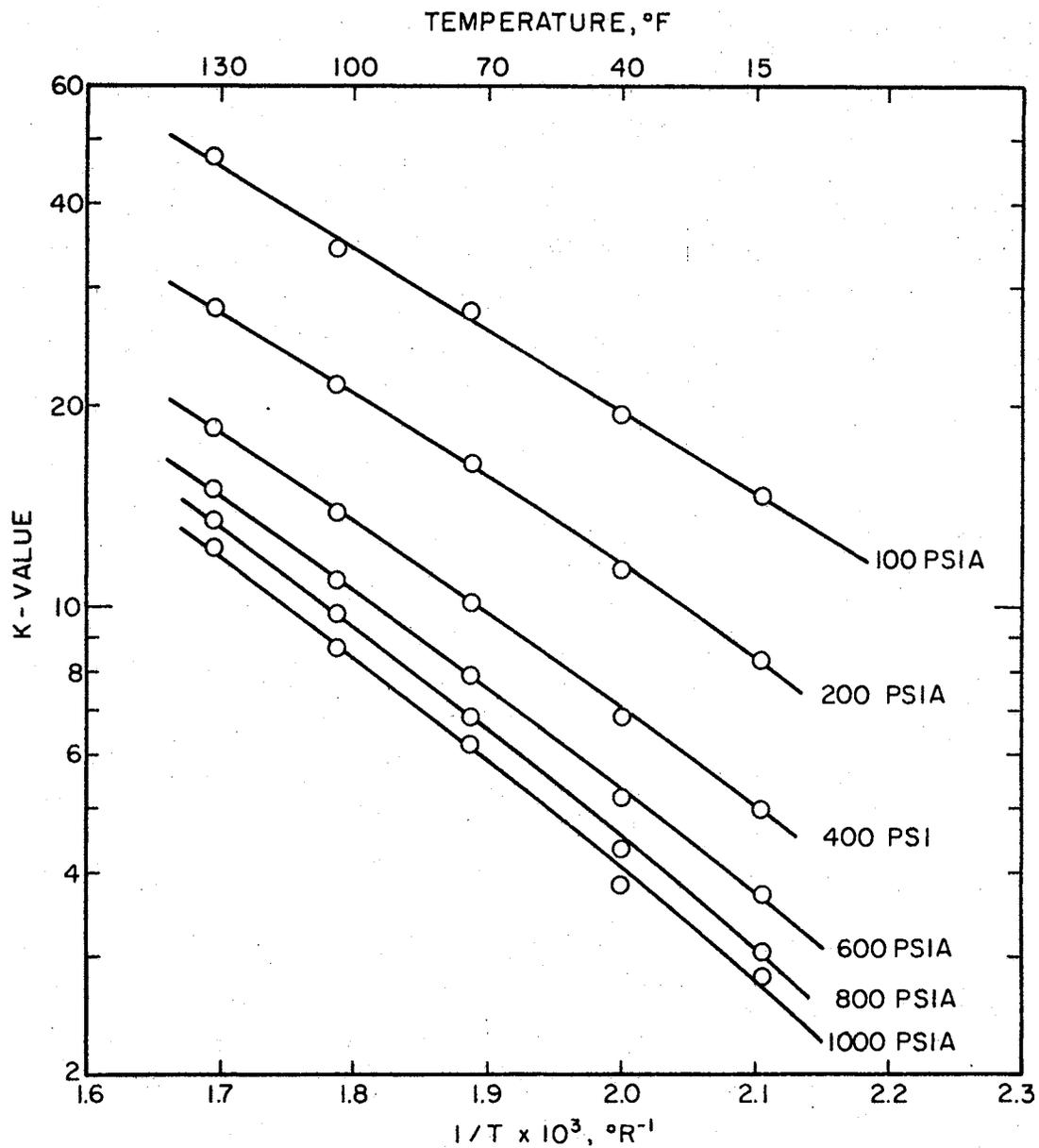
Figure 3. K-Values for Hydrogen Sulfide at Infinite Dilution
in the Methane-n-Decane System as a Function of
Reciprocal Temperature

CHAPTER VII

DISCUSSION OF RESULTS

The experimental data are discussed in this chapter, including

comparisons with existing experimental data and with the correlation

proposed by Yudovich.

Equilibrium K-values for propane at infinite dilution in the

methane-n-decane system were compared to the data of Koonce (31) and

Yudovich (43) at temperatures of $15^\circ F$, $40^\circ F$, and $70^\circ F$ over a pressure

interval of 100 to 1000 psia. As shown in Table III, the K-values

obtained in this work compared very well with the data of both Koonce

and Yudovich. Upon comparing these data with those from the above

sources, the maximum deviation, which was 2.5%, was found to occur at

$40^\circ F$ and 1000 psia. K-values for propane in this work are plotted with

the K-values obtained from the above references as a function of

temperature for isobars of 100, 200, 400, and 600 psia. These are

shown in Figure 4.

A comparison was also made between the equilibrium K-values

calculated by using both polarizability and molecular weight to deter-

mine void volumes. The maximum deviation in the K-values was 0.13%.

This close agreement can be explained by referring to Equation (3-16)

and noting that measured K-values depend directly on the value of

$(V_{Ri} - V_G)$. Since V_G is small and its value differed only slightly

when calculated by the two different methods, the difference of

TABLE III

COMPARISON OF K-VALUES FOR PROPANE AT INFINITE
DILUTION IN THE $C_3H_8-CH_4-nC_{10}$ SYSTEM
WITH THE DATA OF KOONCE (31)
AND YUDOVICH (43)

Pressure, psia	This Work	Koonce (31)	Yudovich (43)
	$40°F$		
100	0.793	0.800	0.791
200	0.428	0.432	0.426
400	0.259	0.265	0.258
600	0.209	0.215	0.207
800	0.195	0.199	0.193
1000	0.195	0.200	0.192
	$70°F$		
100	1.180	1.180	0.179
200	0.626	0.633	0.626
400	0.372	0.377	0.373
600	0.293	0.300	0.292
800	0.257	0.264	0.255
1000	0.245	0.247	0.245
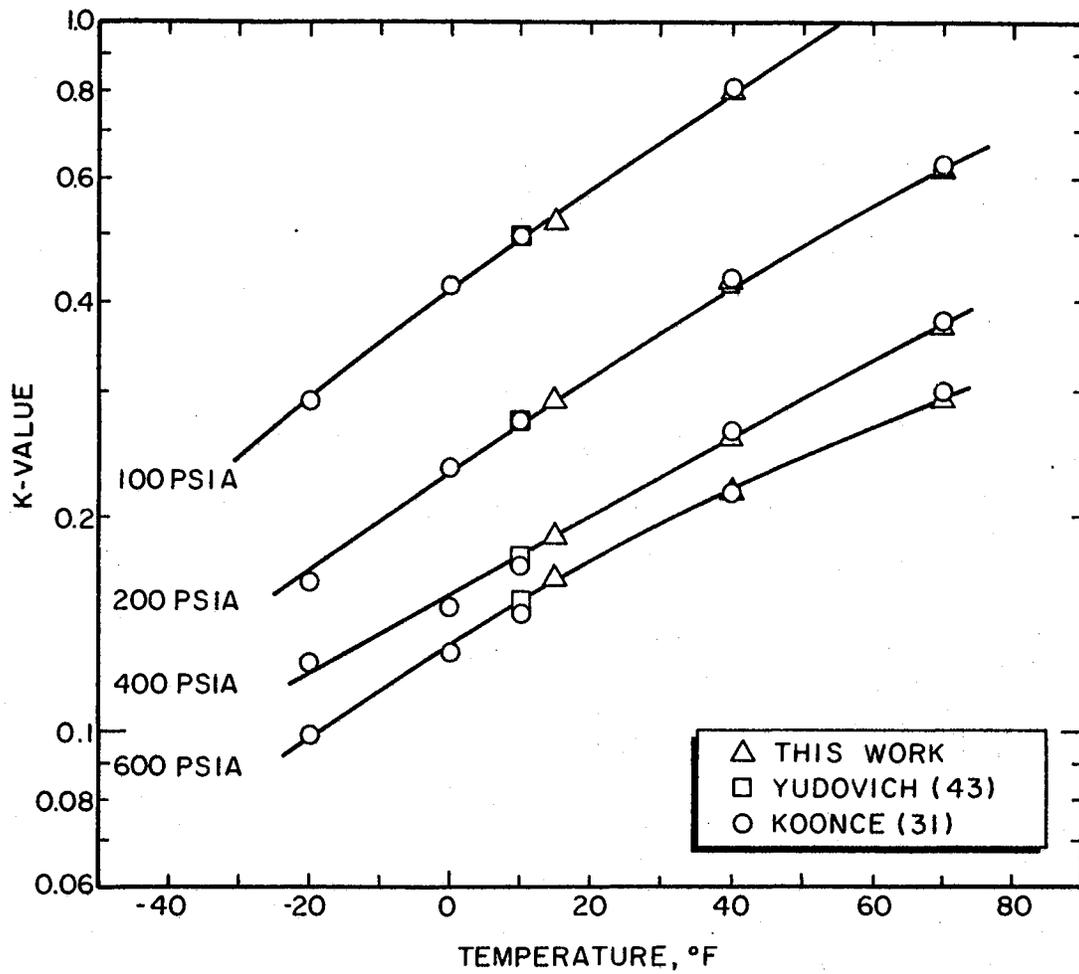
Figure 4. K-Values for Propane at Infinite Dilution in the
Methane-n-Decane System as a Function of
Temperature

$(V_{Ri} - V_G)$ will become less significant when V_{Ri} is large, as is the case in the present work.

The isobars for 800 and 1000 psia in Figure 3 show more scatter than the isobars at the lower pressures with the greatest scatter existing at 1000 psia. Increased scatter at the higher pressures was attributed to problems with the sample valve; small pieces of teflon from the packing in the valve would wear off and lodge between the valve stem and valve seat resulting in improper sealing of the sample valve.

Comparison with Correlation (Equation 3-30)

For the systems studied in this work, the solute, 2, was at infinite dilution in methane the carrier gas (component 1) and n-decane the solvent (component 3). Utilizing Equations (3-29) and (3-30) the equilibrium K-value for the solute at infinite dilution can be represented as:

$$\ln K_2^{\infty} = \frac{\overline{V}_2}{RT} (a_{22} - 2\phi_1 a_{21} - 2\phi_3 a_{23} + \phi_1^2 a_{11} + 2\phi_1 \phi_3 a_{13} + \phi_3^2 a_{33})$$

$$+ \ln \frac{\overline{V}_2}{\overline{V}_m} + \phi_1 (1 - \frac{\overline{V}_2}{\overline{V}_1}) + \phi_3 (1 - \frac{\overline{V}_2}{\overline{V}_3}) + \ln v_2^o - \ln \Psi_2 \qquad (5\text{-}1)$$

where a_{12} represents the cohesive energy density between two different components and a_{11} represents the solubility parameter of component "i" squared, (δ_i^2). The molar volume for component "i" and the mixture is given by $\overline{V}_i$ and $\overline{V}_m$ respectively and were obtained from the literature (48). The parameter x_i, which represents the mole fraction of methane in the saturated methane-n-decane solution, was obtained from the data of Sage and Lacey (30).

The constants a_{12} for the methane-hydrogen sulfide interaction and a_{23} for the hydrogen sulfide-n-decane interaction were evaluated by using Equation (3-21) expressed for a binary system in terms of equilibrium K-values

$$\ln K_2 = \frac{\overline{V}_2 \phi_1^2}{RT} (a_{11} - 2a_{12} + a_{22}) + \ln \frac{\overline{V}_2}{\overline{V}_m} + \ln \frac{f_{2_L}^o}{P} - \ln \Psi_2$$

$$+ \phi_1 (1 - \frac{\overline{V}_2}{\overline{V}_1}) \tag{5-2}$$

and fitting this equation to binary solution phase equilibrium data using the linear least squares method. The constant a_{13} was obtained from Yudovich (43). The constants a_{11}, a_{22}, and a_{33} were obtained from Chao and Seader (48).

Given below are the values for each interaction constant.

$$a_{12} = 53.00 \quad \text{cal/cc}$$

$$a_{13} = 40.79 \quad \text{cal/cc}$$

$$a_{23} = 65.20 \quad \text{cal/cc}$$

$$a_{11} = 32.26 \quad \text{cal/cc}$$

$$a_{22} = 77.44 \quad \text{cal/cc}$$

$$a_{33} = 59.60 \quad \text{cal/cc}$$

The vapor-phase fugacity coefficient of the solute at infinite dilution was calculated by using the Redlich-Kwong equation as modified by Chueh and Prausnitz (52) (as shown in Appendix B). The vapor phase fugacity of hydrogen sulfide over the temperature and pressure ranges covered in this work are tabulated in Table IV.

The pure component liquid fugacity coefficient, v_2^o, was calculated from the data of Sage and Lacey (53) using the following relationships.

TABLE IV

VAPOR PHASE FUGACITY COEFFICIENT OF HYDROGEN SULFIDE
AT INFINITE DILUTION IN METHANE

Pressure Psia	Temperature				
	15°F	40°F	70°F	100°F	130°F
100	.9504	.9570	.9635	.9688	.9731
200	.9023	.9152	.9279	.9383	.9469
400	.8111	.8356	.8599	.8799	.8964
600	.7262	.7612	.7960	.8247	.8486
800	.6477	.6920	.7363	.7729	.8035
1000	.5759	.6282	.6807	.7244	.7610

$$\ln v_2^o = \ln \frac{f_{L2}^o}{P} = \frac{1}{RT}\int_0^{P_{vp}}\left[\bar{V}^V - \frac{RT}{P}\right]dP + \frac{1}{RT}\int_{P_{vp}}^{P}\bar{V}^L\,dP$$

$$+ \ln \frac{P_{vp}}{P} \tag{5-3}$$

Values obtained for the pure component liquid fugacity at the temperature and pressure of the system are given in Table V.

Utilizing Equation (5-1), equilibrium K-values were calculated. The results are given in Table VI. Figure 5 shows a comparison of measured K-values and those calculated from Equation (5-1). This comparison is tabulated in Table VII.

The equilibrium K-values calculated by the combined Scatchard-Hildebrand and Flory-Huggins equations do not compare well with

experimental K-values. The experimental K-values are consistently
higher than the calculated K-values.

TABLE V

PURE COMPONENT LIQUID FUGACITY OF
HYDROGEN SULFIDE, $(f^o_{L_2})$, PSIA

Pressure Psia	Temperature				
	$15^\circ F$	$40^\circ F$	$70^\circ F$	$100^\circ F$	$130^\circ F$
100	96.81	147.95	204.20	310.99	448.70
200	98.81	148.66	208.00	314.80	454.00
400	101.36	152.37	213.60	321.62	464.80
600	103.97	156.18	223.80	329.54	473.40
800	106.66	160.08	229.60	337.67	486.40
1000	109.41	164.08	238.00	345.99	496.00

TABLE VI

K-VALUES OF HYDROGEN SULFIDE AT INFINITE
DILUTION IN THE METHANE-N-DECANE
SYSTEM CALCULATED FROM
EQUATION (5-1)

Pressure Psia	Temperature				
	15°F	40°F	70°F	100°F	130°F
100	1.045	1.586	2.170	3.284	4.712
200	0.576	0.854	1.175	1.755	2.503
400	0.344	0.502	0.680	0.997	1.410
600	0.275	0.393	0.536	0.757	1.053
800	0.248	0.347	0.462	0.645	0.889
1000	0.238	0.326	0.431	0.586	0.795

TABLE VII

COMPARISON OF K-VALUES FOR HYDROGEN SULFIDE AT INFINITE DILUTION IN THE CH_4-H_2S-n-C_{10} SYSTEM WITH VALUES CALCULATED FROM EQUATION (5-1)

Pressure Psia	Temperature														
	T = 15°F			T = 40°F			T = 70°F			T = 100°F			T = 130°F		
	K_{exp}	K_{calc}	% Dev*	K_{exp}	K_{calc}	% Dev*	K_{exp}	K_{calc}	% Dev*	K_{exp}	K_{calc}	% Dev*	K_{exp}	K_{calc}	% Dev.*
100	1.467	1.045	29.8	1.951	1.586	18.7	2.781	2.170	22.0	3.434	3.284	4.4	4.716	4.712	0.1
200	0.836	0.576	32.2	1.140	0.854	25.1	1.644	1.175	28.5	2.164	1.755	18.9	2.798	2.503	10.5
400	0.499	0.344	31.0	0.685	0.502	30.2	1.013	0.680	32.8	1.384	0.997	28.0	1.857	1.410	24.1
600	0.373	0.275	26.3	0.520	0.393	24.4	0.793	0.536	32.4	1.098	0.757	31.1	1.504	1.053	30.0
800	0.306	0.248	19.0	0.434	0.347	20.0	0.687	0.462	32.8	0.982	0.645	34.4	1.350	0.889	34.2
1000	0.280	0.238	15.0	0.385	0.326	15.3	0.622	0.431	30.7	0.873	0.586	32.9	1.229	0.795	35.4

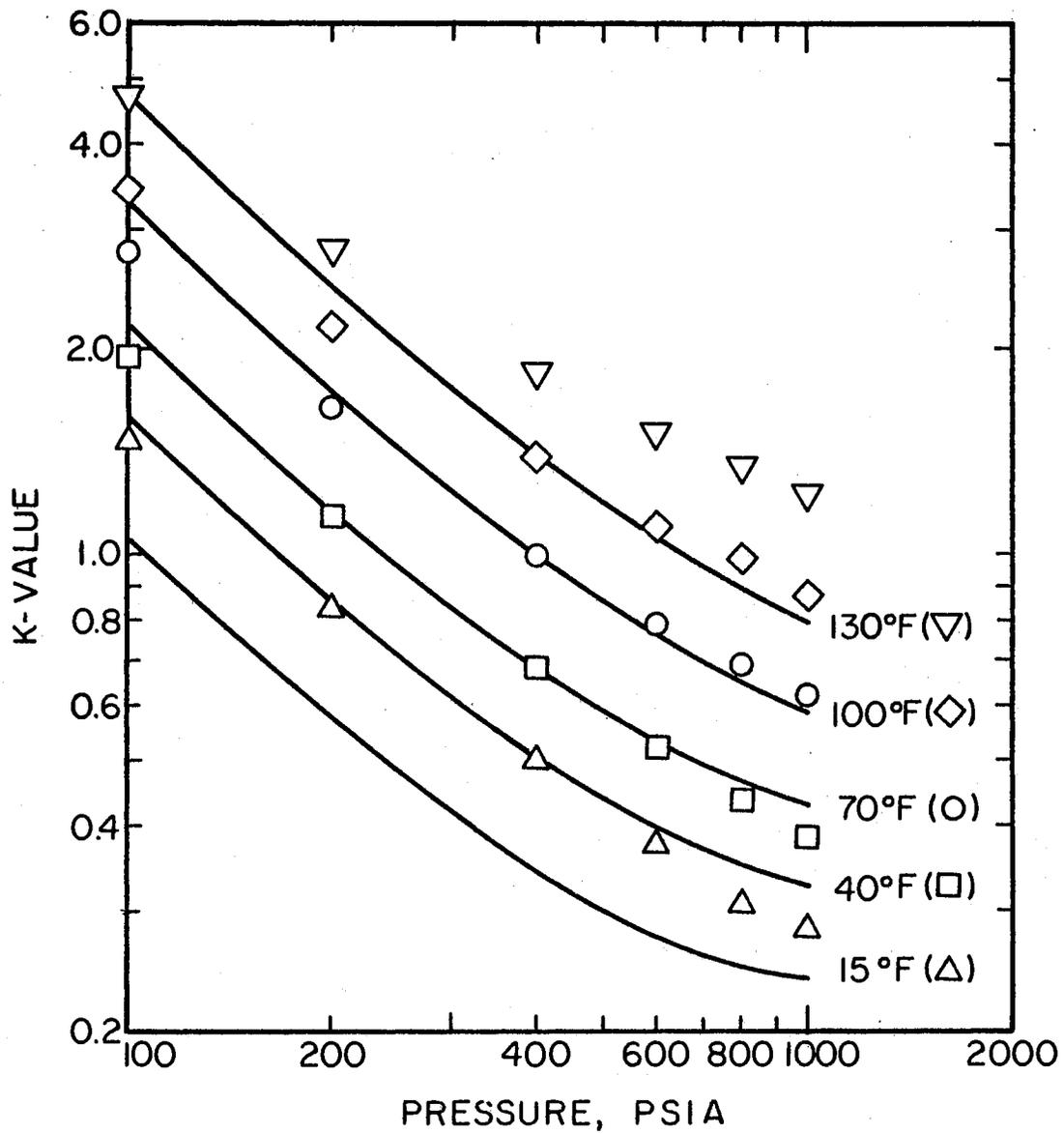* % Deviation = $(K_{exp} - K_{calc})/K_{exp}$ (100)

Figure 5. Comparison of Experimentally Obtained K-Values
Calculated from Equation (5-1)

The source of error in the calculated values is, in part, due to the inability to accurately predict binary K-values in the hydrogen sulfide-n-decane system over the complete range of temperature and pressure after having curve fitted the binary data. By using the curve fitted a_{12} value for the methane-hydrogen sulfide system, the binary K-values could be predicted reasonably well. The maximum error in predicting these values occurred at $160^\circ F$ with the largest error being 4.7% at 1000 psia. The errors at the other temperatures were less than 1.5%. The errors obtained when using a curve fitted value for a_{23} to predict K-values for the hydrogen sulfide-n-decane system ranged from 1% to 18.9%. The maximum error occurred at $100^\circ F$ and 100 psia. However, binary K-values could be predicted more accurately by using a_{12} obtained from the curve fit of the binary data than from a_{12} calculated by using the geometric mean of a_{11} and a_{22}. Since binary K-values could not be predicted from the a_{ij} found by curve fitting the binary data, it would not be possible to predict K-values in a ternary system by using the same a_{ij} values.

Comparison of the K-Value Data with Other Sources

The K-values of hydrogen-sulfide at infinite dilution in the methane-n-decane system determined in this study were compared with infinite dilution K-values of hydrogen sulfide in the methane-n-octane system of Chappelear, et al. (54), who also obtained K-values chromatographically. The comparison was made at $68^\circ F$, $32^\circ F$, and $15^\circ F$ over a pressure range of 100 to 1000 psia. Figure 6 illustrates a comparison of these K-values. The results of this comparison are tabulated in Table VIII.
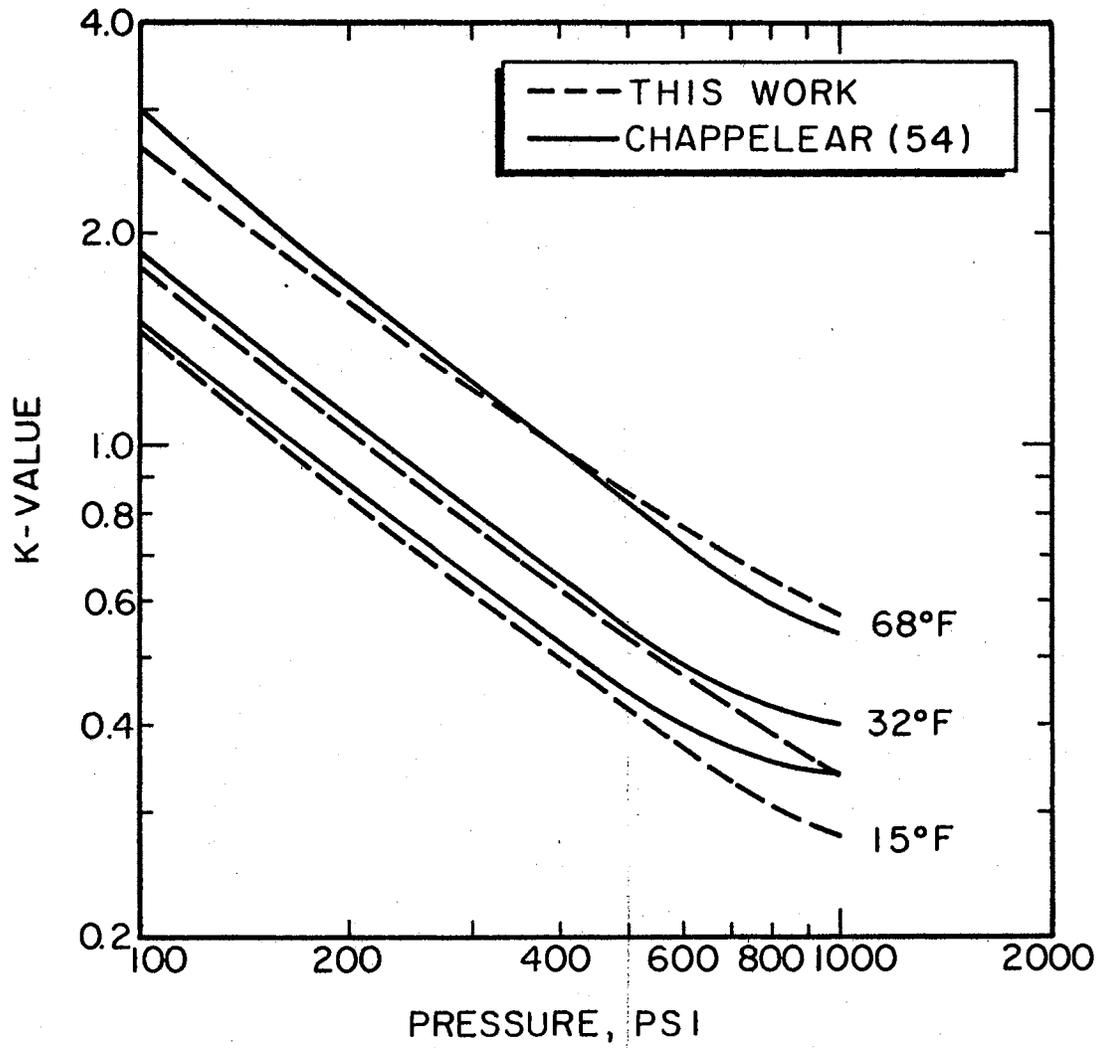
Figure 6. Comparison of Experimentally Obtained K-Values
with K-Values Obtained by Chappelear, et al.
(46)

TABLE VIII

COMPARISON OF K-VALUES FOR HYDROGEN SULFIDE AT INFINITE DILUTION IN THE METHANE-N-DECANE
SYSTEM WITH K-VALUES FOR HYDROGEN SULFIDE AT INFINITE DILUTION
IN THE METHANE-N-OCTANE SYSTEM

Pressure Psia	Temperature								
	$T = 15°F$			$T = 32°F$			$T = 68°F$		
	K_{exp}**	K_c***	% Dev.	K_{exp}	K_c	% Dev.	K_{exp}	K_c	% Dev.
100	1.467	1.51	2.7	1.80	1.90	5.5	2.63	2.99	13.7
200	0.836	0.885	5.9	1.035	1.10	6.3	1.61	1.70	5.6
400	0.499	0.522	4.6	0.618	0.650	5.2	0.979	0.970	-0.92
600	0.373	0.397	6.7	0.467	0.488	4.5	0.762	0.714	-6.3
800	0.306	0.353	15.3	0.389	0.421	8.2	0.653	0.589	-9.8
1000	0.280	0.342	22.1	0.340	0.400	17.5	0.573	0.540	-5.7

* % Deviation = $(K_c - K_{exp})/K_{exp}$ 100
** This Work
*** Chappelear, et al. (54)

As can be seen in Figure 6, the K-values of hydrogen sulfide

obtained in this work are in reasonable agreement with K-values of

Chappelear, et al. (54). As shown in Table VIII, the percent deviation

increases with pressure. This can be explained in part by the fact

that the methane-n-decane system has a greater convergence pressure

than the methane-n-octane system.

From the error analysis presented in Appendix C, the maximum

error due to experimental uncertainty was found to be 1.1% at 100 psia

and 130°F.

CHAPTER VIII

CONCLUSIONS AND RECOMMENDATIONS

This work involved the measurement of equilibrium K-values of
hydrogen sulfide at infinite dilution in the ternary system of methane-
hydrogen sulfide-n-decane by chromatographic techniques. The experi-
mental results from this work are compared to a correlation consisting
of a combination of the Scatchard-Hildebrand and Flory-Huggins equa-
tions. Based on this work, the following conclusions and recommenda-
tions are made.

Conclusions

1. Equilibrium K-values of hydrogen sulfide at infinite dilution
   in the methane-n-decane system were studied successfully by
   using chromatographic techniques.

2. The comparison of equilibrium K-values obtained for propane
   at infinite dilution in the methane-n-decane system with K-
   values from other sources substantiates the techniques used
   in this work.

3. Equilibrium K-values calculated by the combined Scatchard-
   Hildebrand and Flory-Huggins theories do not compare well
   with experimental K-values but were consistently lower.

Recommendations

1. The sample valve used in this work leaked internally at
   moderate and high pressures. The high pressure carrier gas
   leaked into the sample cavity, thus preventing the sample from
   being trapped inside the valve. Before future work is under-
   taken, a new sample valve should be obtained.

2. Difficulties arose in keeping the wheatstone bridge balanced
   as the flow rate was changed. Consequently, before attempting
   further work, a better flow regulator should be obtained to
   replace the one presently in use.

SELECTED REFERENCES

(1) Dal Nogare, S., and R. S. Juvet, "Gas Liquid Chromatography,"
       Interscience Publisher, New York, N. Y. (1962).

(2) Reed, L., Proc. Chem. Soc. 9, 123 (1893).

(3) Tswelt, M., Ber. Deut. Botan. Ges. 24, 316 (1906).

(4) Keulemans, A. I. M., "Gas Chromatography," Reinhold Publishing
       Corp., N. Y. (1957).

(5) Turner, N. C., Nat'l. Pet. News 35, R-234 (1943).

(6) Classen, S., Arkiv. Kemi Mineral Geo. 23A, No. 1, 133 (1946).

(7) Phillips, C. S. G., Trans. Faraday Soc. 7, 241 (1949).

(8) Cremer, E., and F. Prior, Z. Elektrochem. 55, 66 (1951).

(9) Martin, A. J. P., and R. L. M. Synge, Biochem. J. 35, 1359 (1941).

(10) Martin, A. J. P., and A. T. James, Biochem. J. 50, 679 (1952).

(11) Wilson, J. N., J. Am. Chem. Soc. 62, 1983 (1940).

(12) Glueckauf, E., Trans. Faraday Soc. 51, 34 (1955).

(13) Van Deemter, J. J., F. J. Zuiderweg, and A. Klinkenberg, Chem.
       Eng. Sci. 5, 271 (1956).

(14) Purnell, H., "Gas Chromatography," Wiley and Sons, N. Y. (1962).

(15) Martin, A. J. P., Soc. For Anal. Chem. 81, 52 (1956).

(16) Porter, P. E., CH. H. Deal, and F. H. J. Stross, Am. Chem. Soc.
       78, 2999 (1956).

(17) Kwantes, A., and G. W. A. Rijnders, "Gas Chromatography," D. H.
       Desty, ed., Academic Press, N. Y. (1958).

(18) Stalkup, F. I., "The Study of High Pressure Vapor Liquid Equi-
       librium by Gas Liquid Partition Chromatography," Ph.D.
       Thesis, Rice University (1961).

(19) Kurkchi, G. A., and A. V. Iogansen, Akademiia Nauk USSR Doklady
       145, 1085 (1962).

(20) Pierotti, G. J., C. H. Deal, E. L. Derr, and P. E. Porter, J. Am. Chem. Soc. 78, 2989 (1956).

(21) Anderson, J. R., and K. H. Napier, Austral. J. Chem. 10, 250 (1957).

(22) Wilzbach, K. E., and P. Riez, Science 126, 1062 (1957).

(23) Hardy, C. J., J. Chromat. 2, 490 (1959).

(24) Preston, S. T., "Vapor Liquid Equilibrium Constants from Gas Chromatography Data," NGAA Proceedings, April 22-24, 1959).

(25) Natural Gasoline Association of America," Equilibrium Ratio Data Book," Tulsa, Oklahoma (1957).

(26) Lopez, M. G., and R. Kobayashi, Pet. Ref. 39, 125 (1960).

(27) Adlard, E. R., M. A. Khan, and B. T. Whitman, Gas Chromatography, R. P. W. Scott, ed., Butterworths, London (1960).

(28) Everett, D. H. and C. T. H. Stoddart, Trans. Faraday Soc. 57, 746 (1961).

(29) Stalkup, F. I., and R. Kobayashi, AIChE J. 9, 121 (1963).

(30) Sage, B. H., and W. N. Lacey, "Thermodynamic Properties of Lighter Paraffin Hydrocarbons and Nitrogen," American Petroleum Institute, N. Y. (1950).

(31) Koonce, K. T., "Generalization of Gas Liquid Partition Chromatography to Study Multicomponent Vapor-Liquid Equilibria at High Pressures," Ph.D. Thesis, Rice University (1963).

(32) Koonce, K. T., and R. Kobayashi, J. Chem. Eng. Data 9, 490 (1964).

(33) Stalkup, F. I., and H. A. Deans, AIChE J. 9, 106 (1963).

(34) Price, A. R., and R. Kobayashi, J. Chem. Eng. Data 4, 40 (1959).

(35) Martire, D. E., and L. Z. Pollara, J. Chem. Eng. Data 10, 40 (1959).

(36) Cruickshank, A. J. B., D. H. Everett, and M. T. Westaway, Trans. Faraday Soc. 61, 235 (1965).

(37) Chueh, C. F., and W. T. Ziegler, AIChE J. 11, 508 (1965).

(38) Van Horn, L. D., "A Study of Low Temperature Vapor-Liquid Equilibria in Light Hydrocarbon Solvents," Ph.D. Thesis, Rice University (1966).

(39) Van Horn, L. D., and R. Kobayashi, J. Chem. Eng. Data 12, 294

(1967).

(40) Kobayashi, R., P. S. Chappelear, and H. A. Deans, Ind. Eng. Chem. 59, 63 (1967).

(41) Masukawa, S., and R. Kobayashi, J. Gas Chromat. 6, 257 (1968).

(42) Masukawa, S., J. I. Alyea, and R. Kobayashi, Submitted to J. Gas Chromat.

(43) Yudovich, A., "Properties of Gas Mixtures and Liquid Solutions from Infinite Dilution Studies," Ph.D. Thesis, Oklahoma State University (1969).

(44) Yudovich, A., R. L. Robinson, Jr., and K. C. Chao, Chem. Eng. Prog. Symp. Series 64, 85 (1968).

(45) Cheung, H., and E. H. Zander, Chem. Eng. Prog. Symp. Series 64, 34 (1968).

(46) Chang, H. L., P. S. Chappelear, and R. Kobayashi, AIChE J. 14, 318 (1968).

(47) Hildebrand, J. H., and R. L. Scott, "Regular Solutions," Prentice Hall, Englewood Cliffs, N. J. (1962).

(48) Chao, K. C., and J. D. Seader, AIChE J. 7, 598 (1961).

(49) Beaudin, J. M., and J. P. Kohn, J. Chem. Eng. Data 12, 189 (1967).

(50) Reamer, H. H., R. H. Olds, B. H. Sage, and W. N. Lacey, Ind. Eng. Chem. 34, 1526 (1942).

(51) Vennix, A. J., "Low Temperature Volumetric Properties and the Development of an Equation of State for Methane," Ph.D. Thesis, Rice University (1966).

(52) Chueh, P. L., and J. M. Prausnitz, Ind. Eng. Chem. Fund. 6, 492 (1967).

(53) Sage, B. H., and W. N. Lacey, "Some Properties of the Lighter Hydrocarbons, Hydrogen Sulfide and Carbon Dioxide, "American Petroleum Institute, N. Y. (1955).

(54) Chappelear, P. S., K. Asano, T. Nakahara, and R. Kobayashi, Submitted to J. Chem. Eng. Data.

(55) Prausnitz, J. M., "Molecular Thermodynamics of Fluid-Phase Equilibria," Prentice Hall, Englewood Cliffs, N. J. (1969).

APPENDIX A

SAMPLE CALCULATIONS

Calculation of Retention Volumes from Equation (3-17)

$$V_{Ri} = t_{Ri} \ f_a \frac{P_a}{p} \frac{T}{T_a} Z_G \qquad\qquad (3\text{-}17)$$

$T = 70^{\circ}F$

$T_a = 74.5^{\circ}F$

$P = 200$ psia

$P_a = 739.7$ mm H_g

$Z_G = .9749$

The retention times for helium, argon, and hydrogen sulfide are:

	— t_{Ri} —		
	Min	Sec	f_a - cc/min
He	2	15.29	73.439
Ar	2	19.64	73.350
H_2S	3	59.71	73.575
C_3H_8	6	49.83	73.710

The above compressibility factor, Z_G, was obtained from Sage and Lacey (51). The remaining parameters in Equation (3-2) were determined experimentally.

Retention volume for propane: 6 min - 49.83 sec = 6.83046 min.

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$$V_{Ri} = (6.83046)(73.710)\frac{(739.7)(.01934)}{(200)} \times \frac{(70 + 460)}{(74.5 + 460)}(.9749)$$

$$V_{Ri} = 34.808 \text{ cc}$$

Using the experimental data, the retention volumes for helium and argon were also calculated with Equation (3-2). The retention volumes and polarizabilities are given below.

	V_{Ri} – cc	$\alpha \times 10^{24}$ – cc/molecule
He	11.448	.204
Ar	11.802	1.63

The polarizabilities were obtained from the literature.

Calculation of Void Volume

The retention volumes of the above gases were plotted as a function of their polarizabilities. A straight line through these points was then extrapolated to a position on the ordinate which was the polarizability of a hard sphere gas. This point was then used as the void volume of the column. The void volume of the column was also calculated by replacing the polarizability with the molecular weight and extrapolating to a value of zero. Figure 7 shows the technique used to determine void volumes.

Void volume from polarizability:

$$V_G = 11.397$$

Void volume from molecular weight:

$$V_G^* = 11.409$$
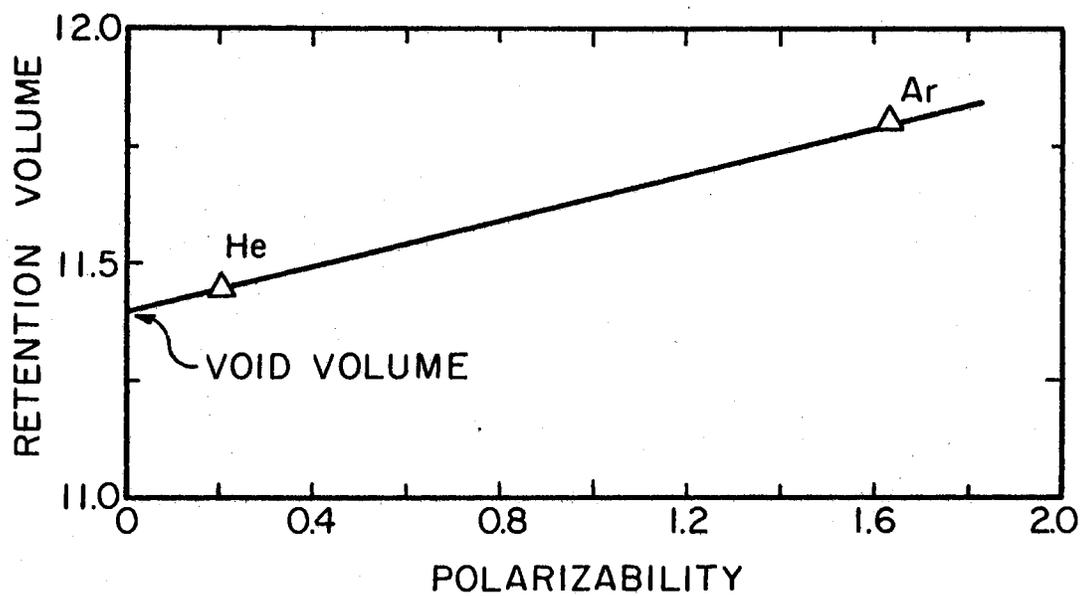
Figure 7. Retention Volume as a Function of Polarizability

Decane in Column

The amount of decane in the column was determined by the procedure outlined in Chapter V.

$$W_L = 1.1207 \text{ gms}$$

$$W_L^O = \frac{1.1207}{142.276} = .00788 \text{ gm-mole}$$

Calculation of K-Value for Propane

The K-value for propane at infinite dilution in the methane-n-decane system was calculated from Equation (3-16).

$$K_i = \frac{W_L^O}{(1 - x_1)(\rho_G)(V_{Ri} - V_G)} \qquad (3\text{-}16)$$

$$V_{Ri} = 34.808 \text{ cc}$$

$$W_L^O = .00788 \text{ gm-mole}$$

$$V_G = 11.397 \text{ cc}$$

$$x_1 = .0702$$

$$\rho_G = .0361 \text{ lb-mole/cu. ft}$$

Values for x_1 and ρ_G were found in Sage and Lacey (30) and Kohn (49).

$$K_i = \frac{.00788}{(1.0 - .0702)(.0361)(34.808 - 11.397)}$$

$$K_i = 0.626$$

APPENDIX B

VAPOR PHASE FUGACITY COEFFICIENT CALCULATED FROM

THE REDLICH-KWONG EQUATION OF STATE AS

MODIFIED BY CHUEH AND PRAUSNITZ

The Redlich-Kwong equation of state is:

$$P = \frac{RT}{v - b} - \frac{a}{T^{0.5} \, v(v + b)} \qquad (B-1)$$

where a and b are characteristic constants that differ from one gas to
another. Both a and b have an approximate physical significance: a
provides a rough measure of the attractive intermolecular forces, and
b gives some indication of molecular size (55). These constants can be
related to the critical pressure and temperature by

$$a = \frac{\Omega_a R^2 T_c^{2.5}}{P_c} \qquad (B-2)$$

$$b = \frac{\Omega_b R T_c}{P_c} \qquad (B-3)$$

where Ω_a and Ω_b are dimensionless constants that can be evaluated from
pure component volumetric data for the saturated vapor as suggested by
Chueh (52). This permits Ω_a and Ω_b to vary for different substances
rather than remain constants as proposed in the two-parameter corre-
sponding states assumption. Values for a and b of a mixture are
calculated by the following relationships:

$$a_m = \sum_{i=1}^{n} \sum_{j=1}^{n} y_i y_i a_{ij} \tag{B-4}$$

where

$$a_{ii} = \frac{\Omega_{a_i} R^2 T_{c_i}^{2.5}}{P_{c_i}} \tag{B-5}$$

$$a_{ij} = \frac{(\Omega_{a_i} + \Omega_{a_j}) R^2 T_{c_{ij}}^{2.5}}{2 P_{c_{ij}}} \tag{B-6}$$

and

$$b_m = \sum_{i=1}^{n} y_i b_i \tag{B-7}$$

where

$$b_i = \frac{\Omega_{b_i} R T_{c_i}}{P_{c_i}} \tag{B-8}$$

$$P_{c_{ij}} = \frac{Z_{c_{ij}} R T_{c_{ij}}}{V_{c_{ij}}} \tag{B-9}$$

$$V_{c_{ij}}^{1/3} = \frac{1}{2}(V_{c_i}^{1/3} + V_{c_j}^{1/3}) \tag{B-10}$$

$$Z_{c_{ij}} = 0.291 - 0.08 \left(\frac{\omega_i + \omega_j}{2}\right) \tag{B-11}$$

$$T_{c_{ij}} = (1 - k_{ij})(T_{c_i} T_{c_j})^{\frac{1}{2}} \tag{B-12}$$

with ω representing the acentric factor, which is a macroscopic measure of the extent to which the force field around a molecule deviates from spherical symmetry. The characteristic binary constant k_{ij} shown above

which represents the deviation from the geometric mean for $T_{c_{ij}}$ is to a good approximation a true molecular constant independent of temperature, composition, and density. The value used for k_{ij} of 0.05 for the hydrogen sulfide and methane system was that of Chueh and Prausnitz (52). Values for ω, Ω_a, and Ω_b obtained from the same source are given below.

System	ω	Ω_a	Ω_b
Methane	.013	.4278	.0867
Hydrogen Sulfide	.100	.4340	.0882
n-Decane	.498	.4930	.1000

By the use of the above equations and mixing rules the equation for the vapor phase fugacity coefficient,

$$RT \ln \Psi_i = \int_{v}^{\infty} \left[\left(\frac{\partial P}{\partial n_i}\right)_{T,V,n_j} - \frac{RT}{V} \right] dV - RT \ln Z \quad (B-13)$$

becomes for component K,

$$\ln \Psi_k = \ln \frac{v}{v-b} + \frac{b_k}{v-b} - \frac{2 \sum_{i=1}^{n} y_i a_{ik}}{RT^{3/2} b^2}$$

$$\left[\ln \frac{v+b}{v} + \frac{ab_k}{RT^{3/2} b^2} \ln \frac{v+b}{v} - \frac{b}{v+b} \right] - \ln \frac{Pv}{RT} \quad (B-14)$$

The molar volume, v, is that of the gas mixture; it was obtained by solving the Redlich-Kwong equation, which is cubic in v, and taking the largest real root as v.

APPENDIX C

ERROR ANALYSIS

An estimate of the random errors associated with the measurement and calculation of the equilibrium K-values can be made from an estimation of errors involved in the individual parameters. Uncertainties in the measurement of experimental variables are given below.

Experimental Variable	Uncertainty
Ambient temperature, T_a	$\pm 0.2\,^\circ F$
System temperature, T	$\pm 0.04\,^\circ F$
Ambient pressure, P_a	$\pm 0.02\%$
System pressure, P	± 2.0 psi
Time, t	± 0.05 sec
Flow rate, f_a	$\pm 0.1\%$
Molar weight of liquid, W_L^O	$\pm 0.02\%$

An estimate of the uncertainties of the concentration of methane in n-decane and the molar volume of saturated methane-n-decane solutions obtained from the literature (30), were taken as $\pm 0.4\%$.

The equilibrium K-values were calculated according to Equation (3-16)

$$K_i = \frac{W_L^O}{(1 - x_1)(\rho_G)(V_{R_i} - V_G)} \qquad (3\text{-}16)$$

However, this equation can be rearranged to show the value of K_i directly in terms of experimentally measured parameters.

The void volume of the column, V_G, can be expressed in terms of t_G, the retention time of an unretained gas by the relationship:

$$t_G = \frac{V_G}{f_a} \qquad (C-1)$$

Using Equation (3-17) and the above relationship:

$$(V_{R_i} - V_G) = (t_{R_i} - t_G)\, f_a\, \frac{P_a}{P}\, \frac{T}{T_a}\, Z_G \qquad (3-17)$$

Substituting the above expression into Equation (3-16)

$$K_i = \frac{RW_L^O T_a}{(1 - x_1)f_a P_a (t_{R_i} - t_G)} \qquad (C-2)$$

Differentiating Equation (C-2)

$$dK_i = \frac{RW_L^O}{(1 - x_1)f_a P_a (t_{R_i} - t_G)}\, dT_a + \frac{RT_a}{(1 - x_1)f_a P_a (t_{R_i} - t_G)}\, dW_L^O$$

$$+ \frac{RW_L^O T_a}{(1 - x_1)^2 f_a P_a (t_{R_i} - t_G)}\, dx_i$$

$$- \frac{RW_L^O T_a}{(1 - x_1)f_a P_a^2 (t_{R_i} - t_G)}\, dP_a - \frac{RW_L^O T_a}{(1 - x_1)f_a^2 P_a (t_{R_i} - t_G)}\, df_a$$

$$- \frac{RW_L^O T_a}{(1 - x_1)f_a P_a (t_{R_i} - t_G)^2}\, d(t_{R_i} - t_G) \qquad (C-3)$$

By representing the above differentials as difference values and dividing each term by Equation (C-2) the following is obtained.

$$\frac{\Delta K_i}{K_i} = \frac{\Delta T_a}{T_a} + \frac{\Delta W_L^o}{W_L^o} + \frac{\Delta x_1}{(1 - x_1)} + \frac{\Delta P_a}{P_a} + \frac{\Delta f_a}{f_a} + \frac{\Delta(t_{R_i} - t_G)}{(t_{R_i} - t_G)} \quad (C - 4)$$

The sign on each term has been chosen to yield the maximum error in K-values. The errors in the K-values were evaluated at pressures of 100 and 1000 psia at 15°F and 130°F and are shown below.

Temperature	Percent Error	
	100 psia	1000 psia
15°F	.5	.4
130°F	1.1	.4

From this analysis the maximum error due to experimental uncertainty was found to be 1.1% at 100 psia and 130°F.

APPENDIX D

TABULATION OF RAW EXPERIMENTAL DATA

The raw experimental data acquired in this study are listed in
the following table.

TABLE IX

TABULATION OF RAW EXPERIMENTAL DATA

Solute	Retention Time, t_{R_i} Min	Sec	Flow Rate, fa, cc/min	Solute	Retention Time, t_{R_i} Min	Sec	Flow Rate, fa, cc/min
He	1	8.37	80.160	He	2	51.47	59.701
Ar	1	10.56	80.160	Ar	2	57174	59.701
H_2S	2	48.37	80.160	H_2S	6	57.20	59.701
C_3H_8	5	44.68	80.160	C_3H_8	14	36.81	59.701

$T = 15^{\circ}F$

$W_L^o = .0076$ gm-mole

$P = 100$ psia

$T_a = 70.6^{\circ}F$

$P_a = 741.0$ mm Hg

$V_G^* = 11.476$ cc

$V_G = 11.464$ cc

$T = 15^{\circ}F$

$W_L^o = .0076$ gm-mole

$P = 200$ psia

$T_a = 70.6^{\circ}F$

$P_a = 741.0$ mm Hg

$V_G^* = 10.531$ cc

$V_G = 10.519$ cc

V_G^* – calculated by extrapolating to zero Molecular Weight

V_G – calculated by extrapolating to zero Polarizability

TABLE IX (Continued)

Solute	Retention Time, t_{R_i} Min	Sec	Flow Rate, fa, cc/min	Solute	Retention Time, t_{R_i} Min	Sec	Flow Rate, fa, cc/min
He	3	51.73	87.336	He	6	20.72	80.699
Ar	4	1.17	87.336	Ar	6	37.45	80.699
H_2S	8	58.31	87.336	H_2S	14	23.64	80.699
C_3H_8	17	29.86	87.336	C_3H_8	24	59.72	80.699

$T = 15\,^{\circ}F$

$W_L^o = .0076$ gm-mole

$P = 400$ psia

$T_a = 70.6\,^{\circ}F$

$P_a = 741.0$ mm Hg

$V_G^* = 10.035$ cc

$V_G = 10.022$ cc

$T = 15\,^{\circ}F$

$W_L^o = .0076$ gm-mole

$P = 600$ psia

$T_a = 70.5\,^{\circ}F$

$P_a = 741.0$ mm Hg

$V_G^* = 9.754$ cc

$V_G = 9.741$ cc

TABLE IX (Continued)

Solute	Retention Time, t_{R_i} Min	Sec	Flow Rate, fa, cc/min	Solute	Retention Time, t_{R_i} Min	Sec	Flow Rate, fa, cc/min
He	9	9.86	76.726	He	8	6.31	111.421
Ar	9	35.07	76.726	Ar	8	29.53	111.421
H_2S	20	14.88	76.726	H_2S	17	4.93	111.421
C_3H_8	30	31.51	76.726	C_3H_8	23	27.73	111.421

$T = 15°F$

$W_L^o = .0076$ gm-mole

$P = 800$ psia

$T_a = 70.4°F$

$P_a = 740.9$ mm Hg

$V_G^* = 9.603$ cc

$V_G = 9.589$ cc

$T = 15°F$

$W_L^o = .0076$ gm-mole

$P = 1000$ psia

$T_a = 70.4°F$

$P_a = 740.9$ mm Hg

$V_G^* = 9.471$ cc

$V_G = 9.456$ cc

TABLE IX (Continued)

	Retention Time, t_{R_i}				Retention Time, t_{R_i}		
Solute	Min	Sec	Flow Rate, fa, cc/min	Solute	Min	Sec	Flow Rate, fa, cc/min
He	1	12.47	73.484	He	2	4.70	80.160
Ar	1	14.62	73.484	Ar	2	8.87	80.160
H_2S	2	34.90	73.484	H_2S	4	17.30	80.645
C_3H_8	4	34.87	73.484	C_3H_8	8	0.16	80.645

$T = 40^{\circ}F$

$W_L^{\circ} = .0076$ gm-mole

$P = 100$ psia

$T_a = 71.0^{\circ}F$

$P_a = 739.3$ mm Hg

$V_G^* = 11.730$ cc

$V_G = 11.719$ cc

$T = 40^{\circ}F$

$W_L^{\circ} = .0076$ gm-mole

$P = 200$ psia

$T_a = 71.0^{\circ}F$

$P_a = 739.3$ mm Hg

$V_G^* = 10.847$ cc

$V_G = 10.835$ cc

TABLE IX (Continued)

Solute	Retention Time, t_{R_i} Min	Sec	Flow Rate, fa, cc/min	Solute	Retention Time, t_{R_i} Min	Sec	Flow Rate, fa, cc/min
He	4	22.90	74.257	He	5	45.90	84.985
Ar	4	32.42	74.349	Ar	5	59.85	84.985
H_2S	8	49.20	74.534	H_2S	11	16.20	84.806
C_3H_8	15	48.40	74.534	C_3H_8	19	12.56	84.806

$T = 40°F$

$W_L^o = .0076$ gm-mole

$P = 400$ psia

$T_a = 71.0°F$

$P_a = 739.3$ mm Hg

$V_G^* = 10.260$ cc

$V_G = 10.248$ cc

$T = 40°F$

$W_L^o = .0076$ gm-mole

$P = 600$ psia

$T_a = 71.0°F$

$P_a = 739.5$ mm Hg

$V_G^* = 9.982$ cc

$V_G = 9.969$ cc

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TABLE IX (Continued)

Solute	Retention Time, t_{R_i} Min	Sec	Flow Rate, fa, cc/min	Solute	Retention Time, t_{R_i} Min	Sec	Flow Rate, fa, cc/min
He	7	9.50	92.166	He	8	41.57	97.009
Ar	7	29.02	92.166	Ar	9	6.66	97.009
H_2S	13	32.81	92.095	H_2S	16	0.37	96.696
C_3H_8	21	18.13	92.095	C_3H_8	23	9.35	96.696

$T = 40°F$

$W_L^O = .0076$ gm-mole

$P = 800$ psia

$T_a = 71.1°F$

$P_a = 740.7$ mm Hg

$V_G^* = 9.736$ cc

$V_G = 9.722$ cc

$T = 40°F$

$W_L^O = .0076$ gm-mole

$P = 1000$ psia

$T_a = 71.1°F$

$P_a = 740.7$ mm Hg

$V_G^* = 9.658$ cc

$V_G = 9.643$ cc

TABLE IX (Continued)

Solute	Retention Time, t_{R_i} Min	Sec	Flow Rate, fa, cc/min	Solute	Retention Time, t_{R_i} Min	Sec	Flow Rate, fa, cc/min
He	1	52.72	45.942	He	2	15.29	73.439
Ar	1	56.24	45.802	Ar	2	19.64	73.350
H_2S	3	29.18	45.767	H_2S	3	59.71	73.575
C_3H_8	5	40.74	45.645	C_3H_8	6	49.83	73.710

$T = 70^\circ F$

$W_L^o = .0079$ gm-mole

$P = 100$ psia

$T_a = 74.5^\circ F$

$P_a = 739.7$ mm Hg

$V_G^* = 12.046$ cc

$V_G = 12.036$ cc

$T = 70^\circ F$

$W_L^o = .0079$ gm-mole

$P = 200$ psia

$T_a = 74.5^\circ F$

$P_a = 739.7$ mm Hg

$V_G^* = 11.409$ cc

$V_G = 11.397$ cc

TABLE IX (Continued)

Solute	Retention Time, t_{R_i} Min	Sec	Flow Rate, fa, cc/min	Solute	Retention Time, t_{R_i} Min	Sec	Flow Rate, fa, cc/min
He	4	6.48	76.726	He	4	11.68	112.254
Ar	4	16.34	76.482	Ar	4	22.96	111.836
H_2S	6	59.32	77.022	H_2S	7	0.25	110.803
C_3H_8	11	57.59	77.320	C_3H_8	11	51.65	109.589

$T = 70^\circ F$

$W_L^\circ = .0079$ gm-mole

$P = 400$ psia

$T_a = 74.5^\circ F$

$P_a = 739.7$ mm Hg

$V_G^* = 10.577$ cc

$V_G = 10.565$ cc

$T = 70^\circ F$

$W_L^\circ = .0079$ gm-mole

$P = 600$ psia

$T_a = 74.5^\circ F$

$P_a = 739.7$ mm Hg

$V_G^* = 10.268$ cc

$V_G = 10.255$ cc

TABLE IX (Continued)

Solute	Retention Time, t_{R_i} Min	Sec	Flow Rate, fa, cc/min	Solute	Retention Time, t_{R_i} Min	Sec	Flow Rate, fa, cc/min
He	6	44.95	93.266	He	7	53.57	101.437
Ar	7	5.49	93.458	Ar	8	17.41	101.01
H_2S	10	46.83	93.313	H_2S	12	14.52	100.840
C_3H_8	17	29.96	93.023	C_3H_8	19	1.71	100.334

$T = 70°F$

$W_L^O = .0079$ gm-mole

$P = 800$ psia

$T_a = 74.5°F$

$P_a = 739.7$ mm Hg

$V_G^* = 10.155$ cc

$V_G = 10.142$ cc

$T = 70°F$

$W_L^O = .0079$ gm-mole

$P = 1000$ psia

$T_a = 74.5°F$

$P_a = 739.7$ mm Hg

$V_G^* = 9.997$ cc

$V_G = 9.962$ cc

TABLE IX (Continued)

Solute	Retention Time, t_{R_i}		Flow Rate, fa, cc/min	Solute	Retention Time, t_{R_i}		Flow Rate, fa, cc/min
	Min	Sec			Min	Sec	
He	1	11.62	69.889	He	2	5.88	75.710
Ar	1	13.40	69.971	Ar	2	9.51	75.710
H_2S	2	1.30	70.46	H_2S	3	22.80	75.614

$T = 100°F$

$W_L^O = .0079$ gm-mole

$P = 100$ psia

$T_a = 72.3°F$

$P_a = 738.8$ mm Hg

$V_G^* = 12.374$ cc

$V_G = 12.363$ cc

$T = 100°F$

$W_L^O = .0079$ gm-mole

$P = 200$ psia

$T_a = 72.1°F$

$P_a = 738.8$ mm Hg

$V_G^* = 11.659$ cc

$V_G = 11.648$ cc

TABLE IX (Continued)

Solute	Retention Time, t_{R_i} Min	Sec	Flow Rate, fa, cc/min	Solute	Retention Time, t_{R_i} Min	Sec	Flow Rate, fa, cc/min
He	3	7.73	98.603	He	3	49.91	119.403
Ar	3	13.91	98.603	Ar	3	58.56	119.403
H_2S	4	46.71	98.603	H_2S	5	39.31	119.403

$T = 100^{\circ}F$

$W_L^{o} = .0079$ gm-mole

$P = 400$ psia

$T_a = 74.3^{\circ}F$

$P_a = 734.6$ mm Hg

$V_G^{*} = 10.981$ cc

$V_G = 10.970$ cc

$T = 100^{\circ}F$

$W_L^{o} = .0079$ gm-mole

$P = 600$ psia

$T_a = 74.3^{\circ}F$

$P_a = 734.8$ mm Hg

$V_G^{*} = 10.642$ cc

$V_G = 10.629$ cc

TABLE IX (Continued)

Solute	Retention Time, t_{R_i} Min	Sec	Flow Rate, fa, cc/min	Solute	Retention Time, t_{R_i} Min	Sec	Flow Rate, fa, cc/min
He	5	36.14	108.893	He	6	38.97	113.529
Ar	5	57.43	109.589	Ar	6	56.22	113.529
H_2S	7	51.73	110.092	H_2S	9	20.82	113.314

$T = 100°F$

$W_L^o = .0079$ gm-mole

$P = 800$ psia

$T_a = 72.9°F$

$P_a = 738.9$ mm Hg

$V_G^* = 10.527$ cc

$V_G = 10.513$ cc

$T = 100°F$

$W_L^o = .0079$ gm-mole

$P = 1000$ psia

$T_a = 72.9°F$

$P_a = 738.9$ mm Hg

$V_G^* = 10.234$ cc

$V_G = 10.219$ cc

TABLE IX (Continued)

Solute	Retention Time, t_{R_i}		Flow Rate, fa, cc/min	Solute	Retention Time, t_{R_i}		Flow Rate, fa, cc/min
	Min	Sec			Min	Sec	
He	1	15.69	65.826	He	2	4.82	74.720
Ar	1	17.51	65.826	Ar	2	8.17	74.720
H_2S	1	55.58	65.681	H_2S	3	5.51	74.720

$T = 130°F$

$W_L^O = .0079$ gm-mole

$P = 100$ psia

$T_a = 75.0°F$

$P_a = 737.4$ mm Hg

$V_G^* = 12.914$ cc

$V_G = 12.904$ cc

$T = 130°F$

$W_L^O = .0079$ gm-mole

$P = 200$ psia

$T_a = 75.0°F$

$P_a = 737.4$ mm Hg

$V_G^* = 11.982$ cc

$V_G = 11.972$ cc

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TABLE IX (Continued)

Solute	Retention Time, t_{R_i} Min	Sec	Flow Rate, fa, cc/min	Solute	Retention Time, t_{R_i} Min	Sec	Flow Rate, fa, cc/min
He	3	56.00	75.758	He	5	11.38	84.926
Ar	4	2.58	75.949	Ar	5	22.06	84.926
H_2S	5	31.42	75.805	H_2S	7	3.82	84.806

$T = 130^\circ F$

$W_L^o = .0079$ gm-mole

$P = 400$ psia

$T_a = 75.0^\circ F$

$P_a = 737.4$ mm Hg

$V_G^* = 11.293$ cc

$V_G = 11.282$ cc

$T = 130^\circ F$

$W_L^o = .0079$ gm-mole

$P = 600$ psia

$T_a = 750.0^\circ F$

$P_a = 737.7$ mm Hg

$V_G^* = 10.962$ cc

$V_G = 10.950$ cc

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TABLE IX (Continued)

Solute	Retention Time, t_{R_i} Min	Retention Time, t_{R_i} Sec	Flow Rate, fa, cc/min	Solute	Retention Time, t_{R_i} Min	Retention Time, t_{R_i} Sec	Flow Rate, fa, cc/min
He	5	59.45	97.800	He	6	32.78	110.599
Ar	6	11.52	98.119	Ar	6	50.32	110.294
H_2S	7	53.75	97.640	H_2S	8	33.10	109.790

$T = 130°F$

$W_L^o = .0079$ gm-mole

$P = 800$ psia

$T_a = 75.0°F$

$P_a = 738.0$ mm Hg

$V_G^* = 10.771$ cc

$V_G = 10.758$ cc

$T = 130°F$

$W_L^o = .0079$ gm-mole

$P = 1000$ psia

$T_a = 75.0°F$

$P_a = 738.0$ mm Hg

$V_G^* = 10.499$ cc

$V_G = 10.485$ cc

NOMENCLATURE

a   - cohesive energy density or Redlich-Kwong equation constant

b   - Redlich-Kwong equation constant

ΔE_i - isothermal molar change in energy of pure i in going from liquid to the ideal gas state

f   - fugacity or carrier gas flow rate

K   - vapor-liquid equilibrium constant

k_i - partition coefficient

k_{ij} - correction factor for binary interaction

L   - length of column

n_i - number of moles of solute sample i

P   - pressure

R   - gas constant

T   - temperature

t_R - retention volume

u_i - average linear velocity of component i

V   - volume

$\overline{V}$ - molar volume

V_L - volume of stationary liquid phase in the GLC column

V_G - volume of mobile gas phase equal to the void volume

V_R - retention volume

W   - weight

x   - mole fraction in liquid phase

y   - mole fraction in vapor phase

Z_G – compressibility factor of the carrier gas at system conditions

Greek Symbols

γ – activity coefficient in liquid solution

δ – solubility parameter

ν – pure component liquid fugacity coefficient

ρ – density

ϕ – volume fraction

Ψ – vapor phase fugacity coefficient

Ω_A – dimensionless constant in Redlich-Kwong equation

Ω_B – dimensionless constant in Redlich-Kwong equation

Subscripts

1   – methane or solvent in a binary solution

2   – solute

3   – n-decane

c   – critical conditions

G   – gas phase

FH   – Flory-Huggins

i, j, k, l   – component in system

L   – liquid phase

m   – mixture

SH   – Scatchard-Hildebrand

V   – vapor phase

vp   – vapor pressure

Superscripts

M   − mixture

∞   − infinite dilution

o   − pure state

VITA

Anthony Loring Hines

Candidate for the Degree of

Master of Science

Thesis: VAPOR-LIQUID EQUILIBRIUM STUDY OF THE METHANE-HYDROGEN
         SULFIDE-N-DECANE TERNARY SYSTEM

Major Field: Chemical Engineering

Biographical:

    Personal Data: Born in Altus, Oklahoma, September 19, 1941, the
        son of Mr. and Mrs. William A. Hines.

    Education: Graduated from Altus High School, Altus, Oklahoma, in
        May, 1959; received an Associate of Science degree from
        Cameron State Agricultural College, Lawton, Oklahoma, in
        May, 1963; received the Bachelor of Science degree from the
        University of Oklahoma in January, 1967, with a major in
        Chemical Engineering; completed requirements for the Master
        of Science degree in May, 1972.

    Professional Experience: Employed as an assistant engineer by
        Texaco, Inc., during the summers of 1965 and 1966; employed
        as a process engineer by Warren Petroleum Corporation from
        January, 1967, to September, 1967, and from March, 1968, to
        September, 1968; employed by International Business Machines
        as a chemical engineer from August, 1969, to the present time.