VAPORIZATION EQUILIBRIUM RATIOS FOR CO_2 AND H_2S IN PARAFFINIC, NAPHTHENIC, AND AROMATIC SOLVENTS

By

CHARLES JOSEPH MUNDIS

Bachelor of Science
Oklahoma State University
Stillwater, Oklahoma
1968

Master of Science
Oklahoma State University
Stillwater, Oklahoma
1970

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of the Oklahoma State University
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Thesis Approved:

Robert L. Robinson, Jr.
Thesis Adviser

R. N. Maddox

Billy L. Crynes

Allen M. Rowe Jr.

D. D. Durham
Dean of the Graduate College

PREFACE

Vaporization equilibrium ratios (K-values) were determined for carbon dioxide and hydrogen sulfide at infinite dilution in the methane - n-heptane, methane - methylcyclohexane, and methane - toluene systems at 20, 0, -20, and -40°F at pressures to 1500 psia. Measurements were made by the chromatographic technique. Results were confirmed by classical measurements on the carbon dioxide, hydrogen sulfide, methane and n-octane system. Results were correlated well by a modified Redlich-Kwong equation.

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CHAPTER I

INTRODUCTION

A knowledge of the vapor-liquid equilibrium relationship is a prerequisite to the description of a variety of processes for separation of the components of a mixture. Information is scarce on the vapor-liquid equilibrium behavior of carbon dioxide (CO_2) and hydrogen sulfide (H_2S) in absorber systems operating at subambient temperatures and moderate pressures. Experience in correlating vapor-liquid equilibrium ratios (K-values) has indicated that the non-hydrocarbons CO_2 and H_2S usually require preferential treatment for the estimation of their K-values. Literature data are especially scarce for K-values of CO_2 and H_2S in aromatic and naphthenic solvents.

The purpose of this study was to (1) construct an apparatus which could be used to determine experimental K-values of H_2S and CO_2 in aromatic and naphthenic solvents, (2) measure the K-values of CO_2 and H_2S in selected paraffinic, naphthenic, and aromatic solvents and (3) provide a suitable correlation for representation of the phase behavior of CO_2 and H_2S in these solvents.

The apparatus constructed for this work employed the chromatographic technique. The literature on the subject of gas-liquid chromatography reveals that chromatography is firmly established as a reliable and applicable technique for studying thermodynamic properties of solutions. The chromatographic method of measurement was used because it is a simple, accurate, and rapid means of obtaining K-value data. In addition, previous studies (17, 51) at Oklahoma State University using the chromatographic technique had resulted in establishment of some expertise in the use of this method.

The specific systems selected for study were designed to fill a critical gap in available data on the hydrocarbons and associated components. The proposed systems for study are:

1. CO_2 in the methane (C_1)-toluene (Tol) system
2. CO_2 in the methane-methylcyclohexane (MCH) system
3. CO_2 in the methane-heptane (C_7) system
4. H_2S in the methane-toluene system
5. H_2S in the methane-methylcyclohexane system
6. H_2S in the methane-heptane system

For each system the data range selected was 20 to -40°F (20°F intervals) at pressures to 1500 psia. The data were measured chromatographically with the CO_2 and H_2S at infinite dilution in all cases.

The systems listed were chosen because they provide the desired combinations of the non-hydrocarbons with naphthenic and aromatic solvents and they are systems for which pertinent binary data are available (methane-toluene, methane-methylcyclohexane, methane-heptane, methane-CO_2, methane-H_2S). The binary data are required for two purposes. First, the methane-solvent binary data are required for calculation of the K-values of H_2S and CO_2 from the chromatographic experiments. Second, the complete set of binary data listed above are useful in development of correlations to predict vapor-liquid equilibrium.

In addition, the K-values of CO_2 and H_2S in the methane-octane system at -20^o and 0^oC were measured both by the chromatographic technique and in a classical windowed cell. The windowed cell data help appraise the validity of the chromatographic data from this study.

The data from this work were correlated in terms of a modified form of the Redlich-Kwong equation of state, employing empirical interaction parameters. The basis for the correlation is the Soave modification of the Redlich-Kwong equation. Two correlational methods were used, one in which an energy term (T_{cij}) is modified and one in which both energy and distance (V_{cij}) terms were modified. The correlation was applied to the experimental results of this work.

CHAPTER II

LITERATURE SURVEY

The literature survey for this study consisted of a search for (1) the binary vapor-liquid equilibrium (VLE) data needed for the experimental calculations, (2) binary VLE data needed for correlation work, and (3) all existing VLE data on K-values of CO_2 or H_2S in heavy (heptane and heavier) alkanes, aromatics, or naphthenic hydrocarbons.

The history of chromatography, the application of gas-liquid partition chromatography to vapor-liquid equilibrium studies, and the theory of chromatography have been discussed in detail by several other investigators (24, 46, 51). The work of Van Horn goes into particular detail on the above subjects.

The binary vapor-liquid equilibrium data required for calculation of K-values at infinite dilution by the chromatographic technique consist of methane in each of the solvents over the range of studied. In this work the data were the following: (1) methane+heptane (2) methane+methylcyclohexane, (3) methane+toluene, and (4) methane+n-octane. Table I gives all the data found and the range of the data source. The data which were used in this work are indicated with an asterick.

The binary VLE data needed for the correlation work consisted of the systems, methane + solvent, methane + gas (CO_2, H_2S) and solvent + gas. The methane + solvent binaries have already been discussed. The data for CO_2 or H_2S in methane are listed in Table I. No data were found for CO_2 or H_2S in the solvents (n-heptane, methylcyclohexane, toluene, or n-octane).

Finally, all VLE data which show the effects of aromatics or naphthenics on the behavior of CO_2 or H_2S were gathered. Very few data are available, thus illustrating the need for the data of this work.

TABLE I

EXPERIMENTAL K-VALUE DATA FROM LITERATURE

System	Temperature Range	Pressure Range (psia)	Data Source
Methane+ n-Heptane	-100 to 0°F	100 to 3000	4*
Methane+ n-Heptane	37 to 137°C	45 to 255	13
Methane+ Toluene	-100 to 0°F	100 to 3000	6*
	150 $^{\circ}$F	100 to 5300	12
Methane Methylcyclohexane	-100 to 0°F	100 to 3500	5*
Methane+ n-Octane	-50 to 150°C	150 to 1500	22*
	-120 to 200°F	200 to 1600	23
	40 to 280°F	50 to 1200	40*
Methane+ Hydrogen Sulfide	40 to 340°F	200 to 10,000	34
Methane+ Carbon Dioxide	-100 to 29°F	200 to 1100	9*
	-40 to 10°C	540 to 1200	20
Carbon Dioxide+ n-Decane	40 to 280°F	50 to 1150	35
Hydrogen Sulfide+ n-Decane	40 to 340°F	50 to 1900	36
Methane+ Carbon Dioxide+ Hydrogen Sulfide	-51 to -34.4°C	300 to 700	15

TABLE I (Continued)

EXPERIMENTAL K-VALUE DATA FROM LITERATURE

System	Temperature Range	Pressure Range (psia)	Data Source
Methane+ Carbon Dioxide+ n-Octane	-20°C	100 to 1000	21
Methane+ Carbon Dioxide+ n-Decane	10 to 150°F	100 to 750	52
Methane+ Carbon Dioxide+ n-Octane	-40 to 20°C	100 to 1500	1
Methane+ Hydrogen Sulfide+ n-Octane	-40 to 20°C	100 to 1500	1
Methane+ Ethane+ Propane+ n-Pentane+ n-Decane+ Toluene+ Hydrogen Sulfide+ Nitrogen+ Carbon Dioxide	-50 to 250°F	100 to 4500	49
Hydrogen Sulfide+ n-Nonane	100 to 400°F	20 to 400	10
Hydrogen Sulfide+ Mystiline	100 to 400°F	20 to 400	10

CHAPTER III

THEORETICAL DEVELOPMENT

The theoretical development of the equations used to calculate experimental K-values is given in this chapter for both experimental methods. The development of the correlation framework is also discussed in this chapter.

Gas-Liquid Chromatography Experiment

The Basic Chromatographic Equations

Pecsar and Martin (31) have presented a somewhat simple derivation of the basic chromatographic equation. A modified version of their derivation will be presented here, the final result being the equations which are appropriate for the systems used in this work.

The assumptions involved in the derivation of the equations are the following:

1. Sample size is inifinitely small.
2. The partition coefficient **k** is constant throughout the column.
3. The pressure drop along the column is negligible.
4. The amount of liquid in the column during solute elution remains constant.
5. The mixing and diffusion effects are negligible.
6. There is no interaction between solute and solid support in the column.

7. Instantaneous equilibrium of sample solute exists between the vapor phase (carrier gas) and the liquid phase (stationary liquid).

The partition coefficient k_i is defined by

$$k_i = \frac{\text{concentration of component i in the liquid phase}}{\text{concentration of component i in the vapor phase}} \tag{3-1}$$

or

$$k_i = \frac{n_{Li}/V_L}{n_{gi}/V_g} = \frac{x_i \rho_L}{y_i \rho_g} = \frac{\rho_L}{K_i \rho_g} \tag{3-2}$$

where n_{Li} = number of moles of component i in the liquid phase

n_{gi} = number of moles of component i in the vapor phase

V_L = volume of stationary liquid in the gas-liquid chromatography (GLC) column

V_g = void volume of the GLC column

x_i = mole fraction of component i in the liquid

y_i = mole fraction of component i in the vapor

ρ_L = liquid density

ρ_g = vapor density

K_i = K-value of component i.

The total number of moles of component i contained in the sample which passes through the column, n_i, is the sum of the moles of component i in the vapor phase, n_{gi}, plus the moles of component i in the liquid phase, n_{Li}, or

$$n_i = n_{gi} + n_{Li} \tag{3-3}$$

A "retention volume" of component i, V_{Ri}, can be defined as

$$V_{Ri} = f\, t_{Ri} \tag{3-4}$$

where f is the carrier gas flow rate and t_{Ri} is the retention time of component i; that is, the time required for a sample pulse of component i to pass through the column.

The average linerar velocity of the sample pulse, u_i, can be defined as

$$u_i = L/t_{Ri} \qquad (3\text{-}5)$$

where L is the length of the chromatograph column. Combining Equations (3-4) and (3-5) gives

$$u_i = Lf/V_{Ri} \qquad (3\text{-}6)$$

Similarly, the carrier gas velocity can be defined as

$$u_g = Lf/V_g \qquad (3\text{-}7)$$

The average linear velocity of the sample pulse (Equation (3-5)) can also be expressed in terms of the velocity of the sample pulse in the vapor, u_{gi}, and in the liquid, u_{Li}. The average linear velocity, u_i, is the velocity of propagation of the impulse through the column and can be expressed as the average velocity of component i moving in the vapor phase and in the liquid phase, or

$$u_i = \frac{n_{gi}\,u_{gi} + n_{Li}\,u_{Li}}{n_i} \qquad (3\text{-}8)$$

Since the liquid phase is stationary, then

$$u_{Li} = 0 \qquad (3\text{-}9)$$

The fraction of the sample pulse which is in the vapor phase will have a velocity equal to the carrier gas velocity, or

$$u_{gi} = u_g = Lf/V_g \qquad (3\text{-}10)$$

Substituting Equations (3-9) and (3-3) into (3-8), the result is

$$(n_{gi} + n_{Li})\,u_i = n_{gi}\,u_{gi} \qquad (3\text{-}11)$$

Equation (3-8) could be written

$$n_i \, u_i = n_{gi} \, u_{gi}$$

or

$$\frac{n_{gi}}{n_i} = \frac{u_g}{u_{gi}}$$

Combining Equation (3-10), (3-6), and the above equation gives the fraction of the sample pulse in the gas phase as

$$\frac{n_{gi}}{n_i} = \frac{V_g}{V_{Ri}}$$

The above illustrates that the ratio of the free gas volume to the sample retention volume is the fraction of the sample in the vapor phase.

Equation (3-11) can be rearranged and combined with Equation (3-6) and (3-10) to give

$$n_{gi} \left(\frac{Lf}{V_{Ri}} - \frac{Lf}{V_g} \right) + n_{Li} \left(\frac{Lf}{V_{Ri}} \right) = 0 \qquad (3\text{-}12)$$

Rearranging Equation (3-12), dividing through by $\frac{n_{Li} \; fL}{V_{Ri}}$, and substituting Equation (3-2) for $\frac{n_{gi}}{n_{Li}}$ gives

$$\frac{V_g \, \rho_g \, K_i}{V_L \, \rho_L} \left[\frac{V_g - V_{Ri}}{V_g} \right] = 1 \qquad (3\text{-}13)$$

The moles of pure stationary liquid are equal to the moles of liquid and gas solution minus the gas in solution, or

$$W_L^o = \rho_L \, V_L - \chi_1 \, \rho_L \, V_L$$

or

$$W_L^o = (1-\chi_1) \, \rho_L \, V_L$$

or finally

$$\rho_L \, V_L = \frac{W_L^o}{(1-\chi_1)} \qquad (3\text{-}14)$$

where

$V_L \rho_L = W_L$ = the moles of stationary liquid and gas solution on the GLC column.

W_L^o = the moles of pure stationary liquid on the GLC column.

χ_1 = mole fraction of carrier gas in the liquid phase.

Equation (3-14) expresses $\rho_L V_L$ in terms of variables which are measureable on the chromatographic apparatus. Equations (3-13) and (3-14) are combined to give

$$\frac{K_i (1-\chi_1) \rho_g (V_g - V_{Ri})}{W_L^o} = -1$$

Solving for K_i gives

$$K_i = \frac{W_L^o}{(1-\chi_1) \rho_g (V_{Ri} - V_g)} \qquad (3\text{-}15)$$

where

K_i = vapor liquid equilibrium constant of the sample pulse i,

W_L^o = moles of pure stationary liquid in the GLC column,

χ_1 = mole fraction of the carrier gas in the liquid phase,

ρ_g = density of the carrier gas

V_{Ri} = retention volume of solute i (sample pulse i).

V_g = free gas volume, or volume of the gas phase in the GLC column.

In this work, V_{Ri} has been calculated using the following equation:

$$V_{Ri} = V_{Ri}^C - V_{Ri}^B$$

where

V_{Ri}^C = retention volume of component i from the sample valve to the detector, including the GLC column

V^B_{Ri} = retention volume of component i from the sample valve to the detector, via the GLC column bypass.

Although V^B_{Ri} should be the same for all components, tests indicated that there was a difference of 0.5 to 5.0 seconds in elution times ($V_{Ri} \alpha t_{ri}$) between helium and CO_2 samples, from 100 psia to 1500 psia, respectively. V^B_{Ri} was measured with the GLC column bypass open and the GLC column blocked out of the system. The above equation can be combined with Equation (3-4) to give

$$V_{Ri} = t^C_{Ri} f^C - t^B_{Ri} f^B \qquad (3\text{-}16)$$

where

f^C = carrier gas flow rate for the column run

f^B = carrier gas flow rate for the bypass run $\cong f^C$

In this work the carrier gas flow rates, f, were measured at ambient conditions with the carrier gas saturated with water vapor.

Thus, f can be expressed as

$$f = f_a \left(\frac{P_a}{P}\right) \left(\frac{T}{T_a}\right) Z_g \qquad (3\text{-}17)$$

where

f, f_a = system and ambient flow rates

P, P_a = system and ambient pressure

T, T_a = system and ambient temperature

Z_g = compressibility of carrier gas at column conditions, T and P.

The carrier gas flow rate at ambient conditions can be expressed in terms of experimentally measurable quantities using

$$f_a = \frac{V_B}{t_B} \left(\frac{P_a - P_{H_2O}}{P_a}\right) \qquad (3\text{-}18)$$

where

V_B = calibrated volume of the bubblemeter

t_B = residence time of the bubble in V_B

P_a = ambient pressure (mm Hg)

P_{H_2O} = water vapor pressure at T_a

The water vapor pressure can be expressed as a function of ambient temperature (in ^oC) by the following equation:

$$P_{H_2O} = 9.412 - 0.266\,T_a + 0.0366\,T_a^2 \qquad (3\text{-}18a)$$

The above equation was derived by a simple second degree polynomial least squares curve fit of water vapor pressure data from the literature (32).

Equations (3-15) to (3-18) are the basic equations used to calculate K-values from GLC elution data.

Determination of GLC Column Void Volume

The void volume, or free gas volumen, V_g, of the GLC column is defined as the volume of gas phase in the GLC column.

The K-values are dependent directly upon the value of $(V_{Ri} - V_g)$, as can be seen from equation (3-15). For highly retained components in which V_{Ri} is large, a high accuracy in calculating V_g is not necessary, since $V_{Ri} >> V_g$. But for very volatile components where the value of V_{Ri} approaches V_g, the free gas volume, V_g, needs to be known very accurately.

In this work the free gas volume was obtained from retention volume measurements on the spherical gases, helium (He) and argon (Ar), by extrapolating retention volumes of these two gases as a function of polarizability to the point of zero polarizability. This method is similar to that used by Yudovich (53). A plot of retention volume as a function of polarizability is shown in Figure 15. A linear extrapolation can be made numerically. The polarizabilities of helium and argon are 0.204 and 1.63, respectively (25). Knowing the retention volumes of He and Ar, V_{RHe} and V_{RAr}, the slopes on Figure 15 can be written as

$$\frac{V_{RAr} - V_{RHe}}{1.63 - 0.204} = \frac{V_{RAr} - V_g}{1.63 - 0.0}$$

or

$$V_g = 1.143 V_{RHe} - 0.143\ V_{RAr} \tag{3-19}$$

where

V_g = free gas volume

V_{RHe} = retention volume of helium

V_{RAr} = retention volume of argon

The retention volumes of helium and argon were calculated using Equation (3-16); that is, runs for two helium samples and two argon samples were required to calculate V_g.

Classical Windowed Cell Experiment

In the classical experiments the samples of liquid and vapor were drawn from a closed equilibrium cell and analyzed either by a hydrogen flame detector (HF) or thermal conductivity detector (TC). The detectors had to be calibrated before the K-value data could be evaluated.

This section will discuss the equations used to calculate detector response factors for each component and the equations used to evaluate K-values from the cell data.

Calculation of Relative Response Factors

Differences in thermal conductivity (for the TC detector) or in the number of carbon atoms per mole (for the HF detector) cause the response of the detectors to differ for different components. Thus, the response factor, RF_i, of component i is defined to be the chromatographic detector output response of component i per mole of component i. The output response for a component is the area under the peak on the strip chart recorder, or for this work, the number of counts on the digital integrator. Thus, the response factor for component i is

$$RF_i = \frac{\text{number of counts of component i}}{\text{number of moles of component i}}$$

The "relative response," R_{1i}, of the component methane, C1, to component i can be expressed as

$$R_{1i} = \frac{RF_1}{RF_i} = \frac{\text{counts C1 / moles C1}}{\text{counts } C_i \text{ / moles } C_i}$$

or

$$R_{1i} = \frac{\text{moles } C_i \text{ / moles C1}}{\text{counts } C_i \text{ / counts C1}} \qquad (3\text{-}20)$$

Thus, the relative response factor can be found by making a mixture in which the numbers of moles of each component is known. A sample of the mixture must then be run through a chromatograph to find the number of counts which result for each component.

Calculation of K-values

The experimental data from the windowed cell consist of the "number of counts" of each component in both a vapor and a liquid sample; that is, the area under the peak of each component. By taking the ratio of the number of counts of component i to the number of counts of C1 and combining this with Equation (3-20), the molar ratio of all components to C1 can be found using

$$\frac{n_{Ci}}{n_{C1}} = (R_{1i}) \quad \left(\frac{\text{counts } C_i}{\text{counts } C1} \right) = \frac{\text{moles } C_i}{\text{moles } C1} \qquad (3\text{-}21)$$

The total moles of mixture in the sample per mole of C1 in the sample can be calculated using

$$\frac{n_T}{n_{C1}} = \frac{\sum_i n_{ci}}{n_{cl}} = \sum_i \left(\frac{n_{ci}}{n_{cl}} \right) \qquad (3\text{-}22)$$

Summing over i components means summing all components, including C_1. The mole fraction can now be calculated using

$$x_i = \frac{n_{ci}}{n_t} = \frac{n_{ci}/\, n_{cl}}{\sum_i (n_{ci}/\, n_{cl})} \qquad (3\text{-}23)$$

The liquid mole fraction, x_i, is calculated using the liquid sample peak areas and the vapor mole fraction, y_i, is calculated using the vapor sample peak areas.

The vapor-liquid equilibrium constant, K_i, is then calculated using the expression

$$K_i = y_i/x_i \qquad (3\text{-}24)$$

Equations (3-20) to (3-24) are the basis for calculations of K-values in the windowed cell.

Correlation Framework

The Soave modification to the Redlich-Kwong (R-K) equation of state is the basis of the correlation of the experimental data taken in this work. The following section will briefly describe (1) the R-K equation of state, (2) the Soave modification of the R-K equation of state, and (3) the application of modified mixing rules to the Soave equation.

Redlich-Kwong Equation of State

The Redlich-Kwong equation of state (37) is commonly considered the best of the two parameter equations of state (11, 41) for predicting thermodynamic properties of hydrocarbons and nonhydrocarbons. The R-K equation was originally proposed for predicting pressure-volume-temperature behavior at temperatures above the critical temperature for any pressure.

The original R-K equation of state is

$$P = \frac{RT}{\bar{V}-b} - \frac{a/T^{1/2}}{\bar{V}\,(\bar{V}+b)} \tag{3-25}$$

where a and b are individual parameters which are evaluated from the critical properties.

Letting

$$Z = \frac{p\bar{V}}{RT} \tag{3-26}$$

$$A = \frac{ap}{R^2T^{2.5}} \tag{3-27}$$

and

$$B = \frac{bp}{RT} \tag{3-28}$$

Equation (3-25) can be written

$$Z^3 - Z^2 + Z\,(A-B-B^2) - AB = 0 \tag{3-29}$$

By setting the first and second derivatives of pressure with respect to volume equal to zero at the critical point, b_c and a_c can be written as

$$b_c = 0.08664\,\frac{RT_c}{P_c} = 0.08664\,V_c' \tag{3-30}$$

and

$$a_c = 0.4275\,\frac{R^2T_c^{2.5}}{P_c} = 0.4275\,R\,T_c^{1.5}V_c' \tag{3-31}$$

where T_c, P_c = critical temperature and pressure

R = gas constant

$V_c'=RT_c/P_c$ = ideal gas critical volume.

The R-K equation can be used to calculate the volumetric and thermal properties of pure compounds and of simple mixtures to a good degree of accuracy. However, its application to multicomponent vapor-liquid equilibrium calculations often gives poor results.

Soave Modification of R-K Equation

Soave (42) believed the shortcomings of the R-K equation could not be attributed solely to the imperfection of the mixing rules (several people have introduced modified mixing rules into the R-K equation (7, 18)). He thought the equation's lack of accuracy in expressing the influence of temperature was partly the cause as reflected in the equation's low accuracy in calculating the vapor pressures of pure substances, which are not influenced by any mixing rule. Soave assumed that an improvement in reproducing saturation conditions of pure substances also leads to an improvement for mixtures. Soave modified the R-K equation by replacing the term $(a/T^{½})$ with a temperature dependent term a'(T). Equation (3-25) is now written

$$P = \frac{RT}{\overline{v}-b} - \frac{a'(T)}{\overline{v}(\overline{v}+b)} \qquad (3\text{-}32)$$

The parameters a' and b can be found at the critical point to be

$$a'(T_c) = 0.4275 \frac{R^2T_c^2}{P_c} = 0.4275\ RT_cV_c' \qquad (3\text{-}33)$$

and

$$b_c = 0.08664\ RT_c/P_c = 0.08664\ V_c' \qquad (3\text{-}34)$$

By introducing a dimensionless factor $\alpha_i(T)$, $a_i'(T)$ may be written as

$$a_i'\ (T) = a_{ci}'\ \alpha\ (T) \qquad (3\text{-}35)$$

where

$\alpha_i(T_c) = 1.$

Soave expressed the empirical factor $\alpha_i(T)$ as

$$\alpha_i(T) = [\ 1+m_i(1-T_{Ri}{}^{0.5})\ ]^2 \qquad (3\text{-}36)$$

where T_{Ri} = reduced temperature of component i = T/T_{ci}

$$m_i = 0.480 + 1.574\ \omega_i - 0.176\ \omega_i{}^2 \qquad (3\text{-}37)$$

and ω_i = the accentric factor of component i.

A complete discussion of the basis of Equations (3-36) and (3-37) is presented by Soave (42).

For mixtures, Soave employed the following mixing rules

$$a' = (\sum_i\ x_ia_i'^{0.5})^2 \qquad (3\text{-}38)$$

$$b = \sum_i x_ib_i \qquad (3\text{-}39)$$

where a_i' and b_i are defined by Equations (3-35) and (3-34), respectively. The terms $\alpha_i(T)$ and a_{c_i} of Equation (3-35) are defined by Equations

(3-38) and (3-33), respectively. Equations (3-32) to (3-39) are the basic equations used by Soave.

Modifications of the Soave Equation for This Work

Soave (42) found that his modified R-K equation fit experimental vapor phase and liquid phase data well for the hydrocarbon systems. He also concluded that the proposed equation was able to predict the phase behavior of mixtures in the critical zone. But large deviations were found for systems containing CO_2, H_2S, and polar compounds although the vapor pressures of the single pure components were reproducible.

In the present work the simple mixing rules suggested by Soave (Equations (3-38) and (3-39)) for applicaltion of the equation to mixtures have been modified further by using more general mixing rules, as follows:

$$a'(T) = \sum_i \sum_j [x_i x_j \, a'_{cij} \alpha_{ij}(T)] \tag{3-40}$$

and

$$b = \sum_i \sum_j (x_i x_j \, b_{ij}) \tag{3-41}$$

where

$$a'_{cij} = 0.4275 \; R \; T_{cij} \; V'_{cij} \tag{3-42}$$

$$\alpha_{ij}(T) = [1+m_{ij} \; (1-T_{Rij}{}^{0.5})]^2 \tag{3-43}$$

$$m_{ij} = 0.480 + 1.574\omega_{ij} - 0.176 \; \omega_{ij}{}^2 \tag{3-44}$$

$$\omega_{ij} = (\omega_i \omega_j)^{1/2} \tag{3-45}$$

$$T_{Rij} = T/T_{cij} \tag{3-46}$$

$$T_{cij} = (T_{ci} T_{cj})^{1/2} \tag{3-47}$$

$$V'_{cij} = [\tfrac{1}{2}(V'_{ci}{}^{1/3} + V'_{cj}{}^{1/3})]^3 \tag{3-48}$$

$$b_{ij} = (b_i + b_j)/2 = 0.08664 \frac{[V'_{ci} + V'_{cj}]}{2} \qquad (3\text{-}49)$$

Empirical correlation factors can be applied to the above generalized mixing rules to improve the Soave modification of the R-K equation. The correlation factors can be considered to be independent of system temperature, pressure, and composition. There are numerous ways in which empirical adjustment factors may be introduced into mixing rules. Direct adjustment factors can be applied to the constants a' and b, such as

$$a'_{ij} = (a'_i a'_j)^{1/2}(1-B_1) \qquad (3\text{-}50)$$

or

$$b_{ij} = \frac{(b_i+b_j)}{2}\,(1+B_2) \qquad (3\text{-}51)$$

or adjustment factors can be applied to parameters such as critical temperature and volume,

$$T_{cij} = (T_{ci}T_{cj})^{1/2}(1-B_3) \qquad (3\text{-}52)$$

$$V'_{cij} = [(\frac{V'^{\,1/3}_{ci} + V'^{\,1/3}_{cj}}{2})(1+B_4)]^3 \qquad (3\text{-}53)$$

Since a'_{ij} is a function of T_{cij} and V'_{cij} (Equation 3-42) and b_{ij} is a function of V'_{cij} (Equation 3-49), correlation factors B_3 and B_4 indirectly affect, a_{ij}, while correlation factor B_4 directly affects b_{ij}.

Lin and Robinson (19, 26) found that modification of both the energy (T_{cij}) and distance (V'_{cij}) parameters was necessary to accurately represent second virial coefficient data. Similar approaches have been used with other solution models (14, 27). In this work, two sets of empirical correlation factors were calculated. One method modified two parameters, as was suggested by Lin and Robinson; the other method modified only the energy term (T_{cij}). The corresponding equations for application of the empirical correlation factors are shown below:

Method 1 - one empirical correlation factor (k'_{ij})

$$T_{cij} = (T_{ci}T_{cj})^{0.5}(1-k'_{ij}) \tag{3-54}$$

Method 2 - two empirical correlation factors (k_{ij}, ℓ_{ij})

$$T_{cij} = (T_{ci}T_{cj})^{0.5}(1-k_{ij}) \tag{3-55}$$

$$V'_{cij} = [\tfrac{1}{2}(V'_{ci}{}^{1/3} + V'_{cj}{}^{1/3})(1 + \ell_{ij})]^3 \tag{3-56}$$

$$b_{ij} = 0.08664\ V'_{cij} \tag{3-57}$$

Equation (3-54) replaces (3-47) in the modified mixing rules for the first method, while Equations (3-55) through (3-57) replace Equations (3-47) through (3-49) for the second method.

Calculation of K-values

The K-value of component i can be expressed in terms of the liquid and vapor fugacity coefficients of component i; that is,

$$k_i = \frac{\emptyset_{iL}}{\emptyset_{ig}} = \frac{f_{iL}/x_iP}{f_{ig}/y_iP} = \frac{y_i}{x_i} \tag{3-58}$$

where

$\emptyset_{iL}$, $\emptyset_{ig}$ = liquid and vapor fugacity coefficients
P = system pressure
x_i, y_i = liquid and vapor mole fractions
f_{iL}, f_{ig} = liquid and vapor fucacities,

and $f_{iL} = f_{ig}$ at equilibrium.

The fugacity coefficient of component i can be calculated using the expression

$$\ell n\ \phi_i = -\ \ell n\ (\frac{P(\bar{V}-b)}{RT}) = \frac{2\sum_i y_i b_{ik} - b}{(\bar{V}-b)} - \frac{2\sum_i y_i a_{ik}}{RT^{1.5} b}\ \ell n\ (\frac{\bar{V}+b}{\bar{V}})$$

$$- \frac{\sum_i y_i b_{ik} - b)}{RT^{1.5} b} [\frac{1}{(\bar{V}+b)} - \frac{1}{b}\ \ell n\ (\frac{\bar{V}+b}{\bar{V}})] \qquad (3\text{-}59)$$

Equation (3-59) can be derived by applying the following general thermodynamic relationship to Equation (3-25):

$$\ln\ \phi_i = \frac{1}{RT} \int_V^\infty [(\frac{\partial P}{\partial n_i})_{T,\ V,\ n_k} - \frac{RT}{V}]\ dV - RT\ \ell n\ Z \qquad (3\text{-}60)$$

The derivation of Equation (3-59) from Equation (3-25) and (3-60) is given in Appendix C.

Equation (3-60) was evaluated using the original R-K equation (Equation (3-25)) rather than the Soave Modification (Equation (3-32)) to derive Equation (3-59). This is valid and can be used if the following modifications are also incorporated.

$$a(T) = a_{ci}\ \alpha_i(T)\ T_{Ri}^{0.5} \qquad (3\text{-}61)$$

where

$$a_{ci} = 0.4275 \frac{R^2\ T_c^{2.5}}{P_{ci}}$$

instead of

$$a_{ci} = 0.4275 \frac{R^2\ T_c^{2}}{P_c} \qquad (3\text{-}62)$$

The above can be proved by expressing the parameter a of the original R-K equation in terms of a' of the Soave modification, or

$$\frac{a}{T^{1/2}} = a' \qquad (3\text{-}63)$$

Substituting Equations (3-33) and (3-35) into (3-63) gives

$$\frac{a_i}{T^{1/2}} = a_i'\ (T) = a_{ci}'\ \alpha_i(T) = 0.4275[\frac{R^2 T_{ci}^{\ 2}\ \alpha_i(T)}{P_{ci}}]$$

or

$$a_i = 0.4275 \left[\frac{R^2 T_{ci}^{2.5}}{P_{ci}}\right]\left[\frac{T}{T_{ci}}\right]^{1/2} \alpha_i(T)$$

Finally, a_i can be written

$$a_i(T) = a'_{ci} \; \alpha_i(T) \; T_{Ri}^{0.5} \qquad (3\text{-}64)$$

where

$$a'_{ci} = 0.4275 \frac{R^2 \, T_{ci}^{2.5}}{P_{ci}}$$

Thus, a_i of the original R-K equation is expressed in terms of $\alpha_i(T)$ of the Soave modification. If Equation (3-64) is used along with the original R-K equation, then Equation (3-59) is valid for use in this work.

CHAPTER IV

EXPERIMENTAL APPARATUS

In this study, vapor-liquid equilibrium constants were measured experimentally on two different types of apparatus. The first apparatus consists of a continuous flow system in which vapor-liquid equilibrium data were measured from the retention time required for an infinitely dilute sample to pass through a chromatographic column. The second consisted of a variable volume static system in which known amounts of the components were mixed in a windowed cell from which vapor and liquid samples were extracted. Mole fractions were then found using a chromatographic system and a detector whose response factors are known.

A detailed description of the two experimental apparatus will be given in this chapter.

Gas-Liquid Chromatography Experiment

The chromatographic method of measurement was used because it is simple, accurate and a rapid means of obtaining K-value data. A schematic diagram of the apparatus is shown in Figure 1.

The main components of the system are the following:

1) the constant temperature bath

2) the sample valve

3) the gas-liquid chromatography column and presaturator

4) the detector and recorder

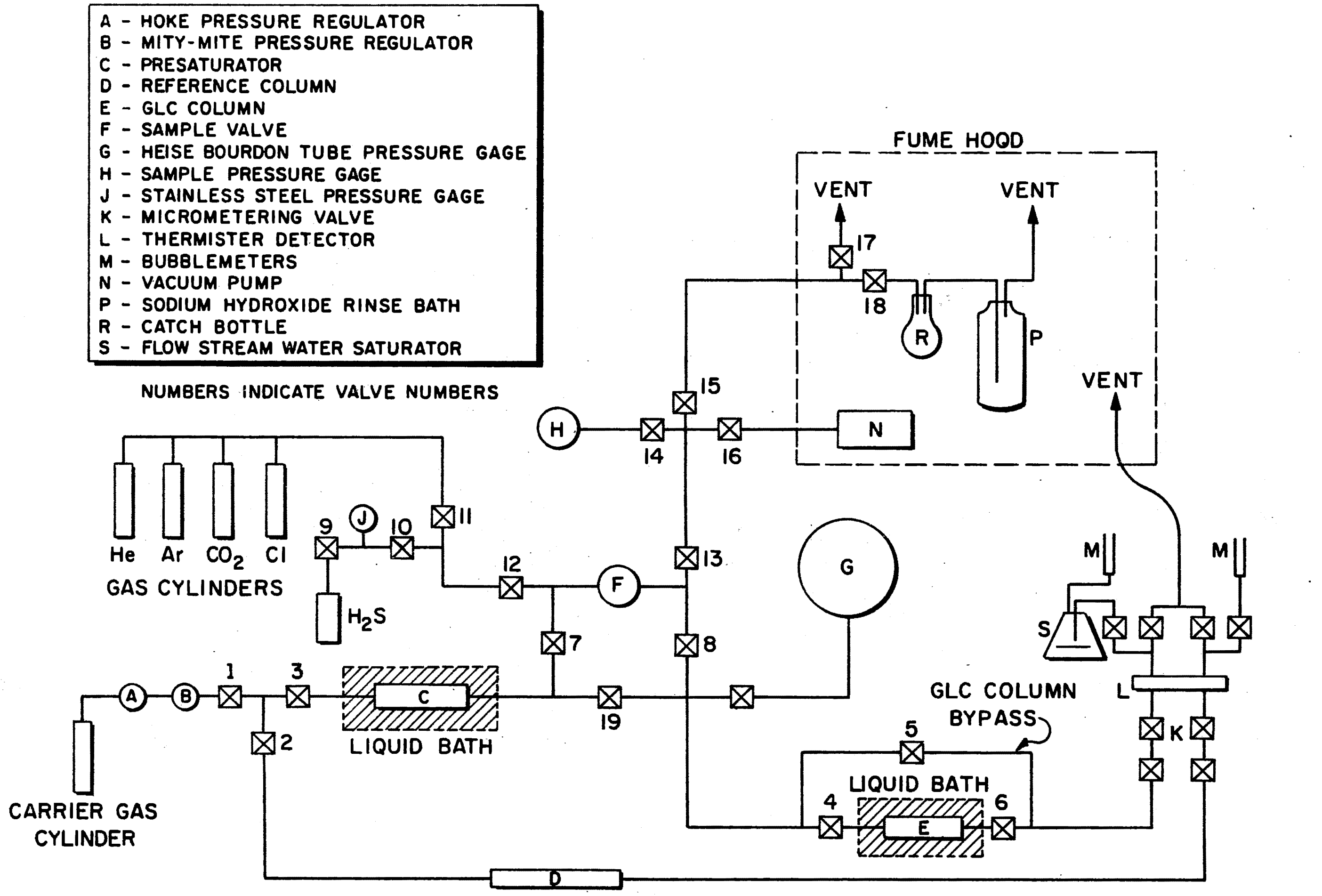

Figure 1. Schematic Diagram of the Chromatographic Equipment

5) the pressure control and measurement
6) the flow control and measurement, and
7) auxiliary equipment.

The apparatus was mounted on an angle iron frame. Plywood platforms were used to support the stripchart recorder, a potentiometer, the controller for the constant temperature bath, the electronic unit for the detectors, and the detectors. The valves, pressure controllers, pressure gauges, bubble meters, and sample valve were mounted on a vertical plywood board. Many of the above mentioned instruments were mounted such that their faces showed through the vertical plywood board. The temperature bath was mounted behind the main angle iron frame. The bath, which was mounted on a screw jack, could be raised and lowered around the gas-liquid chromatography (GLC) column and presaturator. The majority of the connecting tubing was 1/8" O.D. stainless steel tubing. A vacuum pump and sodium hydroxide rinse apparatus were placed in a hood and were connected to the system by 1/4 inch O.D. copper tubing.

The main components of the system will be discussed in detail.

The Constant Temperature Bath

The temperature bath and controller for the bath was made by Ladau and consisted of (1) Model KB-20 bath, (2) Electronic Relay Type R-10 and (3) Relay R-20 (controller).

The model KB-20 bath consists of a double walled bath vessel with coverplate. The inside dimensions of the bath were 8 inches by 8 inches by 14 inches long. The wall thickness is 2 inches. The insulation between the inner bath vessel and the outer housing is glass wool. A circulation pump is mounted on the top of the bath, at one end. The pump includes a propeller at the end of the drive shaft which provides the internal stirring required to maintain good temperature control. Two outlets are available which could be used to circulate to another bath or simply for better agitation in the temperature bath. The pump has a 70 watt motor and a maximum circulation rate of 2 1/4 gal/min. The flow rate in an external circuit can only roughly be controlled. An internal coil allowed cooling of the bath from an external source. A platinum resistance thermometer and heating coil are mounted for optimum temperature control.

The Electronic Relay type R-10 and Relay R-20 contain the main controls for the bath. The R-10 contains the on-off switch for the pump and a potentiometer which controls the heater wattage from 20% to 100% of rated capacity. The R-20 is connected to the platinum resistance thermometer, which is mounted in the constant temperature liquid bath. The R-20 contains the on-off switch of the bath heater and the controls for setting the bath temperature. Cooling was supplied in two ways. For the -40°F isotherms, liquid nitrogen was passed through the internal coil in the bath. For the higher temperature isotherms, the bath liquid was circulated through a second external bath whose temperature could be lowered to -55°C, but which could not be controlled accurately. The liquid from the external bath was not passed through the internal coil due to lack of pumping capacity for the external bath. The pump on the Ladau bath had very good pumping capacity, as was stated earlier.

The bath temperature was controlled by the R-20 relay. The bath temperature was read with a thermopile made of eight copper-constantan thermocouples. The thermopile was calibrated by the investigator (see

Appendix E). A Leeds and Northurp Volt Potentiometer was used to read the thermopile.

Sample Valve

The sample valve was developed by R. H. Jacoby and is very similar to the valve used by Yarborough and Vogel (50). The valve used in this work differs from that of Yarborough and Vogel in that the sample cavity is within a removable capsule. This gives the valve two significant advantages: (1) The fact that the sample cavity is removable makes it possible to machine it very precisely. (2) Since the sample cavity is easily removed, the size of the sample cavity may easily be changed for different types of gases or fluids, and the cavity may easily be replaced if the seat becomes worn or damaged.

The valve stem is non-rotating which should help preserve the seal. The sample cavity used in this work had a volume of 40 μl. The sample sizes could be varied by varying the pressure at which the samples were trapped.

The GLC Column and Presaturator

The GLC columns and presaturators were made from 1/4 inch O.D. stainless steel tubing. The columns were approximately ten inches long. Longer columns gave a larger differences in retention times between helium and the other components, but they also cause the peaks to spread out more. The columns were chosen to give the best compromise between the two effects. The presaturators were approximately 48 inches long. They were bent into a loop five inches in diameter, two and a half times around. The five inch diameter fit nicely into the temperature bath and allowed both the column and presaturator to be submerged completely in the bath.

The chromatograph packing was acid washed, 30/60 mesh Chromosorb P (Tek Lab, catalog number CP-23060). The packing was used because it did not react with the samples. Other packings were tried (Poropak Q, Fluoropack 80), but would react with the samples. The liquid load of the stationary phase was approximately 30% by weight.

Detector and Recorder

The detector system consisted of a thermistor detector and thermistor power supply connected to a stripchart recorder.

The power supply was a Gow-Mac Thermistor Power Supply Control Model 40-002. It is compatible with all thermistor detector thermal conductivity cells and delivers a high quality direct current voltage to the thermal conductivity cell. The unit has a resistance of 8000 ohms at 25°C. An attenuator of sensitivity potentiometer acts as a voltage divider circuit. This enabled the user to adjust the size of the peaks which are displayed on the strip chart recorder. A polarity switch allowed the user to changed the direction of the peaks.

The thermistor detector consisted of the thermal conductivity cell block and the detector elements. The two elements (Gow-Mac, Model 13-504) were mounted in the cell block directly in the gas flow path. The cell block was made from 304 stainless steel. The high sensitivity and rapid response of the thermistor are attributed to its very small volume. The internal volume of the detector cell was 0.012 cc.

The strip chart recorder (Brush Recorder, Mark 10) used a null-balance, potentiometric principle to plot the peaks in response to variations in a dc input from the thermistors. Chart speeds of 2 inch/min and 5 inch/min were mostly used, although speeds of 1 and 10 inches/min were available on the recorder.

The cell block was placed in a metal box and surrounded by foam rubber. A small heater and temperature controller were connected to the cell block, but were not used in this work. As long as the block was well insulated, noise due to temperature fluctuations was negligible.

Pressure Control and Measurement

The system pressure was controlled by two pressure regulators in a series. System pressure was measured between the sample valve and GLC column

The first of the pressure regulators (Hoke, Model 521B20) was a ballast-loaded high precision regulator. The carrier gas cylinders (high pressure methane) were connected directly to the regulator via a manifold. The pressure was reduced from the bottle pressure to approximately 100 psia above the system pressure using the first regulator. The second pressure regulator (Mity-Mite, Model 94) was also a ballast-loaded regulator which was used to drop the pressure approximately 100 psia to the system pressure. Both of these regulators used trapped gas in a sealed dome to regulate the down stream pressure. A 15 inch piece of capillary tubing was in the carrier gas inlet line just after the second regulator. The high resistance to flow in the line helped to overcome any short term pressure fluctuations.

The main gas stream was divided into two streams, the sample stream and the reference stream. The reference stream contained a column which was approximately the length of a GLC column plus a presaturator. The reference column was filled with dry packing. The purpose of the reference column was to provide approximately the same amount of resistance to flow in the reference stream as the GLC column provided to the sample stream.

The system pressure was measured with a Heise bourdon tube pressure gauge. The pressure of the gauge was 0-3000 psia, with 2 psi subdivisions. The pressures were recorded to the nearest 1 psi.

Flow Rate Control and Measurement

The flow rates of the sample stream and reference stream were each controlled with a Whitey micrometer control valve (Cat. No. 21RS2-316). The valve utilizes a 0.020 inch orifice diameter and a spring loaded stem to control flow rates. The stem has a very slight taper and is only 0.010 inch in diameter at the tip. The spring loaded stem guards against heavy handed operators who might overtighten it. The gas flow rates were measured using 50 cc soap bubble flow meters, made from 50 cc burettes. The bubble meter on the sample stream was calibrated with water. The reference stream bubble meter was not calibrated since the flow rate did not need to be known accurately.

The timer used for measuring flow rates was a Brenet (No. 67) stop watch with a 10 second sweep. The smallest divisions were 0.1 seconds and time could be read within 0.02 seconds. A Breno stopwatch with a 30 second sweep, 0.1 second divisions, and which could be read to 0.05 seconds was used, as well as the Brenet, to measure the time required for the samples to pass through the GLC column. The Breno was generally used when long retention times were expected.

Auxiliary Equipment

The auxiliary equipment consisted of (1) a vacuum pump, (2) a balance, (3) a carrier gas saturation flask, (4) a sodium hydroxide (NaOH) rinse bottle, (5) barometer, (6) thermometer, (7) ultra sonic cleaner, and (8) valves and fittings.

The vacuum pump (Welch, Duo-Seal, 1/3 horsepower) was used to evacuate the sample system before samples were injected into the valve. The sample system was purged at least twice with the gas to be used as the sample for the next run. An exception was the H_2S runs where the system was thoroughly evacuated before the samples were trapped. The system was not purged with H_2S to minimize the possibility of leaking H_2S to the atmosphere.

The balance (Mettler Instrument Company, 0-100 gm, 0.05 mg divisions) was used for all weighing done in the course of taking data, which included weighing the empty and packed GLC columns and weighing the solid support, both wet and dry.

The carrier gas saturation flask was used to saturate the sample stream with water after it had passed through the detector and before it passed through the bubble meter. The gas entered the top of the dewar through a 1/4 inch O.D. stainless steel tube, which extended to just above the water level. Bubbling the gas directly into the liquid caused a great deal of noise in the detector due to the flow upsets. Passing the gas into the dewar above the water would probably not thoroughly saturate the gas stream. Thus, cotton was suspended between two corks about three inches up the entry tube. As the gas exited the tube it passed through the cotton, which remained saturated with water. No flow upsets were caused by this system. The gas exited through a side arm.

The sodium hydroxide (NaOH) rinse bottle was used not to neutralize the samples which passed through the GLC column (approximately 40 μl at 300 psi), but rather to neutralize that volume of H_2S which filled the sample stream while charging the sample valve. This volume consisted of the tubing between the H_2S bottle and sample valve, approximately 6 feet of 1/8 inch tubing and dead space in tubing joints. The H_2S was purged through the NaOH solution with methane. The rinse bath was 12 inches high and 2 1/2 inches in diameter. The entry tube extended to within one inch of the bottom of the bath. The bath was filled with a NaOH solution to within two inches of the top. A flask was put in the line ahead of the NaOH rinse bath to prevent the possibility of sucking the NaOH solution back into the sample system. The gas would pass from the NaOH rinse into the fume hood.

A Sonogen-Z ultrasonic cleaner (Branson Instruments, Inc., Catalog No. LTH-126-6 (bath), Model A-300 (electrical unit)) was used to clean the inside of the columns, the 1/8 inch tubing used in the construction of the equipment, and all valves and fittings. All valves (Autoclave, 10V-2071) and fittings were manufactured by Autoclave.

Classical Windowed Cell Experiment

The equilibrium cell used in this work was a variable volume windowed cell. The apparatus, both windowed cell and chromatographic analysis equipment, have been previously described by Yarborough and Vogel (50). The windowed cell employs a sampling valve similar to that used in the GLC work, which allows small samples to be taken and injected into the chromatograph flow stream. A schematic diagram of the windowed cell apparatus is shown in Figure 2.

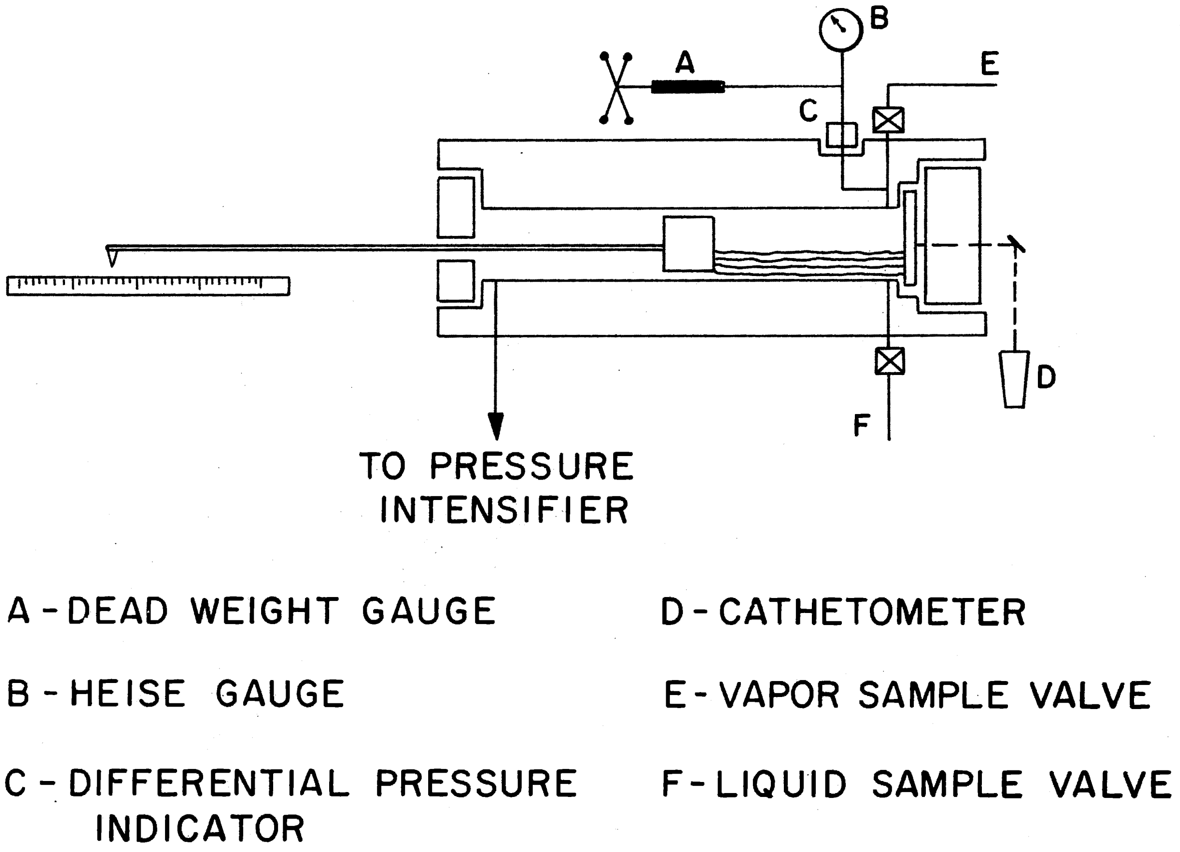

Figure 2. Schematic Diagram of the Classical Windowed Cell Equipment

Only minor modifications have been made to the apparatus for this work. The modifications are as follows:

1. The column used with the hydrogen flame detector was 12 feet of 1/8 inch O.D. stainless steel thinwall tubing filled with 10 weight percent Methyl Silicone Gum Rubber SE-30 on 60/70 mesh Anakron ABS solid support.
2. The original dual hydrogen flame ionization detector was replaced with a Model 5750 flame detector retrofit kit to improve the linearity and sensitivity of response.
3. The filaments in the thermal conductivity detector were tungsten-rhenium "hot wire" filaments. The filaments were new at the beginning of this work and were calibrated for this work.
4. A schematic diagram of the chromatographic switching valves is shown in Figure 3. Also shown are the TC column, the HF column, a heated expander-mixer coil, and a flow stream splitter.
5. The air bath in which the windowed cell was confined was cooled with a Coplematic refrigeration unit (Model KATC-0100-CAH) which had a single stage compressor. The compressor was air cooled and designed for extra low temperature. The compressor was charged with Freon 502 (Monochloro-difluoromethane/chloropentafluoroethane).

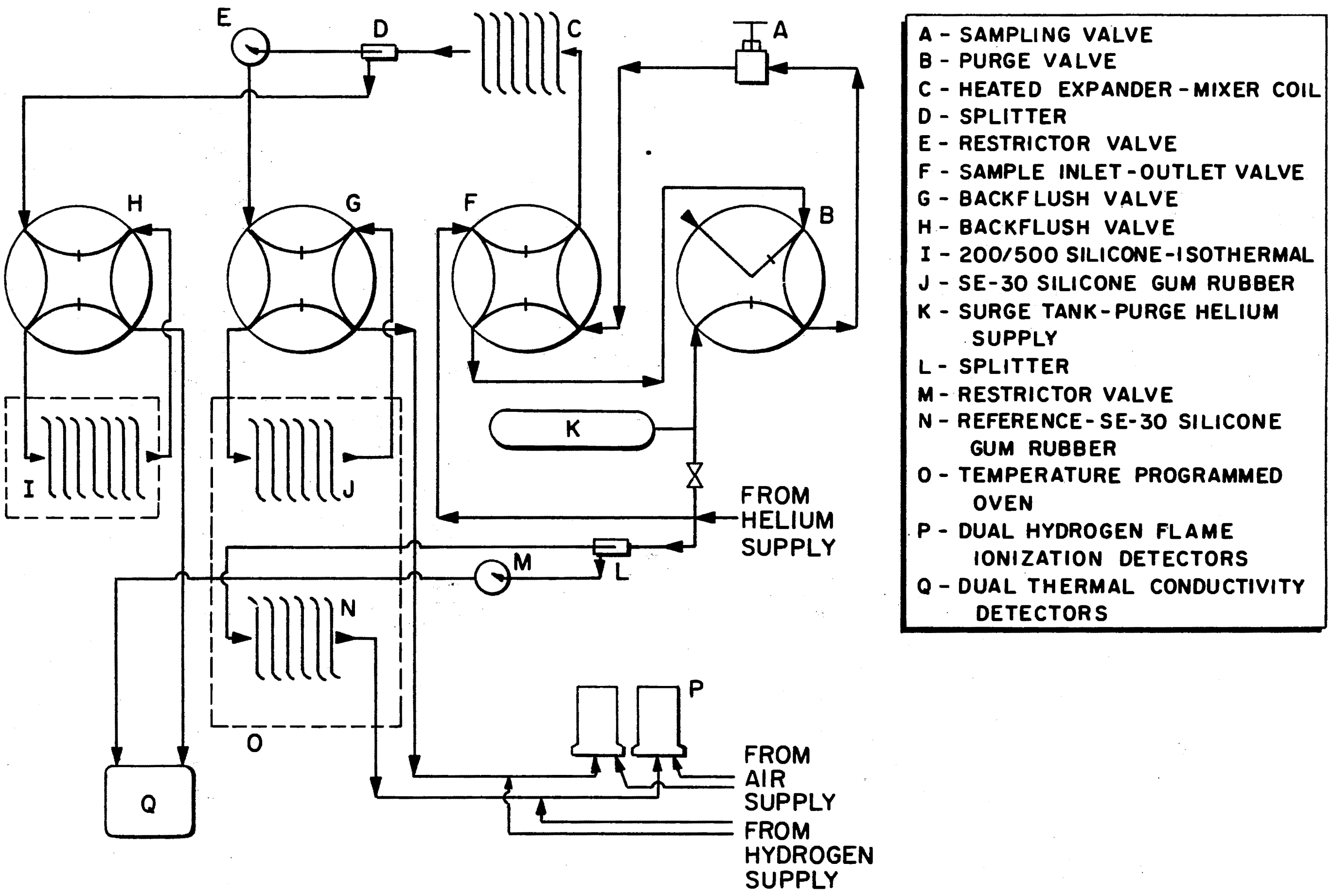

Figure 3. Schematic Diagram of Switching Valves for Chromatographic System of Windowed Cell Experiment

CHAPTER V

EXPERIMENTAL PROCEDURE

The procedures used in taking the experimental data will be described for the two experimental methods, the GLC experiment and the classical windowed cell experiment.

Gas-Liquid Chromatography Experiment

An examination of the equations

$$K_i = \frac{W_L^o}{(1-\chi_1)\,\rho_g(V_{Ri}-V_g)}$$

$$V_{Ri} = t_{Ri}^C f - t_{Ri}^B f$$

and

$$f = f_a\left(\frac{P_a}{P}\right)\left(\frac{T}{T_a}\right)(Z_g)$$

which are the basic equations for determining K-values from chromatography elution data, reveals that the following parameters must be measured experimentally to calculate the K-value from the above equations:

(1) T-system temperature

(2) T_a-ambient temperature

(3) P-system pressure

(4) P_a-ambient pressure

(5) f_a-flow rate of the carrier gas

(6) t_{ri}-retention time of solute i

(7) W_L^o-total moles of pure liquid contained in the GLC column.

The values of χ_1, ρ_g, and Z_g were found in the literature.

The experimental procedure and technique used to obtain the parameters listed above are described below. Unless otherwise stated, the discussion will refer to Figure 1. All preparatory work, preparing columns, and the measurement of the temperature, pressure, and flow rate will be discussed first. The on-stream procedure will be discussed last.

General

The tubing, fittings, and valves were thoroughly cleaned in a sonogen ultrasonic cleaner before they were assembled to remove traces of oil and grease. The equipment was then rinsed with ethanol and thoroughly dried. After the equipment was assembled, carrier gas was passed through the lines to dry out any water vapor that may have condensed on the lines. All fittings were tightened and the system was pressure tested with Helium at 1700 psia.

Preparation of Column Support

A pre-weighed amount of firebrick solid support was put in a clean eight ounce jar. The amount of liquid on the support should be about 30% of the weight of the support plus liquid, thus

$$\frac{L}{L+S} = 0.30$$

or

$$L = \frac{0.3}{0.7} S = 0.43S$$

where

L = weight of liquid needed, and

S = weight of solid.

The calculated amount of liquid was measured in a small beaker and then added to the solid support. The liquid loading needed only to be *approximately* 30%; thus, measurements need only be made roughly. The top was put on the jar and the jar was shaken until the slurry appeared to be homogenous. The mixture was then allowed to set for a few hours with occasional shaking. The jar was tightly sealed.

Preparation of the Column and Presaturator

Care had to be taken in preparing the GLC column to be sure that the number of moles of liquid in the column, W_L^o, was precisely known.

The column was made by installing the proper fittings on a ten inch piece of stainless steel tubing. The column was bent into a semi-circle shape with a five inch diameter. This shape was convenient for weighing, filling, and mounting the column in the liquid bath. The column was thoroughly cleaned in the ultrasonic cleaner, rinsed with ethanol and dried. The column was weighed and recleaned. When the column weight did not change by more than 0.1 mg., the procedure was stopped.

The column was then weighed with a small amount of glass wool (0.03 gm) and the weight was recorded. The column was placed in a vise. The packing was poured into the column with the aid of a funnel and some tygon tubing. A mechanical vibrator was placed on the column to aid in the settling of the packing. When the column was full, the ends were plugged with the weighed glass wool. The filled column was then quickly weighed and connected into the system. The filling and weighing of the column was done quickly to allow as little as possible of the solvent to evaporate from the column. Tests indicated that liquid lost from the column was negiligible over a three to four minute interval. The difference in weights of the column before and after packing represented the weight of the column packing, the solid plus the liquid.

To find W_L^o, the exact amount of liquid in the column must be known. The weight of liquid was found by first cleaning and thoroughly drying a one ounce crucible. The empty crucible was weighed and then reweighed after filling it with some of the packing material from the same jar that was just used to fill the column. The crucible was then placed on a hot plate and the solvent was boiled from the solid. The dry solid was allowed to cool and then weighed. The dry solid was weighed until the weight agreed within 0.1 mg. with the previous weighing to be sure that the crucible had cooled to room temperature.

The liquid loading was calculated using the relationship

$$\text{WFL} = \frac{(\text{Solid weight wet-solid weight dry})}{(\text{Solid weight wet-crucible weight})} = \frac{(\text{SWW-SWD})}{(\text{SWW-CW})} \qquad (5\text{-}1)$$

where

WFL = weight fraction liquid

solid weight wet (SWW) = solid + liquid + crucible

solid weight dry (SWD) = solid + crucible

crucible weight (CW) = crucible

The number of moles of liquid in the GLC column, W_L^o, can be calculated using

$$W_L^o = \frac{(\text{PCF} - \text{PCE})\ (\text{WFL})}{\text{LMW}} \qquad (5\text{-}2)$$

where

PCF = weight of packed column full

PCE = weight of packed column empty

LMW = liquid molecular weight

The weighing and drying of the packing was done very soon after the column was packed to assure that the packing being dried is the same as the column packing. Although negligible change occurred in six hours with the jar tightly sealed, the crucible was filled soon after the column was packed.

Upon completion of an isotherm, the GLC column was isolated from the system (the bypass opened) and the bath was lowered from around the column. The column was given time to warm to room temperature (usually until the next morning, 7 or 8 hours), and then was removed and weighed. The amount of weight loss of liquid in the column was recorded.

The column was changed after most runs. Occasionally, if less than 0.5% of the liquid was lost, the column would be replaced quickly and used for another isotherm. In general, columns were most often used twice for $-40^{\circ}F$ and $-20^{\circ}F$ runs, where the solvent vapor pressure is lowest.

The presaturator was installed in the carrier gas upstream of sample valve. The purpose of the presaturator was to saturate the carrier gas with solvent, thus minimizing the liquid losses in the GLC column. The assumption was made in the theoretical derivation of the equations that the number of moles of liquid on the column is known. If the liquid slowly bleeds off the column, it will cause an error in the calculated K-values. The presaturator was used to minimize this loss.

The procedure for preparing the presaturator was similar to preparing the GLC column. A 48-inch piece of stainless steel tubing and its fittings were thoroughly cleaned. A slurry was made up. Since the amount of liquid need not be known, the slurry was made as wet as possible so that it still poured easily and was not extremely gummy ($\cong$ 35-40% liquid). The slurry was poured into the presaturator and vibrated to ensure a homogenous column. The presaturator was then coiled into a five inch diameter circle and mounted in stream.

The presaturator could be used for both a -40^{o}F and -20^{o}F run, but was generally refilled for the 0^{o}F and 20^{o}F runs. Note that the presaturator could not be bypassed. Thus, if any difficulties occurred that caused a great deal of delay while the equipment was on stream, the presaturator would continue to dry. Long delays are considered to be a minimum of ten hours. One to two hours were not critical.

Temperature and Pressure Measurement

Ambient temperature and pressure had to be measured and system temperature and pressure had to be controlled and measured.

Ambient temperature was measured with a mercury in glass thermometer which was mounted on the side of the main equipment frame, approximately a foot from the bubble flow meters. The temperature was measured and recorded to within 0.1^{o}C just after each sample was run.

Ambient pressure was measured with a mercury barometer which had 0.1 mm Hg divisions. The barometer was read at least once an hour. The readings were extrapolated for samples run between readings.

A thermopile made of eight copper-constantan thermocouples was used to read the bath temperature. (See Appendix E for the calibration of the thermopile). The system temperature was checked every 10-15 minutes.

The system pressure was measured with a Heise bourdon tube pressure gauge at the entrance of the GLC column. The accuracy of the gauge was 0.1% of full scale (3000 psia).

The system pressure was set with the Mity-Mite pressure regulator. Pressure drop along the column was negligible. The system pressure was reduced to atmospheric with a throttling valve after exiting the column. The pressure at the detector and at the flow bubblemeter was atmospheric.

Flow Rate Measurement

Only the flow rate of the sample stream was measured accurately. The flow rate of the reference stream was set so that it was close to the sample stream flow rate.

The sample stream bubble meter had been calibrated with water. The time required for a bubble to rise between two predetermined marks was measured with a stopwatch which had a 10 second sweep and could be read within 0.02 seconds. The runs could be reproduced within 0.05 seconds.

The flow rates were not changed during a run. The flow rate was measured before and after runs with very short elution times, not during the runs. For samples with longer elution times, the flow rate would be measured while the sample was traveling through the column. The bubblemeter times would sometimes vary by 0.1 seconds during a 20 minute elution time. The variance was due to slight drifts in system pressure. The flow rates varied from 45 cc/min at low pressures to about 150 cc/min at 1500 psi.

The expansion valve was heated to prevent condensation of the column solvent in the throttling valve. Difficulties were encountered when the valve was not heated. The condensate would plug the valve, restricting the flow area. The flow rate would slowly decrease. The plugging was a problem only at high pressure.

Sample Trapping and Injection

The high pressure gas cylinders containing the solute gases were connected with a manifold. Each bottle had its own pressure regulator, except H_2S. Two valves and a pressure gauge (stainless steel) were used to regulate the size of the H_2S sample. The outlet of the sample system was vented to a fume hood. The sample system could be evacuated with the vacuum pump. The general procedure was as follows (see Figure 1).

1. With valves 7 and 8 closed, and valve 19 open, the system was purged with the solute gas. Valves 9, 10, and 18 are always kept closed except when trapping H_2S samples. Purging consisted of pressuring the system up to 150 psia and then dropping the pressure to atmospheric. The system was purged twice, then the solute gas was allowed to flow continuously through the system for ten to fifteen seconds. The sample valve was left open during the purging.
2. The sample system was pressured to the appropriate pressure (25-200 psia). Pressure gauge H was used to read the sample pressure.
3. The sample valve was closed, trapping the sample.
4. The sample system was then purged with methane to flush out most of the solute gas between valves 12 and 13. The system does not need to be thoroughly cleaned of solute gas.
5. Valves 12 and 13 were closed. Valve 7 was slightly opened to allow the volume around the sample valve to come to system

pressure without greatly upsetting the pressure in the rest of the system. Valve 8 was opened and valve 19 was closed.

6. Any traces of solute which were not removed by purging were now given time to elute from the system, or at least, they were ahead of the actual solute sample far enough that it did not affect the solute sample. In general, the solute was not injected until the traces of solute showed up on the strip chart recorder. When samples were to be passed through the GLC column, the column was bypassed until the traces showed up on the recorder. Only then was the GLC column put in the main stream.
7. The sample valve was opened and the stopwatch started.

Since purging the system with H_2S twice was inappropriate, a somewhat different procedure was used with the H_2S.

1. Valve 11 was closed to keep H_2S from contaminating the pressure regulators. Valve 14 was kept closed since the sample pressure was read on the stainless steel pressure gauge J. Values 7 and 8 were closed.
2. The system was evacuated back to valve 9 by opening valve 16 (close 15).
3. The H_2S cylinder was opened and the volume between valve 9 and the cylinder was filled to cylinder pressure ($\simeq$ 350 psi).
4. Valve 9 was opened slightly, and the volume between valve 9 and valve 16 was filled to the appropriate pressure. The sample valve was closed.

5. Quickly, valve 9 was opened fully and valve 15 was slightly cracked to bleed the H_2S into the NaOH rinse (valve 17 was not open).
6. The methane cylinder was opened and the manifold filled to 150 psia. When the H_2S pressure dropped to atmospheric pressure in the sample system, valve 11 was slightly opened and the system was purged with methane. Care had to be taken that the NaOH rinse was not blown out of the bottle. After a few minutes of purging valves 11 and 15 were closed and the system was evacuated with the vacuum pump.
7. Valves 12 and 13 were closed. The rest of the procedure was the same as for the other samples.

Recording Sample Times

The retention time, t_{Ri}, is the time required for the sample to elute from the sample valve to the detector. The sample was considered to have reached the detector when the deflection (the peak) on the strip chart recorder reached its maximum. The exact maximum could not be seen visually, especially at high pressures, where the top ½ inch of a 6 inch peak would sometimes stretch out for one to two minutes.

The following method was used to find the exact time to the peak maximum. The recorder paper had a vertical line every 0.5 inches. As the pen passed over a selected vertical line, the stopwatch was stopped and the line marked. The line that was chosen was the first one passed by the stripchart recorder needle after the peak maximum came out. For peaks that were slow coming out, the line that seemed to be nearest the maximum was chosen. A ruler was then laid horizontally across the peak and the midpoint of the peak was found at several points between the baseline and the maximum height of the peak. The midpoints should all lie on the same vertical line, but due to a small amount of tailing they did not. Extrapolating from these midpoints to the top of the peak gave position of the peak maximum. Knowing the chart speed and the distance from the peak maximum to the line at which the stopwatch was stopped, the exact elution time, t_{Ri}, was calculated. The timer was stopped at a vertical line as near the peak maximum as possible to minimize any error that might be caused by faulty chart speed or poorly spaced chart paper.

On-Stream Procedure

This section describes the general procedure used in taking data for an entire isotherm. The procedure described in the previous sections will be joined together. All isotherms for one solvent were run before a new solvent was begun. The $-40^{o}F$ isotherm was run first, then $-20^{o}F$, $0^{o}F$ and $20^{o}F$. For a given isotherm, the lowest pressure, 100 psia, was run first, 1500 psia was run last. For each pressure eight samples were injected, four blanks, that is, the GLC column was bypassed, and then four samples were passed through the GLC column. They were usually run in the following order: He, Ar, CO_2, and H_2S. All isotherms for one solvent were completed before runs with a new solvent were begun.

Column packing for the GLC column and presaturator were made up separately and allowed to set overnight. The GLC column and presaturator were thoroughly cleaned and allowed to dry overnight.

Runs were generally begun in the morning so that an entire isotherm could be completed without stopping ($\tilde{=}$ 16 hours). The temperature of the constant temperature bath was checked the first thing in the morning. Any overnight drift in temperature was corrected. The presaturator was filled with packing and connected into the system. A helium pressure of 1500 psia was applied to the system and the system was checked for leaks. The liquid temperature bath was raised up around the GLC column and presaturator. The helium was bled off the system and carrier gas flow was begun. The system pressure was set at 100 psia with the Mity-Mite pressure regulator and the flow rate was adjusted to about 45 cc/min.

The carrier gas was allowed to flow through the GLC column for a few minutes to sweep out any air and helium in the column, but then the GLC column was blocked out of the system and the bypass was opened (valve 5). The system flow rate and the detector took about 30-60 minutes to reach steady state. The current setting to the detector filaments was 4.5 miliamperes. The attenuator was set on 64 for the 100 psia runs. During this time, the crucible was weighed and a sample of the GLC column packing was weighed. The drying of the sample was begun. The dry solid was weighed sometime later when the crucible had cooled.

A helium sample was trapped and the helium traces were allowed to pass through to the detector. The ambient temperature and pressure were recorded. This could be done at about the time the flow rate and recorder were lining out. The system temperature was checked for drift. The flow rate was recorded, the helium sample injected, and the retention time was recorded after the peak came out. An argon sample was then trapped, the traces allowed to pass, the flow rate recorded, and then it was injected. The procedure was continued for CO_2 and H_2S. Note that the GLC column was being bypassed for these four samples.

The bypass was now closed and the GLC column opened to the flow stream. The four samples were run again. The bypass was opened when the traces of solute were being flushed before sample injection. The ambient pressure was recorded after the four samples.

Upon completion of the above eight sample injections, the system pressure was raised to 200 psia and the above procedure repeated, the GLC column was closed off and allowed to dry and warm to room temperature overnight. The next morning the GLC column was weighed to check for liquid loss.

Classical Windowed Cell Experiment

The operating procedure for preparing for and taking the experimental data will be discussed in this section. Two types of data were taken with the windowed cell apparatus. First data were needed to calibrate the thermistor, that is, to find response factors for each component. For these runs the exact composition of the mixture must be known. The second type of data taken consisted of the K-value data. For these runs the exact composition of the mixture need not be known. The following topics will be discussed in this section: (1) preparation of mixtures, (2) sampling, (3) sample injection and chromatographic run, (4) calibration of detectors, and (5) measurement of K-value data.

The first three items above apply to both the taking of calibration data and K-value data. The fourth and fifth items explain the two procedures and the differences between them.

Preparation of Mixtures

This section contains a discussion of the procedure for preparation of a mixture for a calibration run, one in which the quantity of each component is known precisely. For K-value measurement runs the exact amount of each component in the mixture need not be known, although the mixture was usually made so that it had approximately a predetermined composition. The mixtures contained methane (C_1), hydrogen sulfide (H_2S), carbon dioxide (CO_2), and n-octane (C_8). The procedure was as follows.

The windowed cell was thoroughly cleaned and dried. With the piston pushed forward (small volume) the cell was purged with methane several times. The windowed cell was then filled with methane to a predetermined volume and pressure. Two to three hours were allowed for the methane to reach cell temperature (approximately room temperature). The cell pressure was occasionally adjusted so that it was kept within 2 psia of the charging pressure. The number of moles of methane in the cell was calculated using the cell volume, temperature, pressure, and compressibility data from the literature (39).

The H_2S, CO_2, and C_8 were added to the system as liquids by means of a screw pump. The H_2S and C_8 were charged at 1000 psia (the pressure most often used in charging the methane). The CO_2 was charged at 500 psia or 1500 psia, depending on the size of the charge and total amount of mixture in the cell. The number of moles of each component was calculated from the liquid densities at the charging temperature and pressure. Liquid densities were obtained from the literature (40, 45).

Sampling

The method used in sampling is described by Yarborough and Vogel (50). Slight variations in the procedure will be described below.

1. The sample valve, purge valve, and short pieces of tubing were brought up to a temperature above the system temperature for vapor samples to avoid condensation of the vapor samples and brought to system temperature for liquid samples to avoid flashing the liquid.
2. Two valves were used in the sampling. An 8 μl valve was used for the liquid samples. A 20 μl valve was used for vapor samples.
3. In general, samples were taken in the following order: vapor, liquid, liquid, vapor. After the first vapor and liquid samples were taken and while the samples were being run through the chromograph, the cell was rocked, mixing the contents. The final liquid and vapor samples were then taken. A visual check was made of the size of the peaks recorded on the strip chart recorder to see if any of the four samples were visibly bad. If so, they were repeated.

Sample Injection and Chromatograph Runs

The chromatograph system consisted of the carrier gas flow stream, two chromatograph columns in series with the two detectors (hydrogen flame ionization, HF, and thermal conductivity, TC), the strip chart recorders and the Infotronics unit.

After a sample had been trapped in the sample valve, the sample valve was disconnected from the windowed cell and reconnected to the chromatograph system. The sample valve was placed in a heating block. The heating block was used to heat (75-100°C) the sample valve, thus insuring that the liquid samples were in a vapor state. This would allow the entire sample to go directly into the carrier gas stream when the sample valve was opened. The sample valve dead space was purged with helium. The switching valves (see Figure 3) were then set so that the sample valve was in the main carrier gas flow stream.

The sample valve was opened, thus injecting the sample into the stream. Both strip chart recorders and the Infotronics unit were turned on. In general, the peaks came out in the following order: (1) methane (HF -1:15), (2) methane (TC-2:30), (3) carbon dioxide (TC-3:15), (4) hydrogen sulfide (TC-4:30), and (5) n-octane (HF-5:00). The notation in parenthesis indicates which detector the component passed through and the time from injection in minutes and seconds, where 1:15 is one minute 15 seconds. At about 7:30 the n-octane peak would show up on the TC detector. The strip chart recorder gave a visual record of what was happening in the chromatograph system, while the Infotronics unit recorded on tape a signal proportional to the peak area. The tape was played back at a later date. A digital integrator converted the tape output to "number of counts," which was directly proportional to peak area.

Calibration of Detectors

The chromatograph detectors must be calibrated so that the detector response can be converted into "moles of a component." The calibration procedure was the following.

A mixture was made in the windowed cell. The pressure was raised to 5500 psia and the cell rocked for three to four hours to insure that the mixture existed as a single phase. Four samples were taken from the cell, two from the top and two from the bottom. If the samples all had very nearly the same composition, the mixture was considered to have been in single phase. If the top and bottom compositions were not equal the cell was rocked for a longer period of time. Four more samples were taken. This procedure was continued until the mixture was in a single phase. In this work, the series of four samples never had to be taken more than twice.

The method of relative response was used to calculate the response factors for the two detectors (see Chapter III). The component response relative to the methane response was obtained for CO_2, H_2S, and n-C_8 on the thermal conductivity detector and for n-C_8 on the hydrogen flame ionization detector.

K-value Data

The general procedure used in taking the K-value data is discussed in this section. The overall procedure incorporates all the above subsections except that concerning the calibration of the detectors.

The cell was charged with mixture 6 (see Table XVI). All the K-value data were taken using this mixture. The cell was not recharged between isotherms.) The mixture was made at this composition so that the H_2S and CO_2 mole fractions would be relatively small ($\cong 0.10$). Six moles of mixture were made up because this amount fit two criteria which made easier operation of the windowed cell. Too small of a charge is difficult to pressurize into the single phase region because the windowed cell volume can be decreased to only a given minimum amount. On the other hand, too large a charge cannot be dropped to 200 psia for the needed data, that is, the windowed cell volume can be increased only to a given maximum amount.

After the mixture reached the single phase region at 5500 psia and the calibration mixture run, the system was cooled down and the pressure was dropped to about 1500 psia. Since the oil on the dead weight gauge side of the diaphragm contracted while the system cooled down, the system has to be checked occasionally so too great of a pressure difference did not build across the diaphram. Once the cell reached $0^{o}C$, the cell was rocked for an hour at 1500 psia. The pressure was then gradually (30-60 minutes) lowered to 1000 psia while the cell was continually rocked. After reaching 1000 psia rocking was continued for 30 minutes.

The cell was stopped in the level position. The system temperature and pressure were recorded. The system pressure was raised about 10-20 psi again. Two samples were taken, one liquid and one vapor. The cell was rocked while the two samples were run through the chromatograph. Two more samples were then taken, liquid, then vapor. After running the latter two samples, the pressure was gradually dropped to 800 psia. The procedure was continued through 200 psia.

Upon completion of the $0^{o}C$ isotherm, the temperature was lowered to $-20^{o}C$ and the system pressure raised to 1500 psia. The cell was rocked for an hour, then the pressure was gradually lowered. The above procedure was repeated for the $-20^{o}C$ isotherm.

CHAPTER VI

EXPERIMENTAL RESULTS

During this study, experimental K-value data were obtained for CO_2 and H_2S in several hydrocarbon systems over a range of temperatures and pressures. The experimental results are presented in tabular and graphical form in this chapter. Appendix I contains the raw experimental data from which the results reported here were obtained.

The data were taken on the following systems at the following conditions:

Chromatographic K-value data:

(a) carbon dioxide - methane - n-heptane
(b) hydrogen sulfide - methane - n-heptane
(c) carbon dioxide - methane - toluene
(d) hydrogen sulfide - methane - toluene
(e) carbon dioxide - methane - methylcyclohexane
(f) hydrogen sulfide - methane - methylcyclohexane
(g) carbon dioxide - methane - n-octane
(h) hydrogen sulfide - methane - n-octane

K-value data from windowed cell:

(i) hydrogen sulfide - carbon dioxide - methane - n-octane

Systems (a) through (f) were run at temperatures of $-40^{\circ}F$ to $20^{\circ}F$ ($20^{\circ}F$ intervals) and eight pressures from 100 to 1500 psia. Systems (g) and (h) were run at $0^{\circ}C$ and $-20^{\circ}C$ at six pressures from 100 to 1000 psia.

Although the K-value data for CO_2 and H_2S in methane - n-octane were not an original goal of this work, they were taken in order to confirm the reliability of the experimental technique as discussed in the following chapter. The experimental K-values of the systems (a) through (h) listed above are given in Table II. The results of the windowed cell work, liquid and vapor mole fractions and K-values for CO_2, H_2S, methane, and octane, are given in Table III.

Figures 4 through 6 illustrate the K-values of systems (a) through (f). Isothermal plots of the six systems are given. Figures 7 through 12 show isobaric plots of K-values as a function of reciprocal temperature.

TABLE II

CHROMATOGRAPHIC K-VALUES FOR CARBON DIOXIDE (HYDROGEN SULFIDE) AT INFINITE DILUTION IN FOUR METHANE+SOLVENT BINARY SYSTEMS

Pressure, psia	Temperature			
	-40°F	-20°F	0°F	20°F
		Methane + Heptane		
100	4.62(0.968)	5.93(1.348)	7.00(1.687)	8.43(2.164)
200	2.42(0.534)	3.09(0.726)	3.63(0.918)	4.20(1.153)
400	1.37(0.328)	1.66(0.425)	2.05(0.543)	2.32(0.659)
600	1.02(0.267)	1.22(0.339)	1.49(0.425)	1.63(0.507)
800	0.88(0.250)	1.05(0.311)	1.23(0.381)	1.40(0.444)
1000	0.82(0.260)	0.94(0.299)	1.12(0.362)	1.23(0.410)
1250	0.84(0.285)	0.89(0.314)	1.03(0.362)	1.17(0.409)
1500	0.85(0.314)	0.91(0.351)	0.94(0.375)	1.07(0.408)
		Methane + Methylcyclohexane		
100	5.90(1.020)	7.52(1.408)	8.78(1.826)	11.36(2.454)
200	3.08(0.558)	3.79(0.742)	4.66(0.984)	5.45(1.257)
400	1.70(0.335)	2.06(0.437)	2.47(0.562)	2.96(0.707)
600	1.24(0.266)	1.49(0.343)	1.81(0.440)	2.15(0.550)
800	1.07(0.246)	1.27(0.306)	1.47(0.379)	1.70(0.467)
1000	0.96(0.245)	1.13(0.297)	1.35(0.359)	1.44(0.420)
1250	0.94(0.270)	1.07(0.305)	1.23(0.351)	1.33(0.408)
1500	0.99(0.321)	1.03(0.328)	1.18(0.368)	1.24(0.407)
		Methane + Toluene		
100	4.27(0.411)	5.78(0.626)	7.55(0.923)	10.71(1.246)
200	2.21(0.221)	2.94(0.331)	3.76(0.477)	4.63(0.653)
400	1.26(0.132)	1.61(0.194)	2.03(0.272)	2.45(0.365)
600	0.93(0.105)	1.21(0.152)	1.48(0.209)	1.83(0.277)
800	0.81(0.097)	0.96(0.133)	1.23(0.183)	1.47(0.238)
1000	0.77(0.099)	0.89(0.128)	1.09(0.173)	1.32(0.223)
1250	0.78(0.112)	0.89(0.134)	1.02(0.169)	1.14(0.213)
1500	0.82(0.128)	0.91(0.148)	1.00(0.178)	1.09(0.207)

TABLE II (Continued)

Pressure, psia	Temperature -40°F	 -20°F	 0°F	 20°F
		Methane + Octane*		
100	---	6.72(1.537)	9.37(2.442)	---
200	---	3.45(0.822)	4.86(1.276)	---
400	---	1.95(0.490)	2.65(0.723)	---
600	---	1.42(0.382)	1.89(0.550)	---
800	---	1.16(0.339)	1.52(0.467)	---
1000	---	1.03(0.319)	1.40(0.438)	---

* Temperatures in °C

TABLE III

K-VALUES OF CARBON DIOXIDE, HYDROGEN SULFIDE, METHANE, AND n-OCTANE FROM WINDOWED CELL

		-20°C			0°C		
Composition	Pressure (psia)	Vapor Mole Fraction Y	Liquid Mole Fraction X	K-Value K	Vapor Mole Fraction Y	Liquid Mole Fraction X	K-Value K
CO_2	200	0.0418	0.0116	3.59	0.0443	0.0085	5.22
	400	0.0398	0.0209	1.90	0.0428	0.0175	2.44
	600	0.0418	0.0295	1.42	0.0423	0.0234	1.80
	800	0.0411	0.0350	1.18	0.0417	0.0284	1.47
	1000	0.0405	0.0381	1.06	0.0410	0.0312	1.31
H_2S	200	0.0204	0.0255	0.798	0.0284	0.0226	1.25
	400	0.0177	0.0376	0.470	0.0257	0.0371	0.693
	600	0.0227	0.0579	0.392	0.0239	0.0444	0.538
	800	0.0214	0.0614	0.348	0.0224	0.0472	0.474
	1000	0.0194	0.0605	0.322	0.0201	0.0472	0.427
Methane	200	0.938	0.096	10.59	0.927	0.081	11.85
	400	0.942	0.185	5.44	0.931	0.165	5.70
	600	0.935	0.265	3.70	0.934	0.232	4.19
	800	0.937	0.331	2.91	0.936	0.302	3.09
	1000	0.939	0.390	2.48	0.938	0.362	2.73
Octane	200	0.000153	0.867	0.000177	0.000375	0.888	0.000423
	400	0.000093	0.756	0.000122	0.000286	0.781	0.000366
	600	0.000114	0.648	0.000176	0.000253	0.700	0.000361
	800	0.000125	0.573	0.000218	0.000162	0.623	0.000261
	1000	0.000554	0.512	0.00108	0.000731	0.560	0.00131

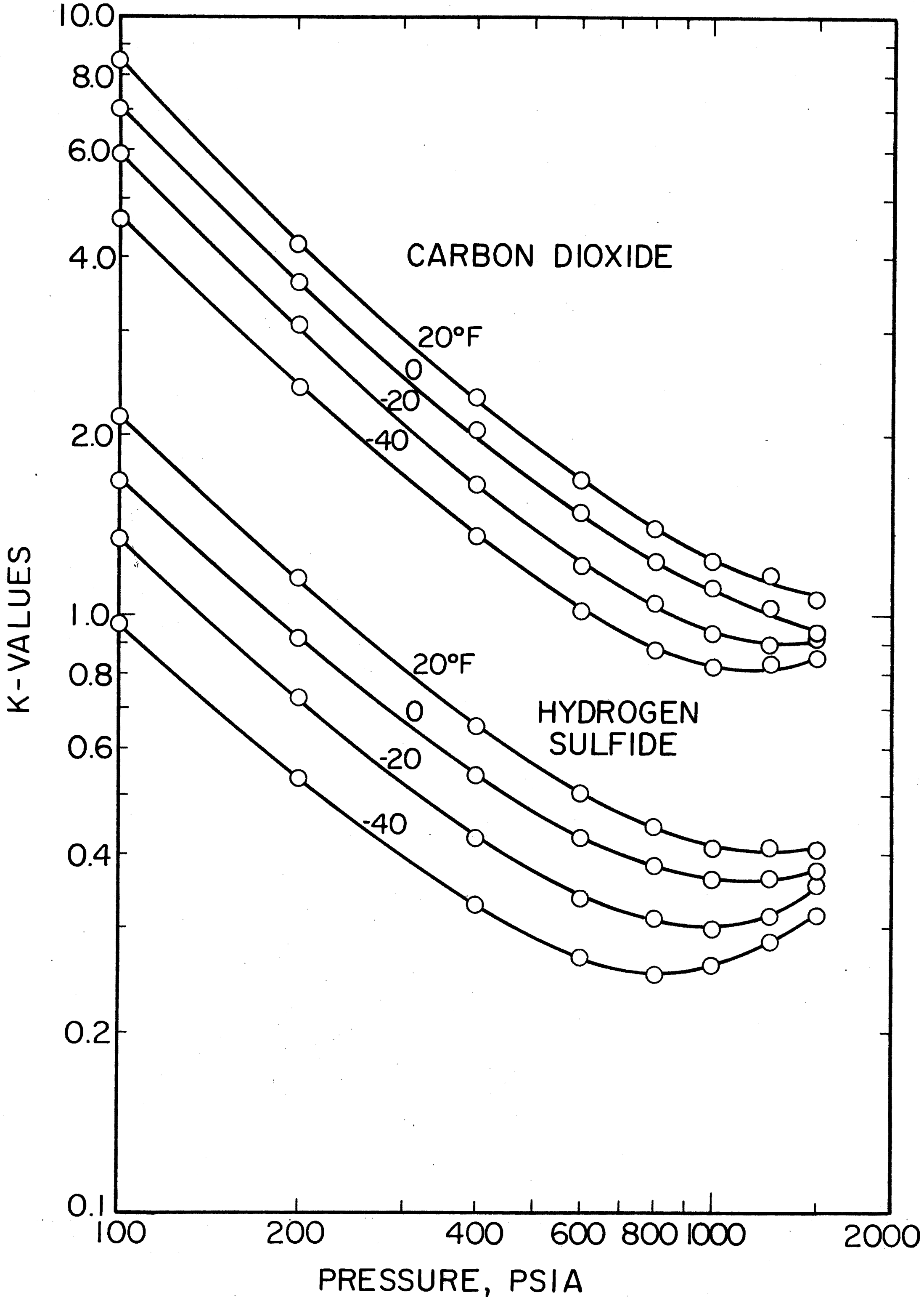

Figure 4. K-values for Carbon Dioxide and Hydrogen Sulfide at Infinite Dilution in the Methane+ n-Heptane System

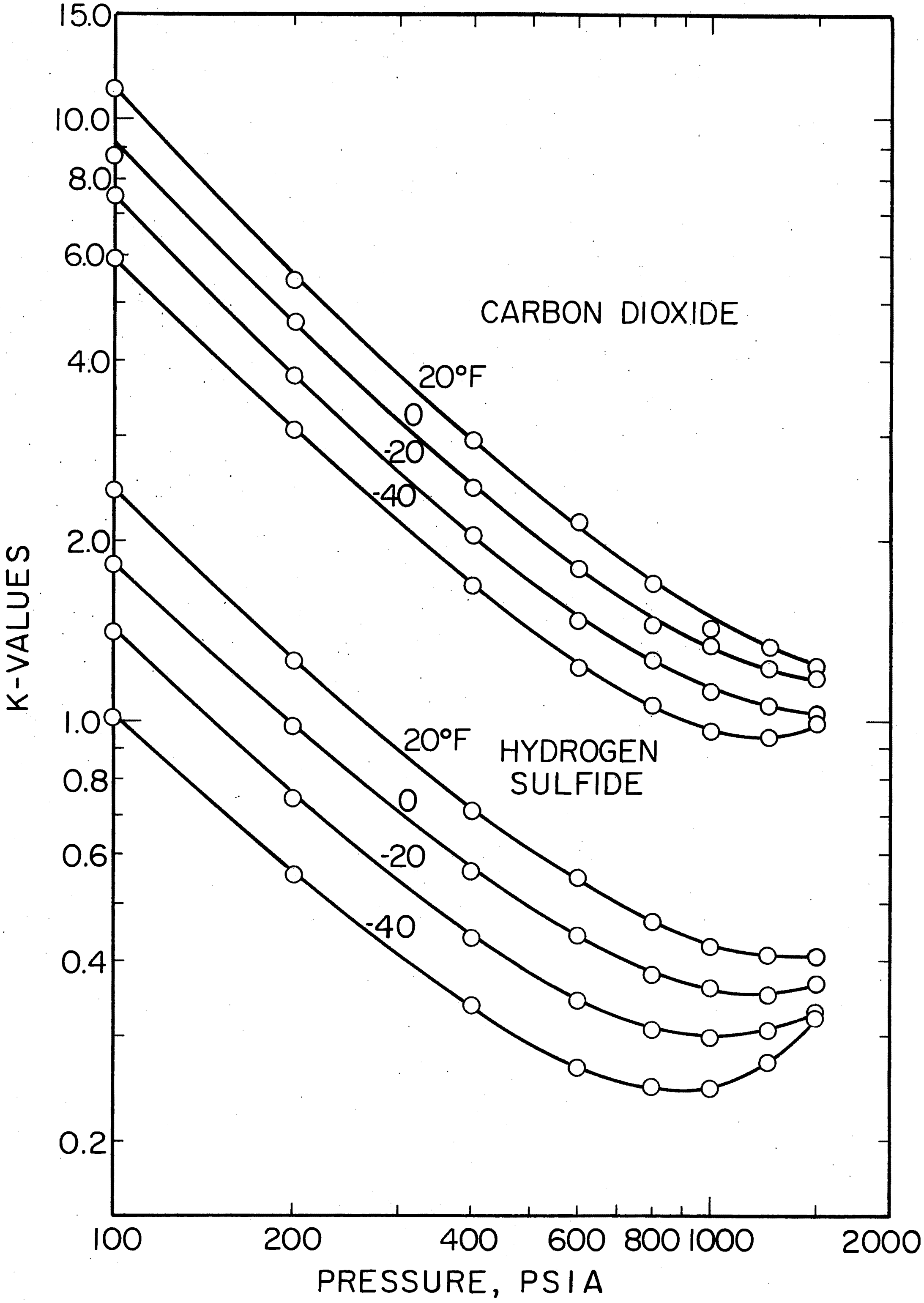

Figure 5. K-values for Carbon Dioxide and Hydrogen Sulfide at Infinite Dilution in the Methane+ Methylcyclohexane System

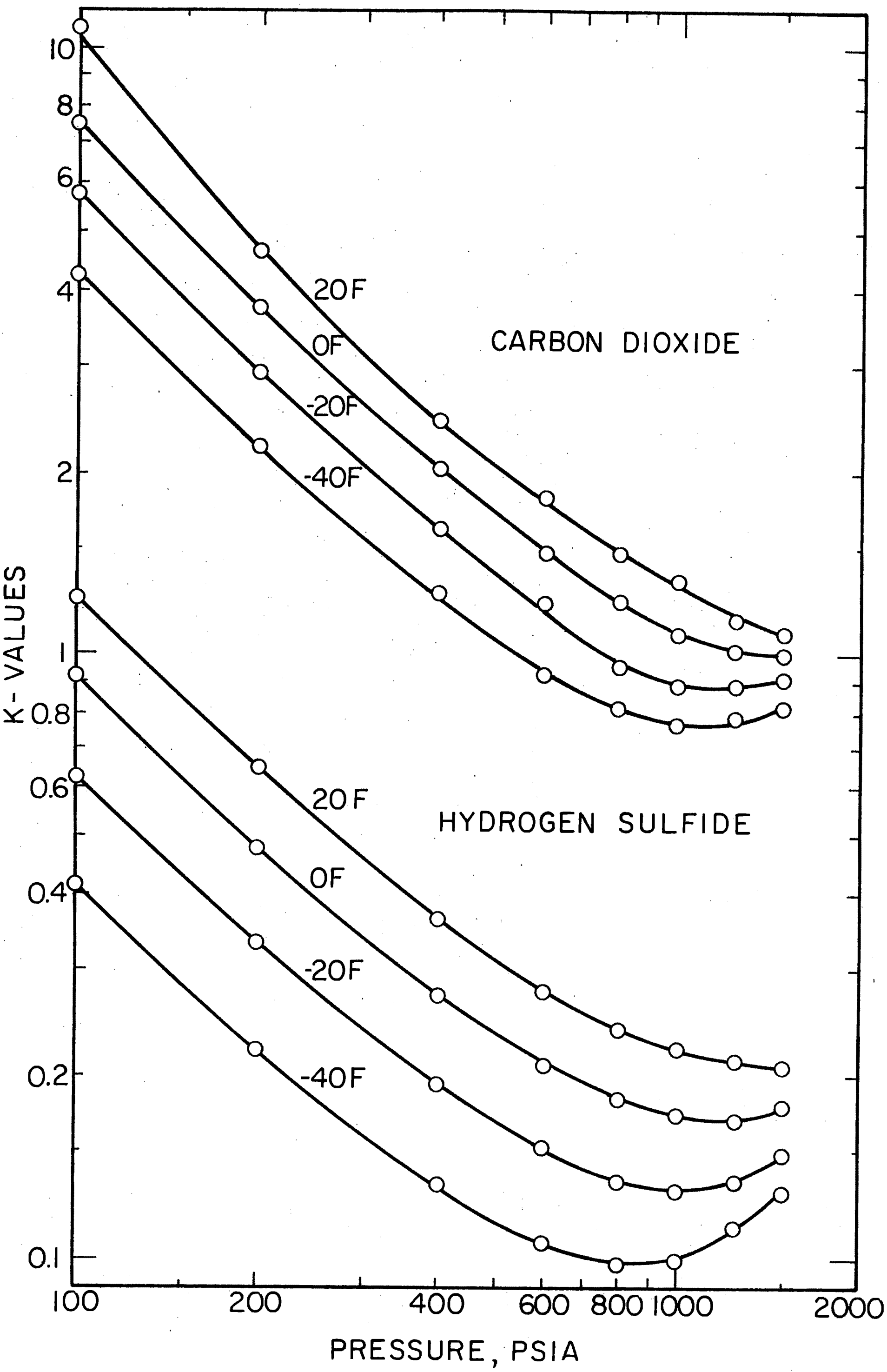

Figure 6. K-values for Carbon Dioxide and Hydrogen Sulfide at Infinite Dilution in the Methane+ Toluene System

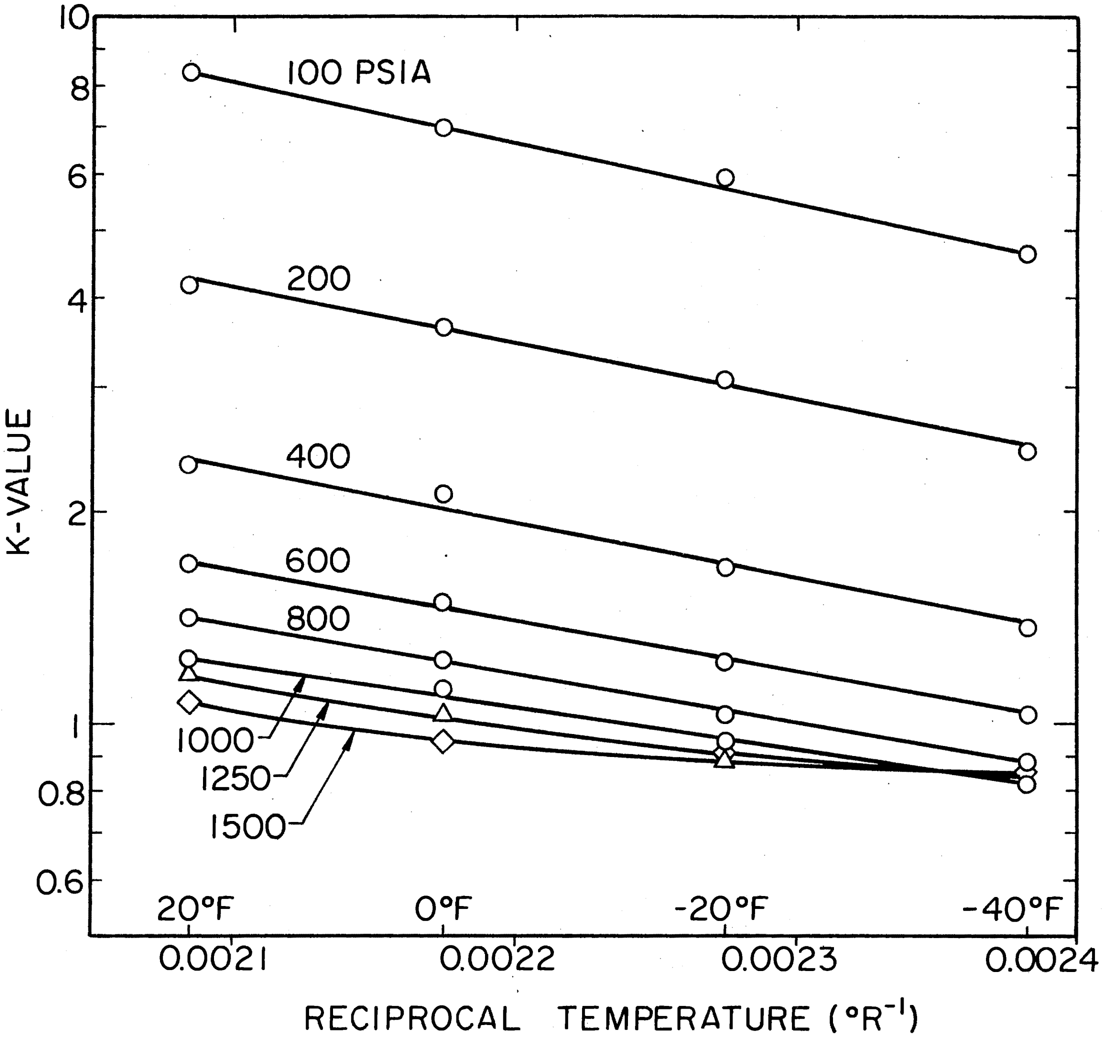

Figure 7. K-values for Carbon Dioxide at Infinite Dilution in the Methane+n-Heptane System as a Function of Reciprocal Temperature

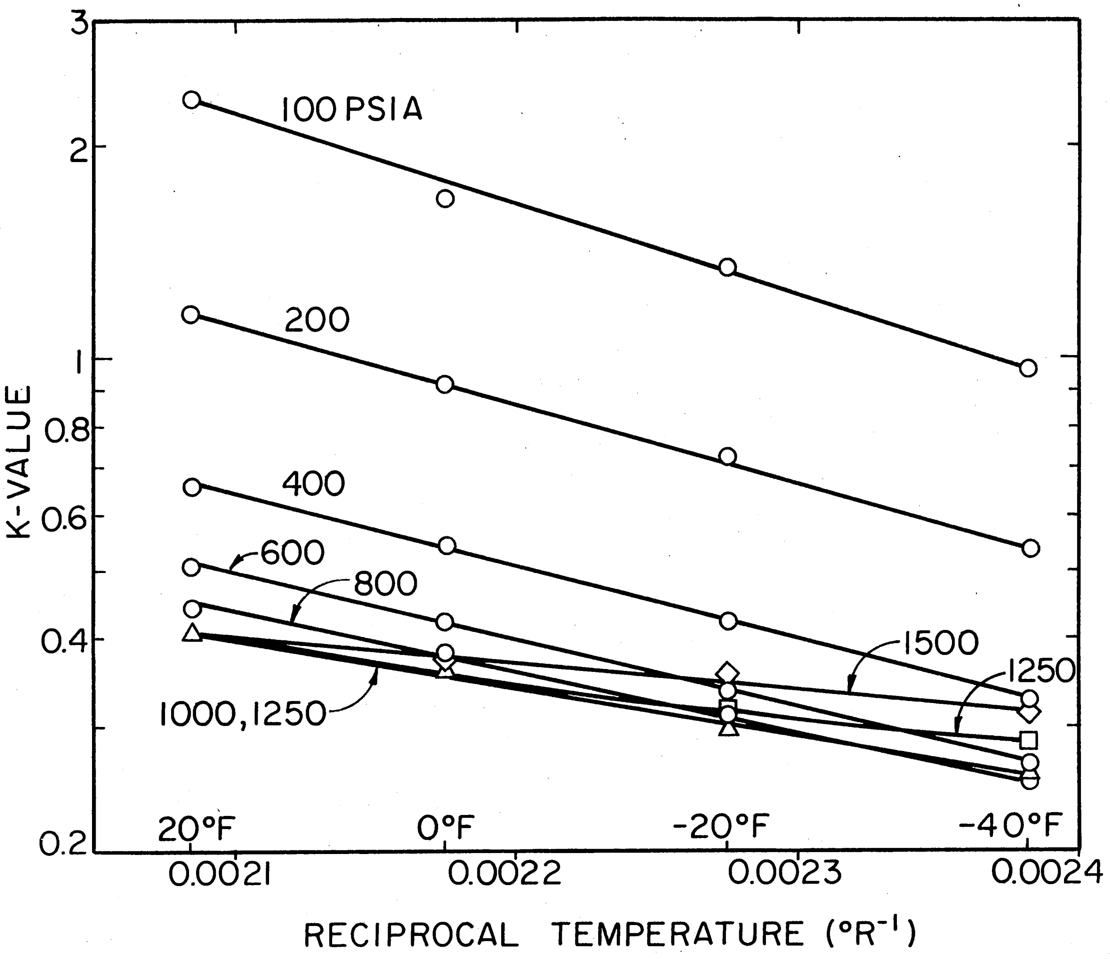

Figure 8. K-values for Hydrogen Sulfide at Infinite Dilution in the Methane+n-Heptane System as a Function of Reciprocal Temperature

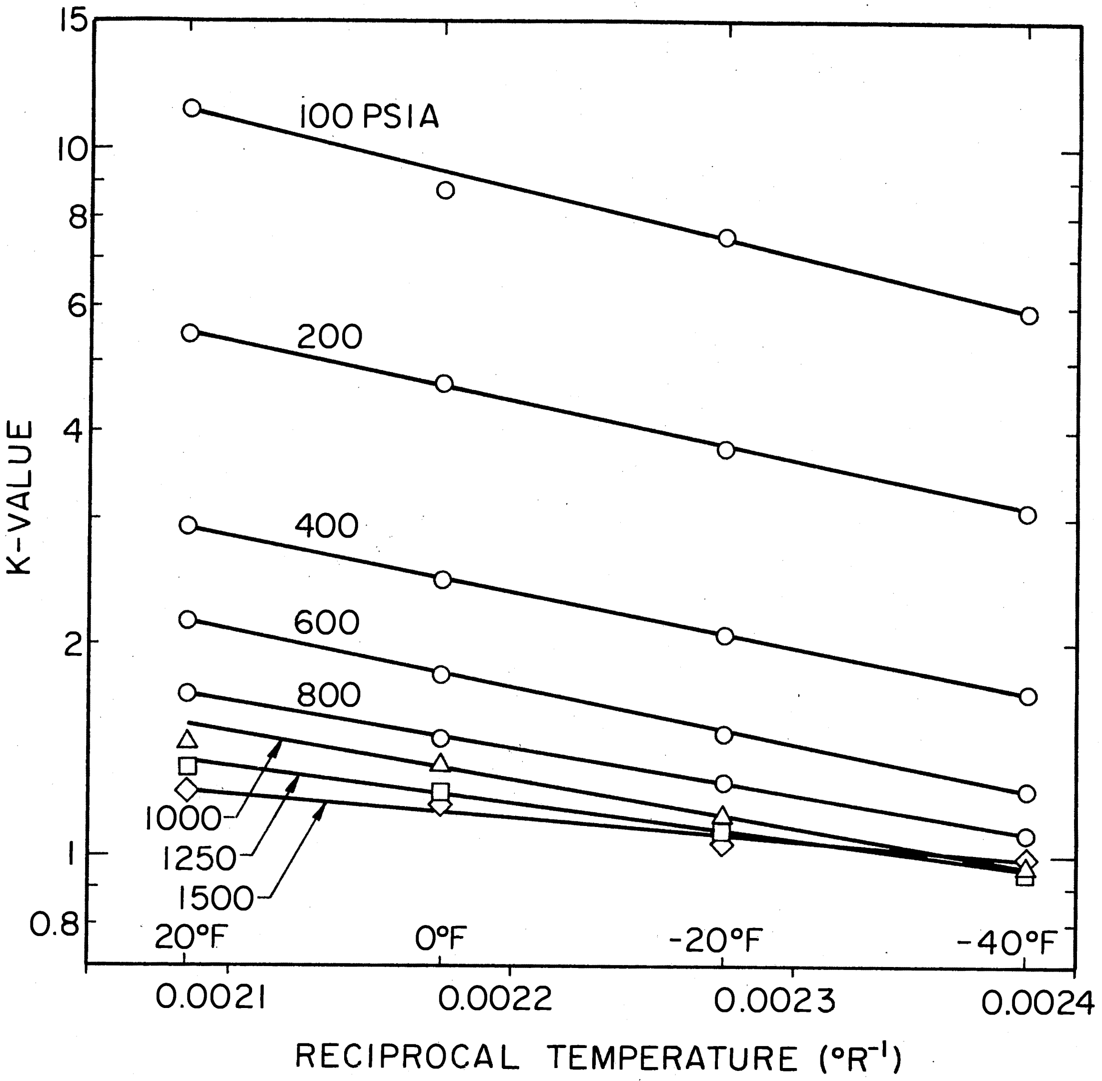

Figure 9. K-values for Carbon Dioxide at Infinite Dilution in the Methane+Methylcyclohexane System as a Function of Reciprocal Temperature

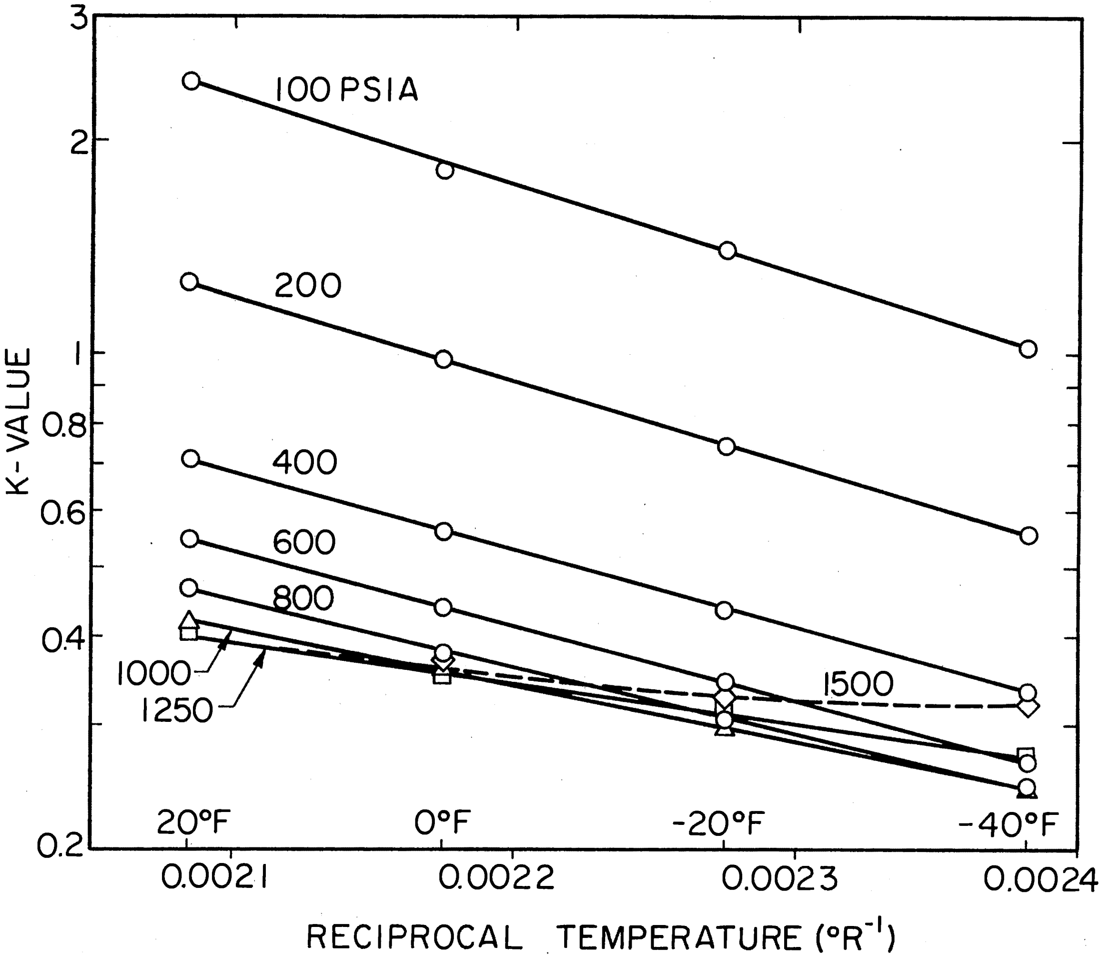

Figure 10. K-values for Hydrogen Sulfide at Infinite Dilution in the Methane+Methylcyclohexane System as a Function of Reciprocal Temperature

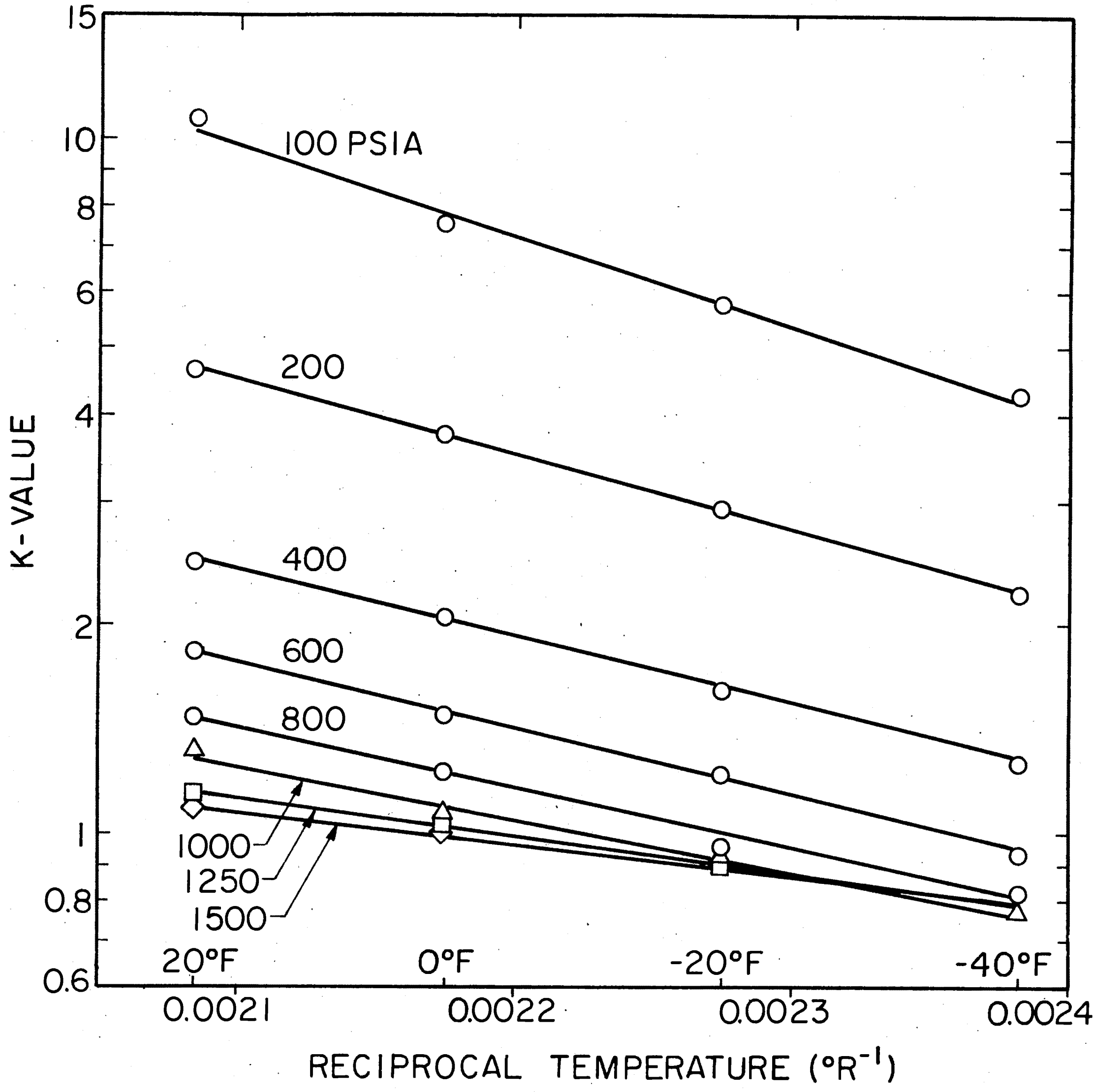

Figure 11. K-values for Carbon Dioxide at Infinite Dilution in the Methane+Toluene System as a Function of Reciprocal Temperature

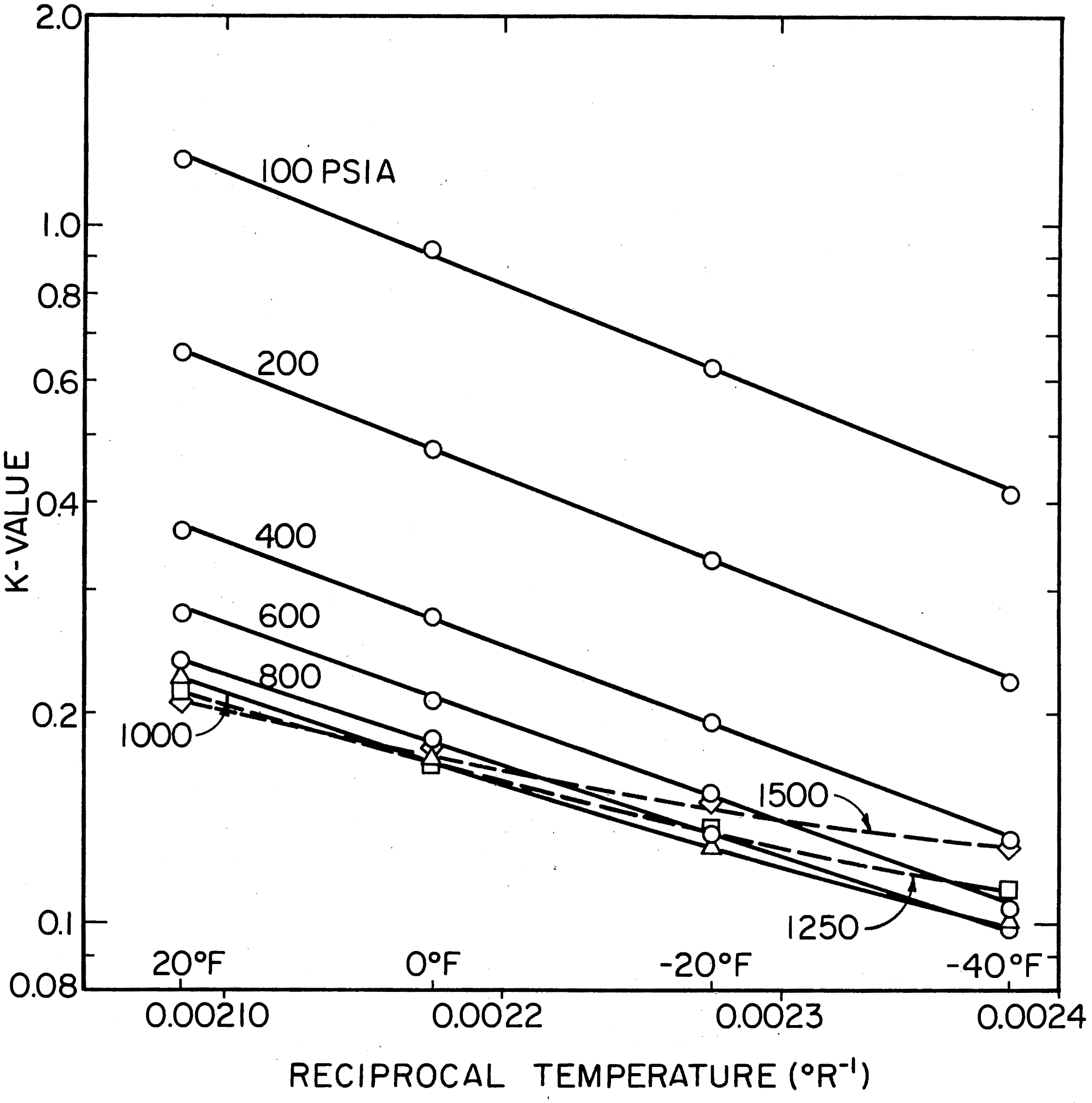

Figure 12. K-values for Hydrogen Sulfide at Infinite Dilution in the Methane+Toluene System as a Function of Reciprocal Temperature

CHAPTER VII

DISCUSSION OF RESULTS

This chapter presents the results of an examination, analysis and correlation of the experimental results which were cataloged in the previous chapter. The chapter begins with a discussion of the expected experimental uncertainty of this work. The results of this work, both windowed cell and chromatographic, are compared to available literature data on similar systems. The correlation framework described in Chapter III is tested using data from this work as well as data from the literature.

Error Analysis

The total expected error in any measured quantity is the sum of the contributions made by errors in measurement of each individual variable used to calculate the final quantity.

Details of the development of the equations necessary to calculate expected experimental uncertainty of the K-values measured by the chromatographic technique appear in Appendix A. The estimated uncertainties involved in the measurements of experimental parameters are listed in Table IV. The results of the error analysis are shown in Table V.

From Table V the experimental uncertainty is greatest for the lighter solute (CO_2) at higher temperatures and lower pressures. At

TABLE IV

ESTIMATED UNCERTAINTIES IN MEASUREMENT OF EXPERIMENTAL PARAMETERS

Experimental Measurement	Estimated Uncertainty
1. Measurements made on Mettler balance for calculation of weight of liquid on column (SWW, SWD, CW, PCF, PCE)	0.00020 gm
2. Solubility of methane in stationary liquid - χ_1	0.2%
3. Ambient Pressure - P_a	0.2 mmHg
4. Standard deviation in the calibration of bubblemeter - V_B	0.019 cc
5. Time required for volume of gas V_B to pass pass through the bubblemeter - t_B	0.05 sec
6. Ambient temperature - T_a	0.1°C
7. Retention times - t_{Ri}, t_{RHe}, t_{RAR}	0.6 sec ($2\frac{\text{inch}}{\text{mm}}$ chart speed) 0.3 sec ($5\frac{\text{inch}}{\text{mm}}$ chart speed)

TABLE V

ESTIMATED PERCENTAGE ERRORS IN EXPERIMENTALLY DETERMINED K-VALUES

Chromatographic Experiment

System	Conditions	CO_2	H_2S
C1-TOL	20°F, 100 psia	2.9	0.4
	-40°F, 1500 psia	1.0	0.5
C1-MCH	20°F, 100 psia	2.5	0.6
	-40°F, 1500 psia	0.6	0.4

Windowed Cell Experiment

Component	Conditions	
	0°C 200 psia	0°C 1000 psia
C1	3.2	2.0
C8	10.3	10.4
H_2S	6.3	5.8
CO_2	4.9	4.3

these conditions the retention time is smallest, thus the value ($V_{Ri}-V_g$) is smallest. Several authors (8, 24, 43, 46) have discussed the importance of determining V_g accurately.

Error analysis for the classical windowed cell indicates that an uncertainty of approximately 4.6% for CO_2 and 6.0% for H_2S is expected. Table V gives the results of the error analysis.

Appendix A discusses the development of the equations used in the error analysis for both the chromatographic experiment and the windowed cell experiment.

In an effort to access experimentally the uncertainties in the calculated K-values from the chromatographic experiments, three separate and complete runs were made for the K-values of CO_2 and H_2S in the methane-octane system at 0^oC. For each run, all preparations and operations were done separately from those of any other runs; that is, separate columns and separate batches of column packing were employed for each run. Figure 13 and 14 illustrate the experimental scatter among these three separate runs. The greatest deviation was less than 4% while the average deviation from the average was only approximately 2%, which was slightly larger than the calculation expected experimental uncertainty. The conclusion is drawn that there are some unknown factors other than random experimental measurement.

Discussion of V_g

In the present work the free gas volume, V_g, was calculated by measuring the retention volumes of two noble gases, helium (He) and argon (Ar), and extrapolating these retention volumes as a function of the polarizability linearily back to a polarizability of zero. At zero polarizability the gas was assumed to be unretained.

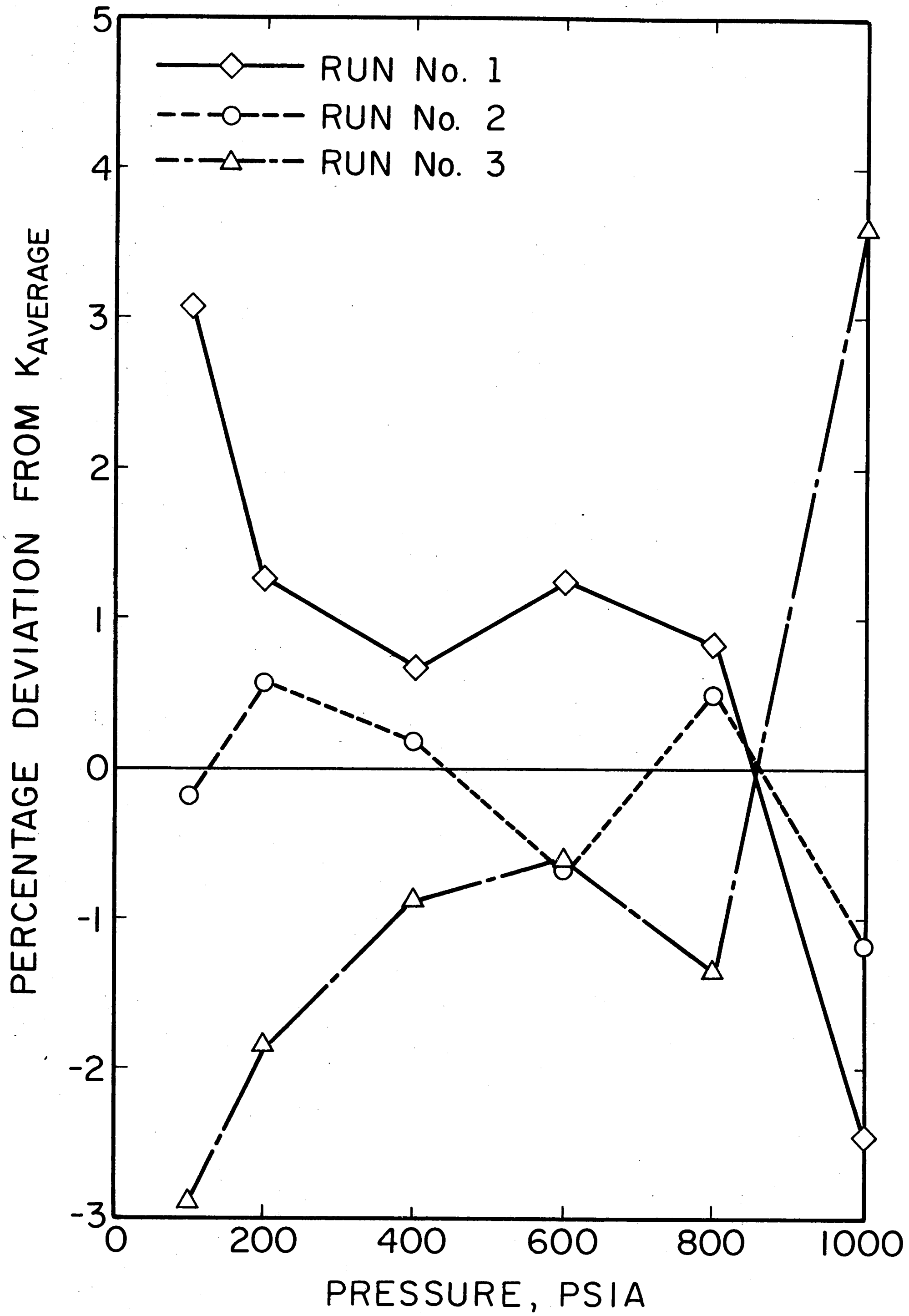

Figure 13. Consistency of Carbon Dioxide K-values for Three Runs at 0^oC in the Methane+n-Octane System

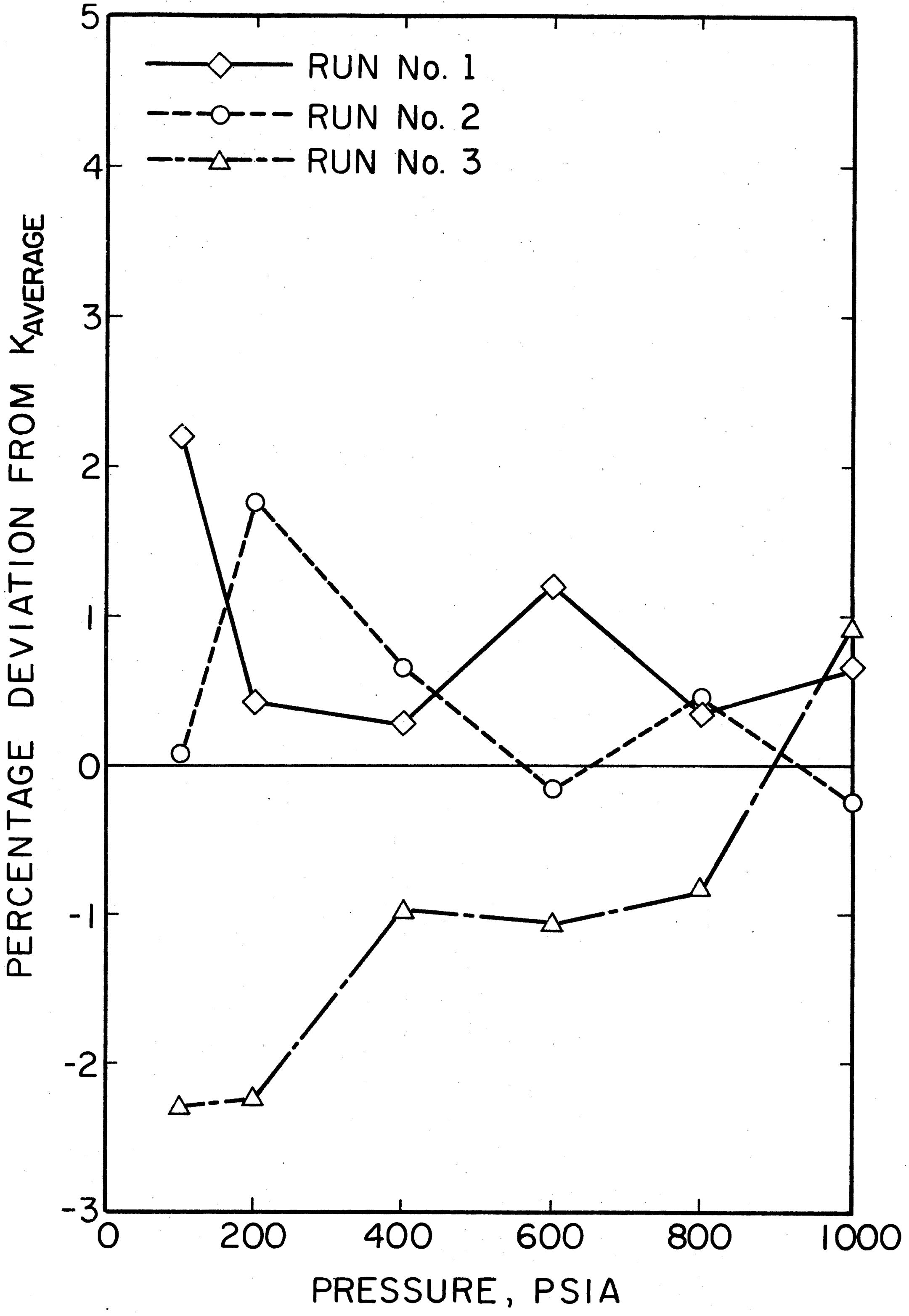

Figure 14. Consistency of Hydrogen Sulfide K-values for Three Runs at $0^{o}C$ in the Methane+n-Octane System

The identification of the retention time of a substance with zero polarizability as being unretained is not substantiated by any rigorous theory. In fact, Masukawa (28) has discussed the hypothetical perfect gas perturbation method in detail and has suggested several alternative extrapolating parameters for determining retention volumes of an unabsorbed gas, such as, critical temperature, Lenord Jones potential parameter, or heat of adsorption.

The free gas volume, V_g, can be expressed in terms of a general extrapolation parameter, β, in the following way. From a plot of V_R vs β, V_R will equal V_g at $\beta = 0$, or for helium and argon, the following identity can be written,

$$\frac{V_g - V_{He}}{0 - \beta_{He}} = \frac{V_{AR} - V_{He}}{\beta_{AR} - \beta_{HE}} \tag{7-1}$$

Solving for V_g, the result is

$$V_g = V_{He} - \frac{V_{AR} - V_{He}}{\left(\frac{\beta_{AR}}{\beta_{He}} - 1\right)} \tag{7-2}$$

Two possible extremes exist for the minimum and maximum values of V_g.

1. In the case where $\beta_{He} << \beta_{AR}$, Equation (7-2) indicates that V_g will approach V_{He}. Since helium is definitely retained to a finite extent as it passes through the GLC column, the free gas volume must be less than V_{He}. Thus, the value of V_g which is calcualted when $[\beta_{AR}/\beta_{He}]$ is very large is the maximum value that V_g could have. The use of a larger value of V_g in the calculation of K-values can in no way be justified.
2. The opposite extreme would be the case where $[\beta_{AR}/\beta_{He}]$ is small. Of the extrapolation parameters suggested by Masukawa, the

parameter with the lowest ratio of values of argon to helium is heat of adsorption where $[\frac{\beta AR}{\beta He}] = [\frac{\Delta H_{AR}}{\Delta H_{He}}] = 5.81$.

Table VI lists the K-values which were calculated using the highest and lowest values of V_g from the two methods mentioned above. Changes in the K-values of 3.1% for CO_2 and 1.0% for H_2S were caused by the variation in V_g. The K-values shown in Table VI are for the methane-MCH system. The small deviations in the calculated K-values indicate that the method used in this work for calculating V_g should not cause appreciable error. Figure 15 illustrates the method used to calculate V_g using the three extrapolation parameters.

Comparison of Results with Other Work

In this section both the chromatographic results and static cell results of this work are examined along with available literature data to test the mutual consistency among the various data sources.

Asano et al. (1) measured the K-values of CO_2 and H_2S in the methane-octane system at 0^oC and -20^oC for pressures from 100 to 1000 psia using a technique quite similar to the method used in this work. The techniques differed only in the calculation of V_g, where Asano used binary K-value data from the literature and radioactively tagged methane to experimentally find a retention volume for methane. Table VII gives the results of Asano and this work (chromatographic and static cell) over the same range of conditions. Figures 16 and 17 present comparisons of the data of Table VII. In the figures the results from the static cell of this work and the results of Asano are presented in terms of their percent deviations from the chromatographic K-values of this work. The chromatographic K-values of this work have an estimated

TABLE VI

EFFECT OF EXTRAPOLATION PARAMETER ON CALCULATION OF K-VALUES

System	Pressure (psia)	Calculated K-Values 1 Polarizability $\beta / \beta = 7.0$	2 $\beta / \beta = 8.0$	3 Heat of Adsorption $\beta / \beta = 4.81$	Percent of Deviation $\frac{2-1}{1}$	$\frac{3-1}{1}$
CO_2 -40°F	100	5.90	5.97	5.87	1.19	-0.51
	800	1.07	1.09	1.066	1.87	-0.37
	1500	0.99	1.02	0.977	3.03	-1.31
CO_2 20°F	100	11.35	11.57	11.26	1.94	-0.79
	800	1.70	1.74	1.68	2.35	-1.18
	1500	1.24	1.28	1.22	3.23	-1.61
H_2S -40°F	100	1.02	1.02	1.019	0	-0.10
	800	0.246	0.247	0.245	.41	-0.41
	1500	0.321	0.324	0.319	.93	-0.62
H_2S 20°F	100	2.45	2.46	2.45	.41	0.0
	800	0.467	0.477	0.465	2.41	-0.43
	1500	0.407	0.411	0.405	.98	-0.49

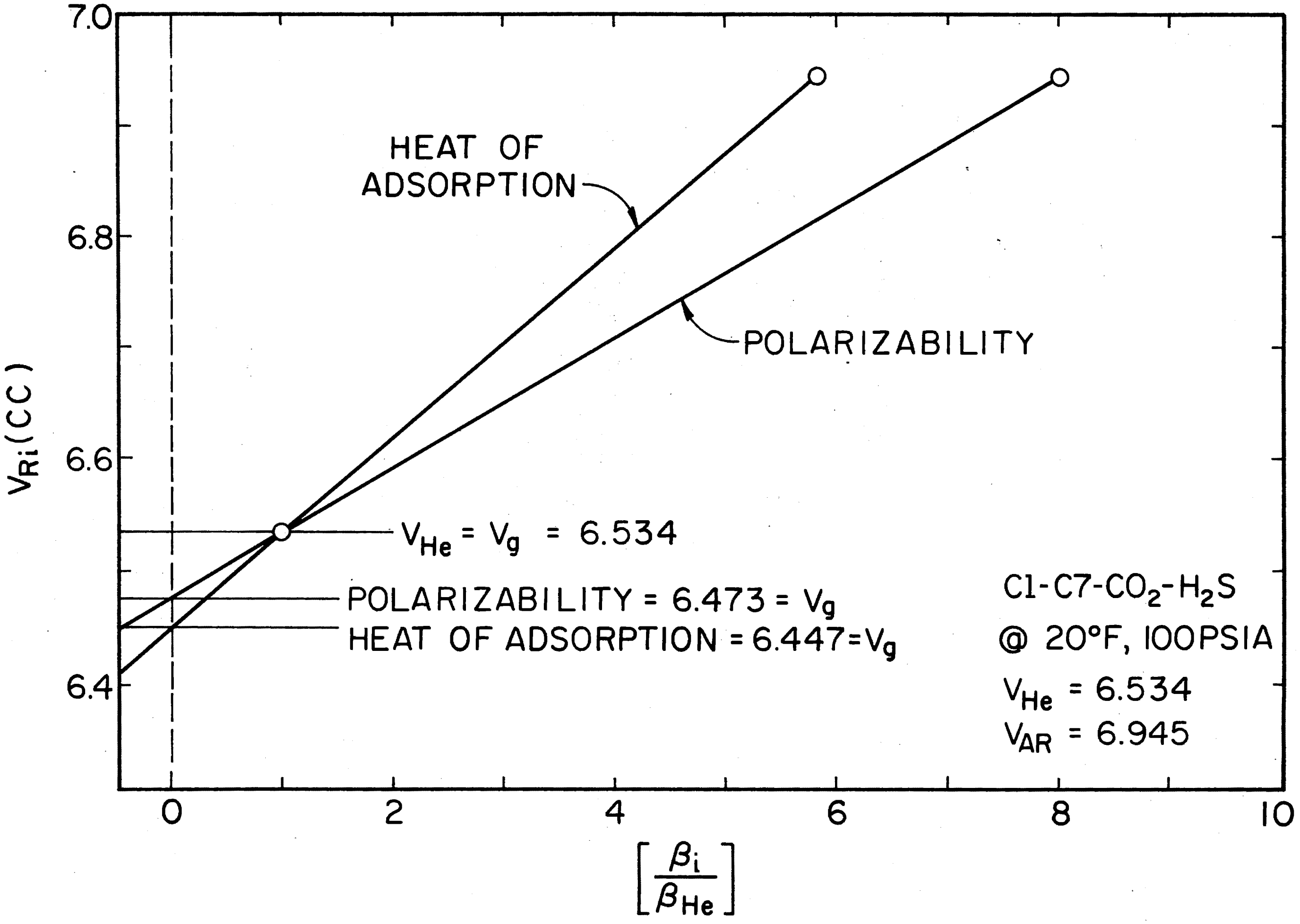

Figure 15. Extrapolation of Retention Volumes to Unretained Gas Using Different Extrapolation Parameters

TABLE VII

K-VALUES OF CARBON DIOXIDE AND HYDROGEN SULFIDE IN THE METHANE+n-OCTANE SYSTEM FROM CHROMATOGRAPHIC WORK, WINDOWED CELL WORK, AND DATA OF ASANO

		This Work		
	Pressure (psia)	Chromatography	Static Cell	Asano (1)
CO_2 -20°C	100	6.72	--	6.17
	200	3.45	3.59	3.11
	400	1.95	1.90	1.77
	600	1.42	1.42	1.33
	800	1.16	1.18	1.11
	1000	1.03	1.06	0.985
CO_2 0°C	100	9.37	--	8.45
	200	4.86	5.22	4.46
	400	2.65	2.44	2.41
	600	1.89	1.80	1.80
	800	1.52	1.47	1.46
	1000	1.40	1.31	1.31
H_2S -20°C	100	1.537	--	1.16
	200	0.822	0.798	0.670
	400	0.490	0.470	0.400
	600	0.382	0.392	0.310
	800	0.339	0.348	0.284
	1000	0.319	0.322	0.280
H_2S 0°C	100	2.44	--	1.90
	200	1.28	1.25	1.10
	400	0.723	0.693	0.650
	600	0.550	0.538	0.488
	800	0.468	0.474	0.421
	1000	0.438	0.427	0.400

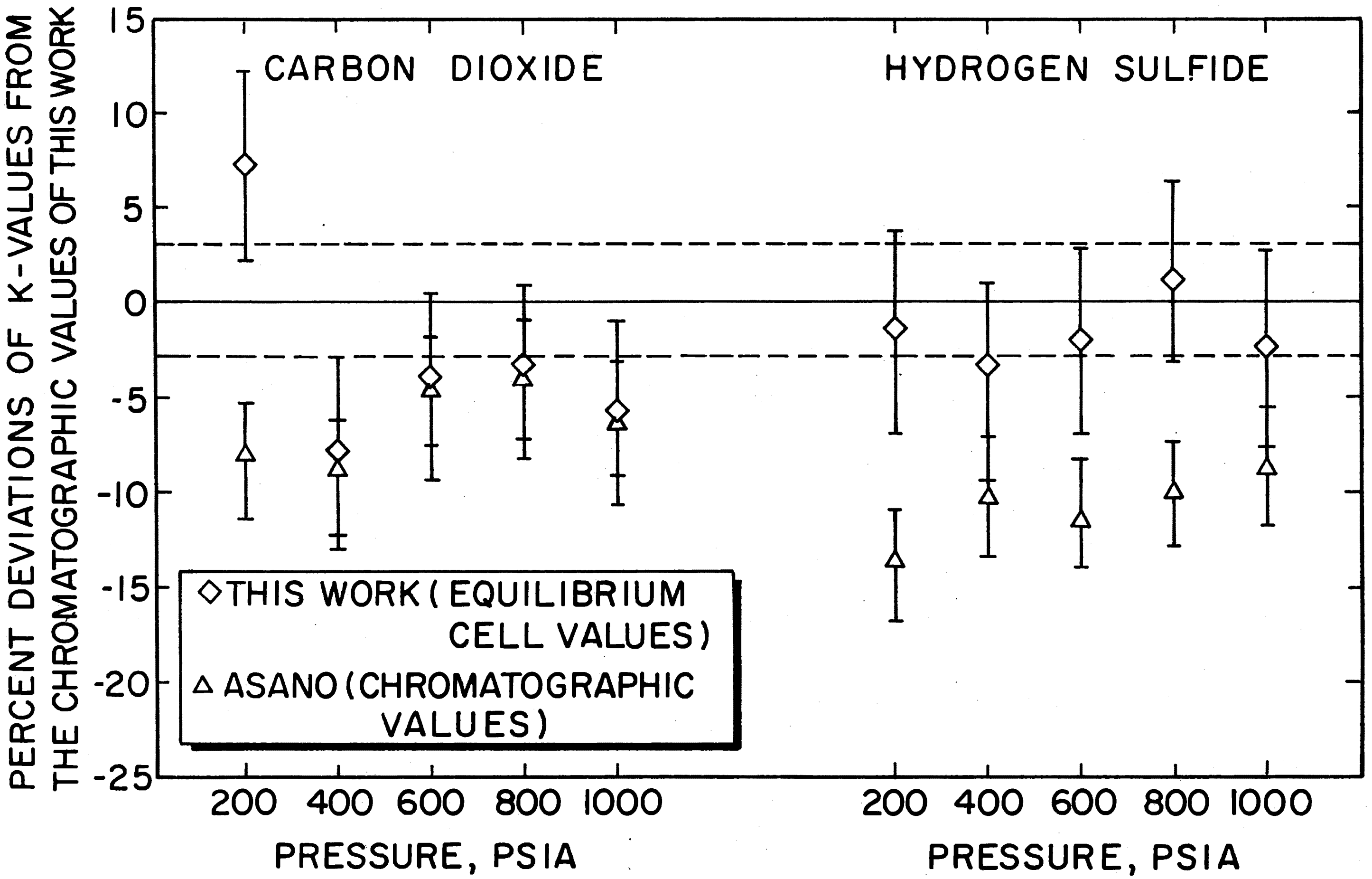

Figure 16. Comparison of K-Values for Carbon Dioxide and Hydrogen Sulfide in the Methane+n-Octane System at 0°C

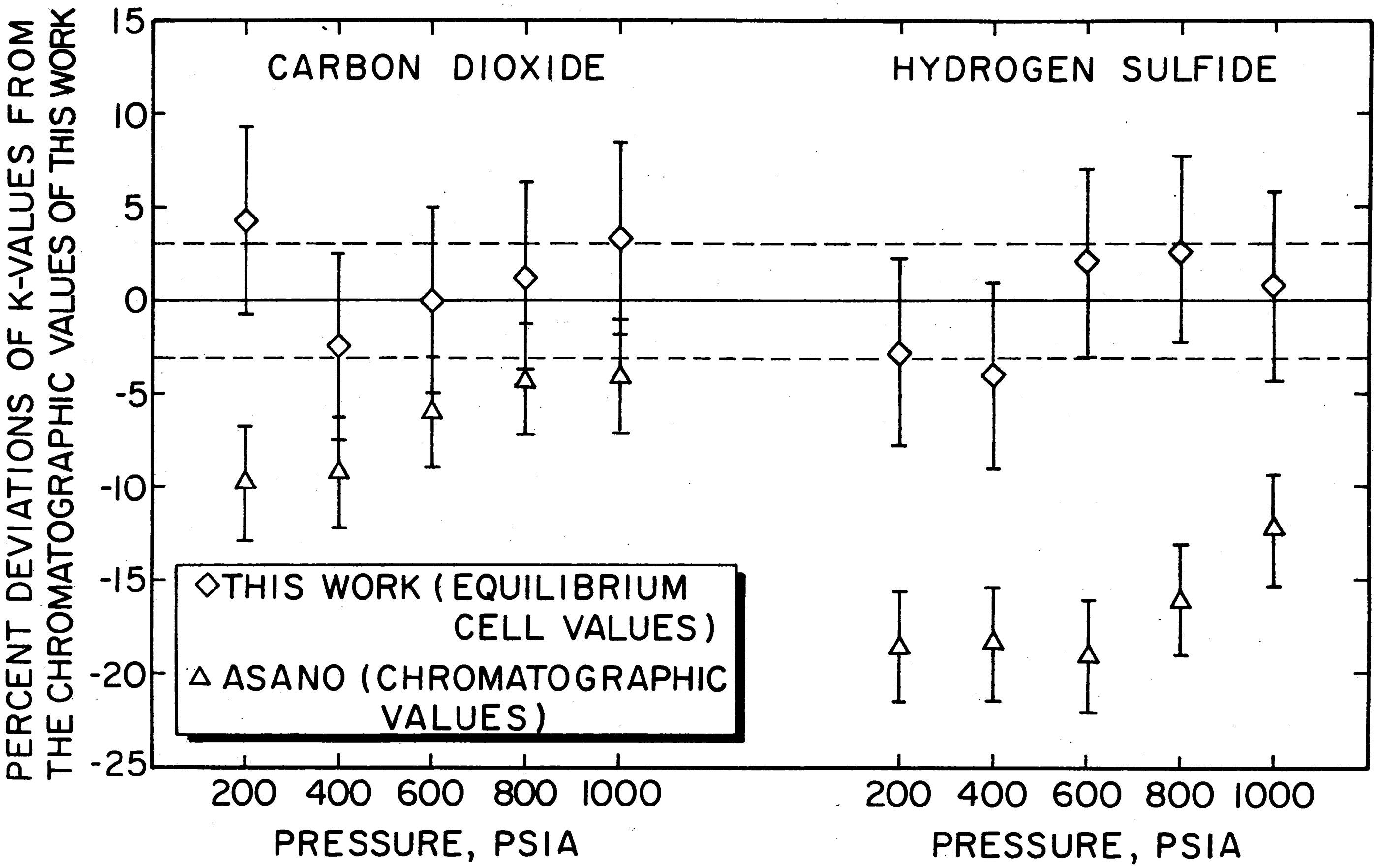

Figure 17. Comparison of K-values for Carbon Dioxide and Hydrogen Sulfide in the Methane+n-Octane System at -20°C

uncertainty of ± 3% (as denoted by the horizontal dashed line at ±3% in Figures 16 and 17); the static cell results, 5% (bars drawn above and below diamond); and an uncertainty of ±3% was arbitrarily assigned to the results of Asano.

Figure 16 shows the CO_2 K-values of the static cell work and Asano to be in excellent agreement at $0^{\circ}C$ (except for 200 psia). The chromatographic data of this work appear somewhat higher than the others, although three of the five data points are within the combined experimental uncertainty. Figure 17 shows the CO_2 K-values at $-20^{\circ}C$ to be in reasonable agreement for all three data sets with somewhat better agreement between the two methods of this work. Khoury and Robinson (21), however, reported good agreement with the CO_2 K-values of Asano at $-20^{\circ}C$. They claimed agreement within 1% although they presented no discreet numerical results. They also employed the chromatographic technique in their studies.

The comparison of H_2S K-values in Figure 16 and Figure 17 show the data of Asano to be 9-12% below the K-values of the chromatographic work at $0^{\circ}C$ and 12-20% below at $-20^{\circ}C$. This difference is well outside the expected experimental uncertainties. The static cell data are in good agreement with the chromatographic data of this work. The disagreement illustrated in Figure 17 between the present chromatographic data and those of Asano was, in fact, the compelling reason for undertaking the windowed cell measurements.

Additional indirect comparisons of the experimental data of this work can be made with the CO_2 and H_2S K-values measured by Yarborough (49) in multicomponent systems. Yarborough made measurements in

(1) a system containing the hydrocarbons methane, ethane, propane, heptane and decane, and nonhydrocarbons nitrogen, carbon dioxide, and hydrogen sulfide, and

(2) a system differing from the above-mentioned system in that toluene was also added to the mixture to make the C_{7+} fraction contain 64% toluene.

Thus, the mixtures were identical except that the C_7+ fraction for the first mixture consisted of heptane and decane while the second mixture had a C_{7+} fraction consisting of heptane, decane, and 64% toluene. The measurements were made on the identical static cell apparatus used in this work. Figure 18 through 21 present comparisons of the CO_2 and H_2S K-values of Asano (dashed line), this chromatographic work (in toluene and heptane) and the work of Yarborough (solid lines). The figures show the effect of temperature on CO_2 and H_2S K-values at 500 and 1000 psia.

Figure 18 reveals fair agreement among the K-values of CO_2 at 500 psia for the data of all investigators. The K-values in n-heptane from this work are about 20% above the other investigators at low temperature, but approach the data of Yarborough at higher temperatures. The K-values of Asano show excellent agreement with Yarborough at low temperatures but begin to deviate at higher temperatures. Figure 19 shows the K-value of CO_2 at 1000 psia for Asano and Yarborough to be in excellent agreement, while the K-values in n-heptane from the present study are some 10% higher. Again, the K-values of this work approach those of Yarborough at higher temperatures while the K-values of Asano begin to deviate from those of Yarborough. The presence of toluene does not have a great effect on the CO_2 K-values in the work of Yarborough or in this

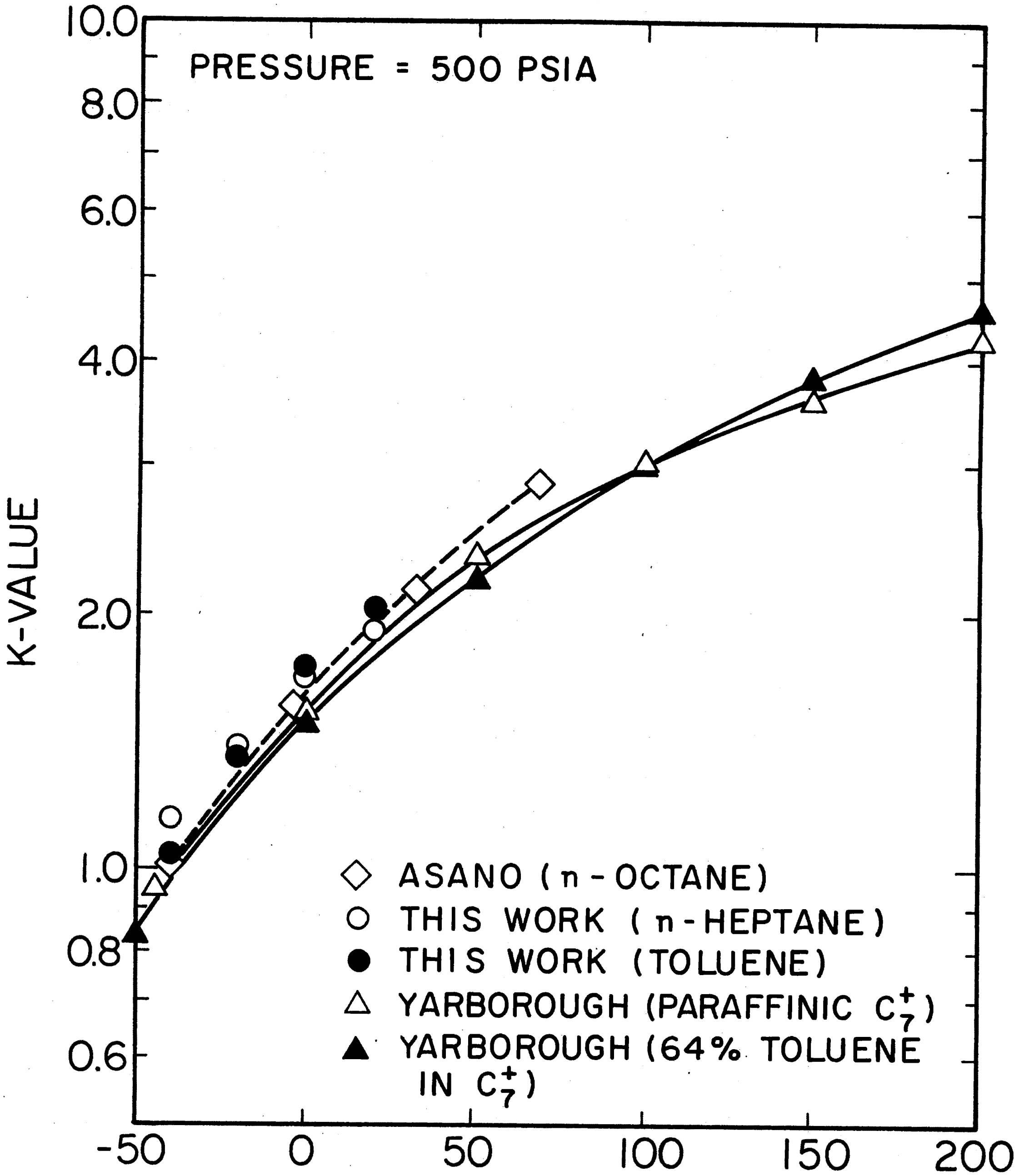

Figure 18. Comparison of K-values for Carbon Dioxide at 500 psia

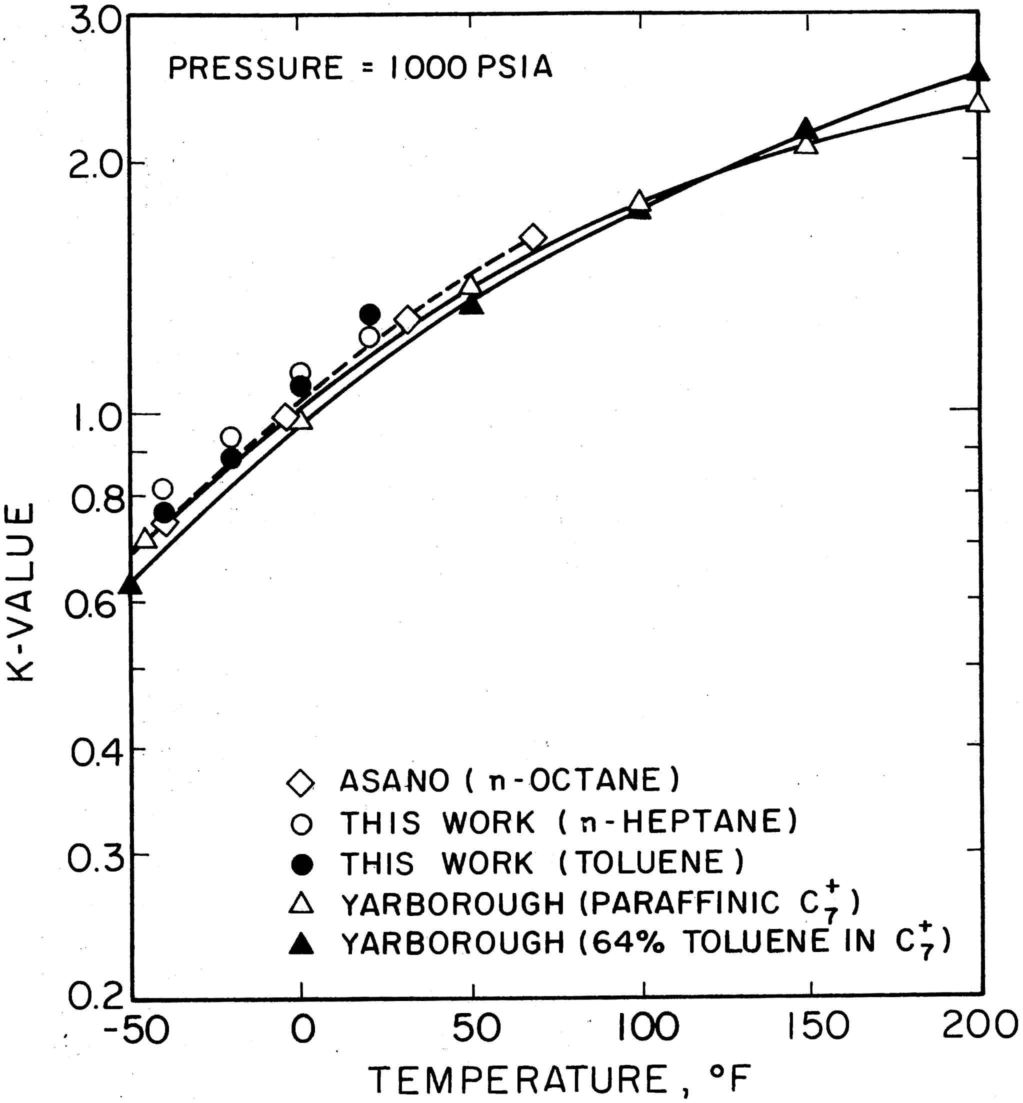

Figure 19. Comparison of K-values for Carbon Dioxide at 1000 psia

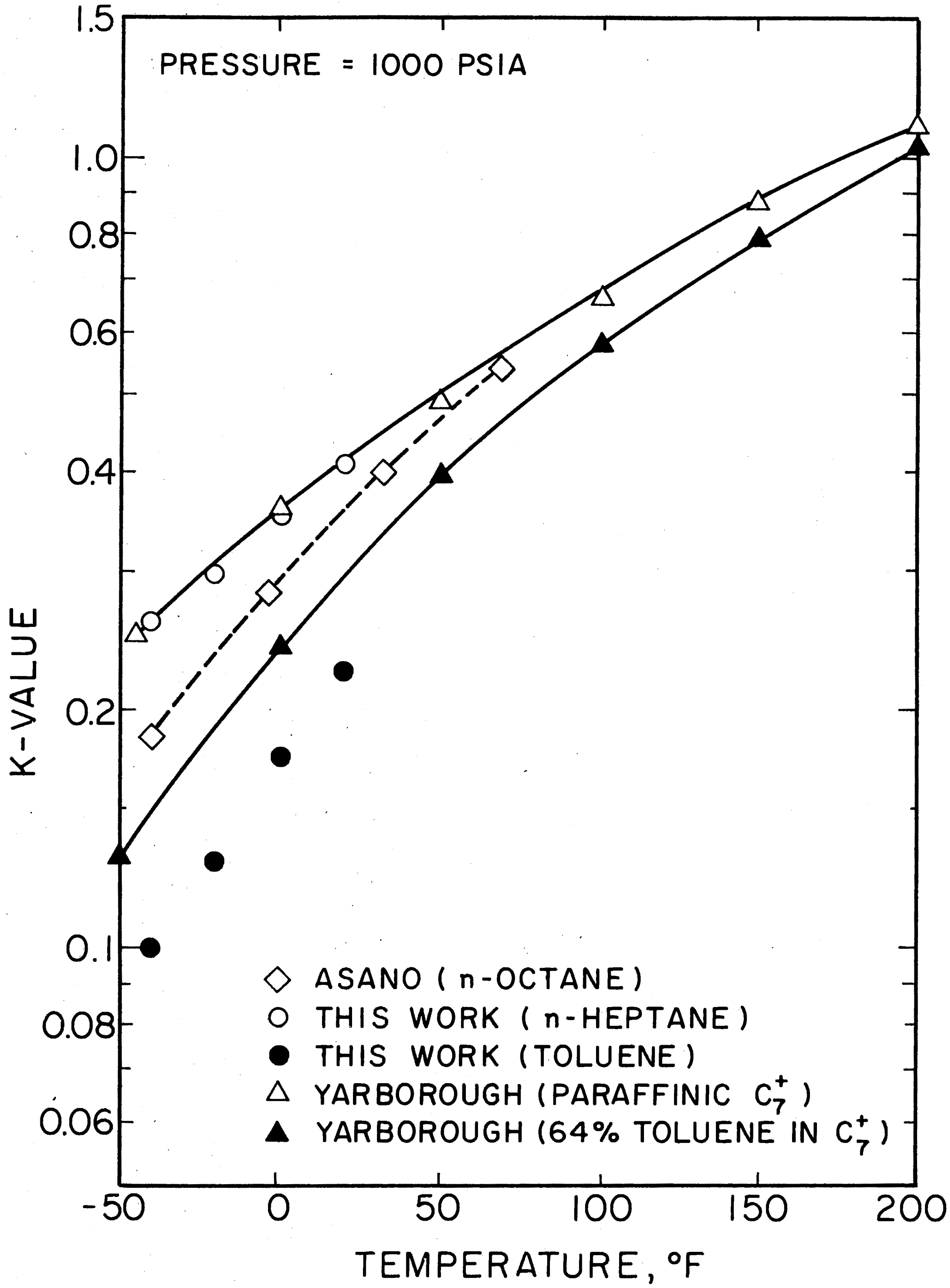

Figure 20. Comparison of K-values for Hydrogen Sulfide at 1000 psia

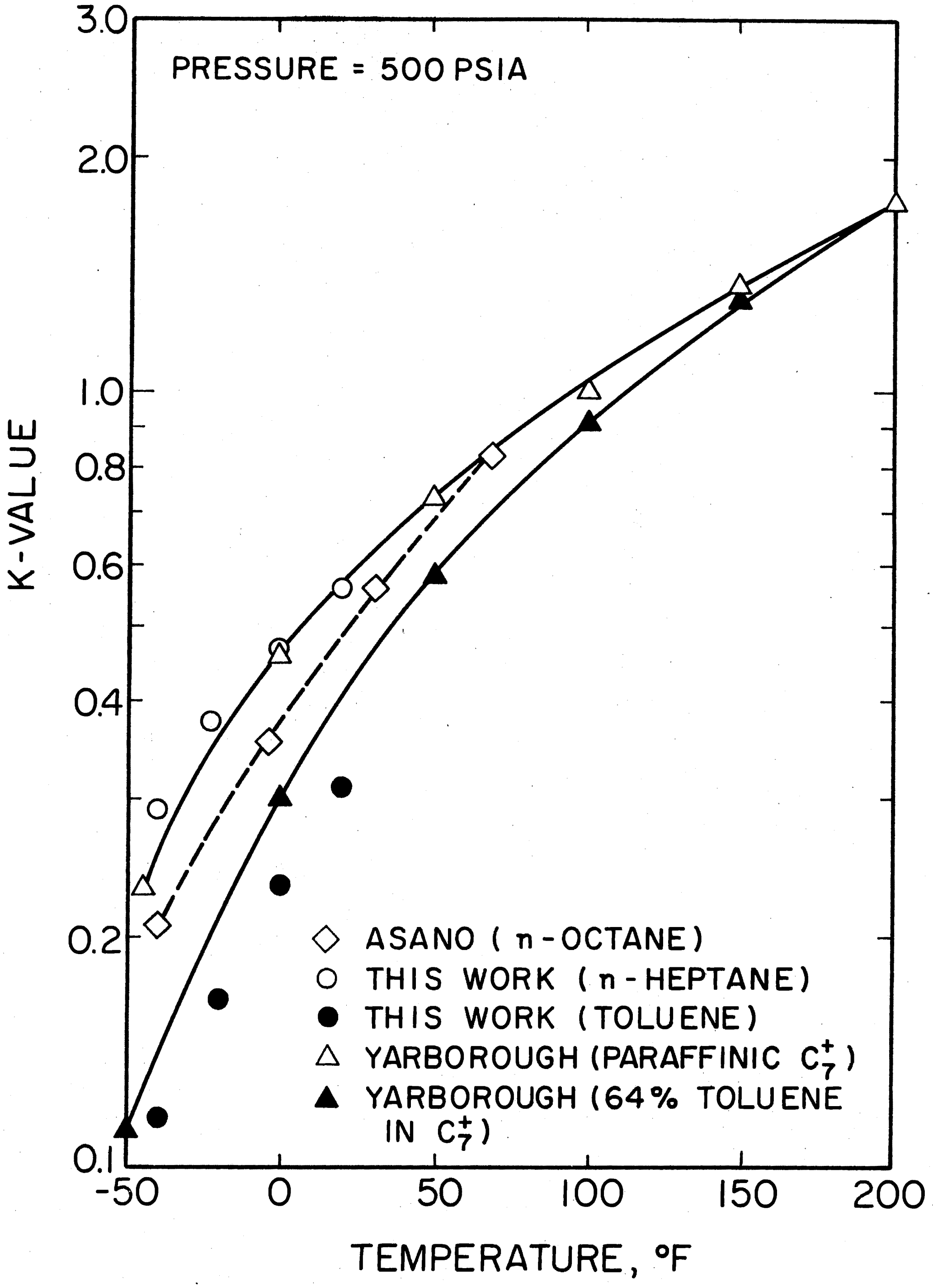

Figure 21. Comparison of K-values for Hydrogen Sulfide at 500 psia

work. The isobars for the two systems of Yarborough do cross at high temperatures in the two plots, while the isobars of this work would cross, but at a much lower temperature. This trend shows up in both figures.

Figure 20 shows the K-values for H_2S at 1000 psia in heptane for this work to be in excellent agreement with the data of Yarborough (for paraffinic C_{7+}), while the data of Asano are as much as 25% lower at -40^oF. Further, the indicated effect of toluene on the H_2S K-value is quite consistent between this work and that of Yarborough; that is, the presence of 64% toluene reduced the H_2S K-values of Yarborough below the value in the paraffinic C_{7+} by about 2/3 of the amount that the chromatographic data of this work indicated. Figure 21 shows similar trends for H_2S K-values at 500 psia, but to a lesser extent. Eakin and DeVaney (10) measured the K-values of H_2S in n-nonane and in mesitylene (an aromatic) using a static cell. They compared their results with those of Yarborough in heptane and toluene. They concluded that "both sets of data are consistent." Eakin and DeVaney found the aromatic reduced the H_2S K-values at low temperatures and enhanced them at higher temperatures.

K-values for the methane and heavy solvent were not measured in the chromatographic work; however, both methane and octane K-values were determined as part of the windowed cell measurements (see Table III). Figure 22 shows those K-values, along with the methane K-values (in octane) measured by Kohn and Bradish (22). Due to the low concentration of octane in the vapor, Kohn did not calculate octane K-values. The solid lines in Figure 22 show the methane and octane K-values which were predicted by correlating the data of Kohn and Bradish using the

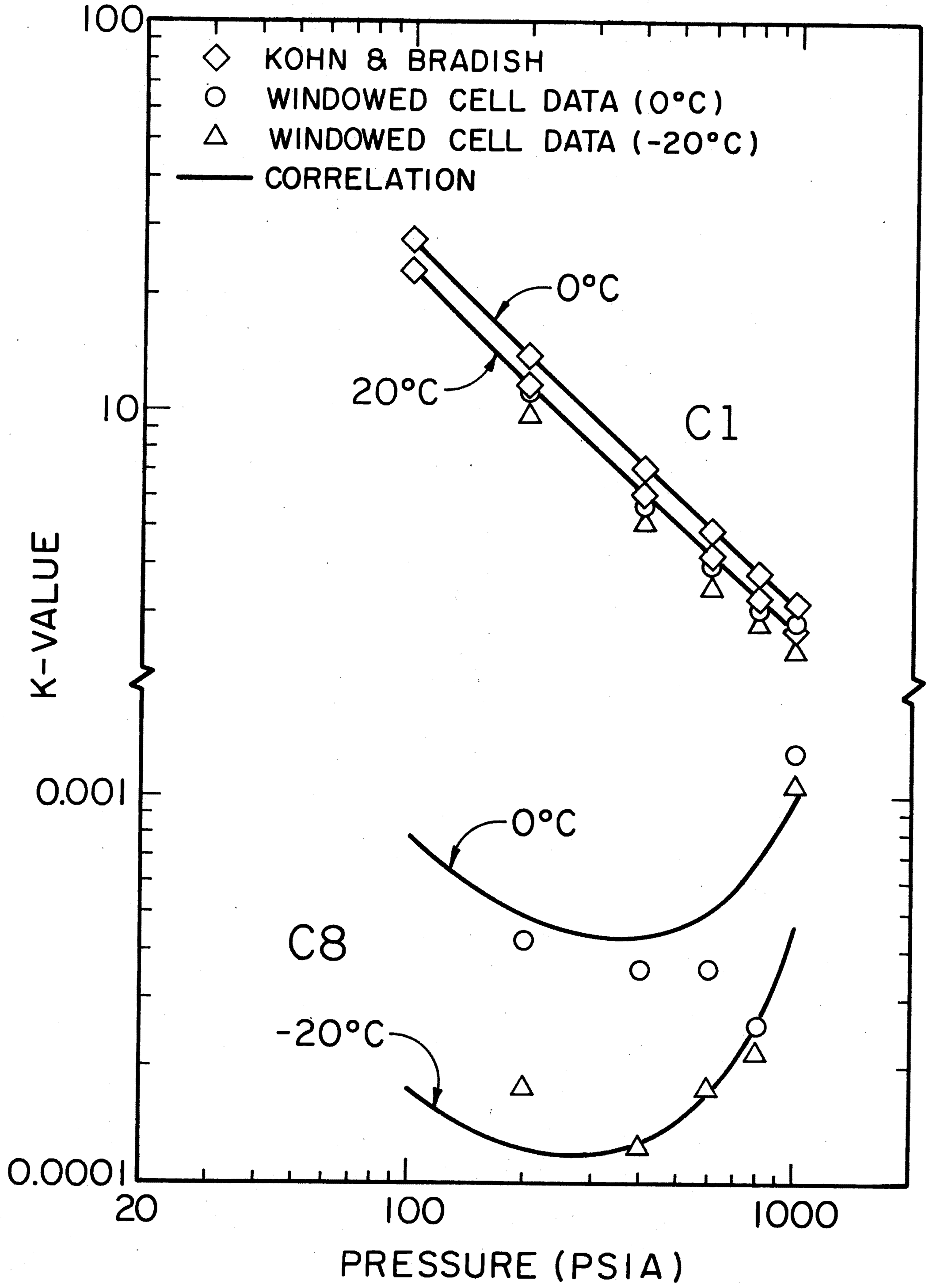

Figure 22. Comparison of K-values for Methane and n-Octane from the Classical Windowed Cell Experiment

Soave modification of the R-K equation of state with one empirical factor added. The figure shows the methane K-values of this work to be 15-20% below those of Kohn and Bradish. Yarborough (49) compared the methane K-values of his work with other investigators and found his K-values (taken on the identical windowed cell apparatus as this work) to be 10-15% lower than the others. The octane K-values appear to be in quite reasonable agreement with the correlation considering the very low concentrations of octane in the vapor phase which led to rather high uncertainties in the octane K-values.

Data Trends

Based on the experimental results of this work, some general comments are possible regarding the effects that naphthenic and aromatic components in an absorber oil would have on the K-values of CO_2 and H_2S.

For CO_2, the K-value in MCH is from 15 to 30% higher than in the paraffinic solvent n-heptane over the complete temperature range -40 to 20°F. The greater deviations are at lower pressures and higher temperatures. Toluene has much less effect on the CO_2 K-values, reducing them by about 7% at the -40°F and increasing them by 7% at 20°F.

Just the opposite effect is seen for the H_2S K-values. In MCH, the H_2S K-values are approximately 1 to 7% higher than in the paraffinic n-heptane, but in toluene the K-values are reduced from 45 to 60%. This effect of toluene is substantiated for both CO_2 and H_2S by the work of Yarborough (49).

Finally, Figure 23 shows the ratio of the H_2S K-values in toluene to the H_2S K-values in n-heptane as a function of pressure. The general trends illustrated in the figure are similar to results obtained for the

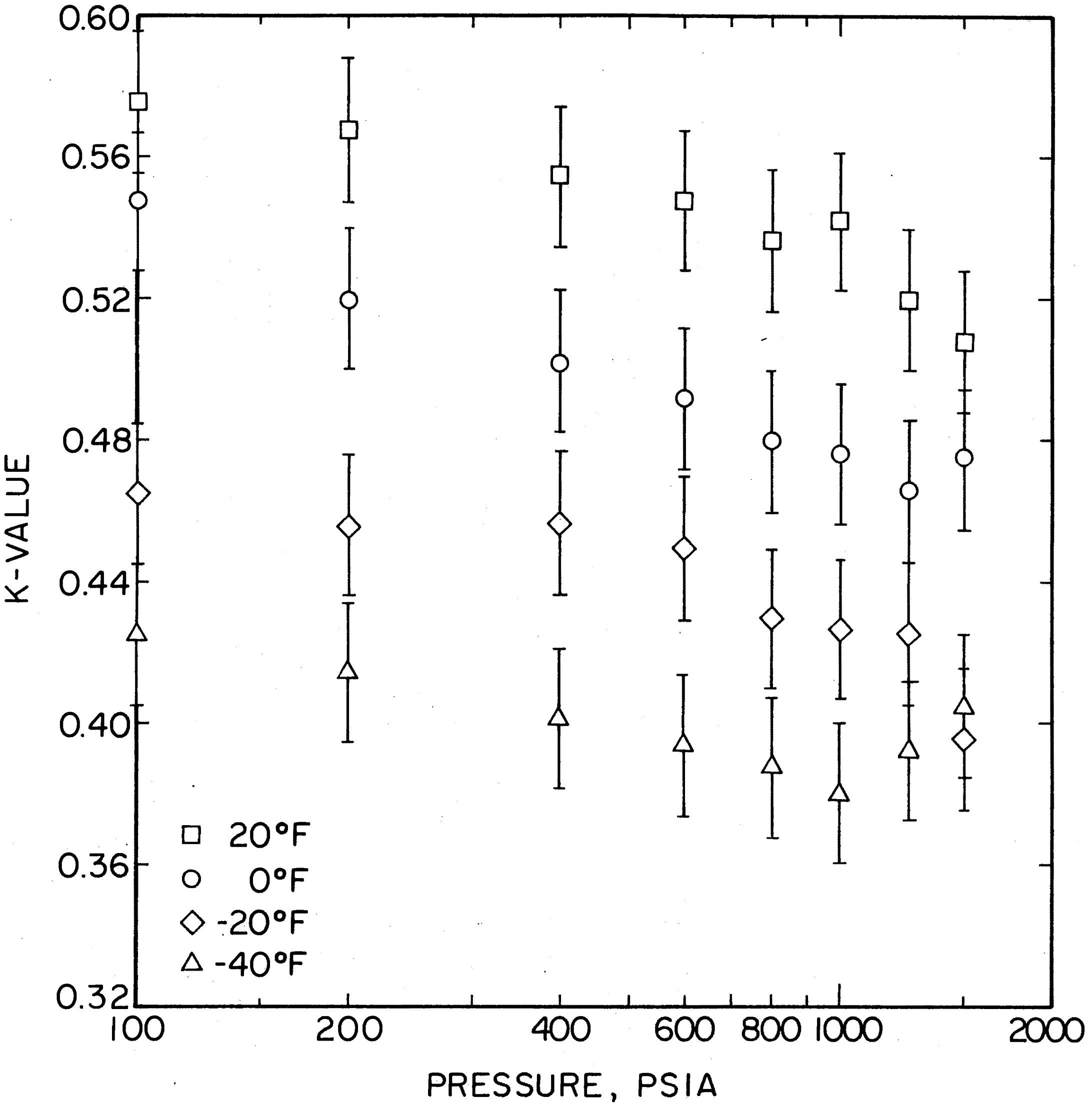

Figure 23. Ratio of K-values for Hydrogen Sulfide in the Methane+ Toluene System to K-values of Hydrogen Sulfide in the Methane+n-Heptane System

K-values of CO_2 and H_2S in MCH relative to those in heptane. As the pressure increased, or the temperature decreased, the K ratio decreased in solvents MCH or toluene relative to heptane. Plots of the other systems showed considerably more fluctuations of data points and much more overlapping of isotherms, but the general conclusions were still the same.

Correlation of Data

The data of this work have been correlated in terms of a modified form of the Redlich-Kwong equation of state, employing empirical interaction parameters. The basis for the correlation is the Scave modification of the Redlich-Kwong equation. In this section the steps taken in correlating the data are discussed in detail, along with the difficulties encountered in the correlation effort. The results are then compared with the basic Soave correlation.

Discussion of Correlation Parameter

The Soave modification of the Redlich-Kwong equation of state is discussed in detail in Chapter III. In the present work the mixing rules which were suggested by Soave have been modified into a more generalized form, which is given in Equation (3-40) through (3-49). Two sets of empirical correlation factors were calculated in this work. One set (k'_{ij}) modified the energy term (T_{cij}) while the other set (k_{ij}, ℓ_{ij}) modified both the energy term and the distance term (through V'_{cij}). The equations showing the application of the two sets of empirical correlation factors are given in Equations (3-54) through (3-57). The use of the two separate methods was undertaken to determine whether or not there is a need for more than one empirical correlation parameter to adequately represent the experimental data.

The correlation equations indicate that critical temperature, critical pressures ($V_c' = RT_c/P_c$) and accentric factors are needed for the pure components used in this study. Critical temperatures and pressures have been found in the literature (30) and are given in Table VIII. Although available in the literature, acentric factors for each of the pure components were calculated in this work to optimize the accuracy of the Soave equation. Vapor pressure data were used along with the Soave modification of the Redlich-Kwong equation of state to find the acentric factors which resulted in the best prediction of vapor pressure data. Table IX shows the range of the vapor pressures used for each component and the acentric factors which were calculated. The vapor pressures of five of the systems were taken from one source (3). The original sources of the data are also listed.

The model used in this work thus required empirical factors (k_{ij}' or k_{ij} and ℓ_{ij}) for each binary pair appearing in the mixture. The empirical correlation factors were determined by non-linear regression to provide the best fit to binary phase equilibrium data taken from the literature. Binary data are available only for the methane binary system. For binary systems involving CO_2 and H_2S with heavy solvents phase equilibrium data are not available. Thus, the empirical correlation factors for these systems were determined by direct fit of the model to the infinite dilution K-values for H_2S and CO_2 determined in the present study. In all evaluations of empirical correlation factors the objective function which was minimized in the non-linear regression was the sum of squares of the deviations between the experimental K-values

TABLE VIII

CRITICAL PROPERTIES OF METHANE, SOLUTES, AND SOLVENTS (30)

Component	Critical Temperature (°K)	Critical Pressure (atm)
Methane	190.59	45.441
n-Heptane	540.27	27.001
Methylcyclohexane	572.20	34.261
Toluene	591.80	40.548
n-Octane	568.83	24.537
Carbon Dioxide	304.21	72.877
Hydrogen Sulfide	373.54	88.868

TABLE IX

VAPOR PRESSURE DATA AND CALCULATED ACENTRIC FACTORS

Component	Temperature and Pressure Range of Data	Calculated Acentric Factor	Number of Data Points	Data Source
Heptane, C_7	47.78 - 779.37 mmHg 25.93 - 99.28 °C	0.345	20	(3, 48)
Methane, C_1	105.03 - 2220.5 mmHg (-181.0) - (-146.65) °C	0.002	24	(3, 16, 44)
Toluene, TOL	47.66 - 779.33 mmHg 35.37 - 111.50 °C	0.260	25	(3, 48)
Methylcyclohexane, MCH	47.66 - 779.33 mmHg 25.59 - 101.83 °C	0.234	21	(3, 48)
Octane, C_8	57.53 - 779.33 mmHg 52.93 - 126.57 °C	0.394	19	(3, 48)
Carbon Dioxide, CO_2	31027. - 54300. mmHg 6.76 - 30.04 °C	0.239	19	(40)
Hydrogen Sulfide, H_2S	10343. - 67229. mmHg 10.44 - 100.00 °C	0.107	12	(40)

and the calculated K-values. For the binary systems containing methane and a heavy solvent, the methane K-values are three to four orders of magnitude greater than the solvent, thus the objective function of the minimization was much larger for the methane. In effect, only the methane K-values had any effect on the optimization. For the methane-CO_2 and methane-H_2S binaries, both components affected the optimization. Appendix B explains the program used and shows a general flow chart of the program.

Results

The results of the two correlations are given in this section. Table X presents the empirical correlation factors (k_{ij} and k_{ij}, ℓ_{ij}) which resulted from the two correlational methods. Table XI lists the results of the correlation of the binary K-value data from the literature. The table gives the average absolute percent deviation between the K-values predicted by the correlation and the experimental K-values from the literature. Since the correlation minimized the square of the difference between the experimental and predicted K-values, the correlation, in effect, was fitting only the methane K-values for the systems C1-C7, C1-TOL, C1-MCH, and C1-C8. The results illustrate this point in that the average deviations for the solvents are much higher than for methane. For CO_2 and H_2S, where the K-values are within an order of magnitude of the C1, the correlation fits both components more evenly. The general trend seems to be that the two constant correlational method fits the binary data slightly better than the one constant method.

Figures 24 through 34 illustrate the results of the correlation of the binary K-values. All data points that were used in the correlational fits are shown in the figures to demonstrate the range of the data used.

TABLE X

EMPIRICAL INTERACTION PARAMETERS EMPLOYED IN K-VALUE CORRELATION

Components "i" and "j"	k'_{ij}	k_{ij}	ℓ_{ij}	Data Reference
C_1/C_7	0.0464	0.1452	0.0634	4
C_1/C_8	0.0598	0.1719	0.0735	22
C_1/MCH	0.0675	0.1454	0.0514	5
C_1/Toluene	0.0784	0.1206	0.0500	6
C_1/CO_2	0.0441	0.0445	−0.0382	9
C_1/H_2S	0.0414	0.0643	−0.0440	40
CO_2/C_7	0.1536	0.2758	0.0398	this work
CO_2/C_8	0.1590	0.2918	0.0526	this work
CO_2/MCH	0.1719	0.2725	0.0310	this work
CO_2/Toluene	0.1339	0.2237	0.0249	this work
H_2S/C_7	0.0934	0.2297	0.0307	this work
H_2S/C_8	0.0930	0.2431	0.0465	this work
H_2S/MCH	0.1031	0.2240	0.0173	this work
H_2S/Toluene	0.0365	0.1549	0.0033	this work

TABLE XI

RESULTS OF CORRELATION OF BINARY K-VALUES

	Average Absolute Percentage Deviation In Predicted K-Value			
	One Parameter Method		Two Parameter Method	
System	C_1	Other	C_1	Other
$C_1 - C_7$	1.9	23.3	2.6	19.4
C_1 - MCH	2.8	71.40	1.5	56.9
C_1 - TOL	10.4	58.8	2.3	62.1
$C_1 - CO_2$	9.4	2.9	6.0	3.1
$C_1 - H_2S$	12.9	1.6	11.1	5.4
$C_1 - C_8$	1.7	68.5	1.7	68.1

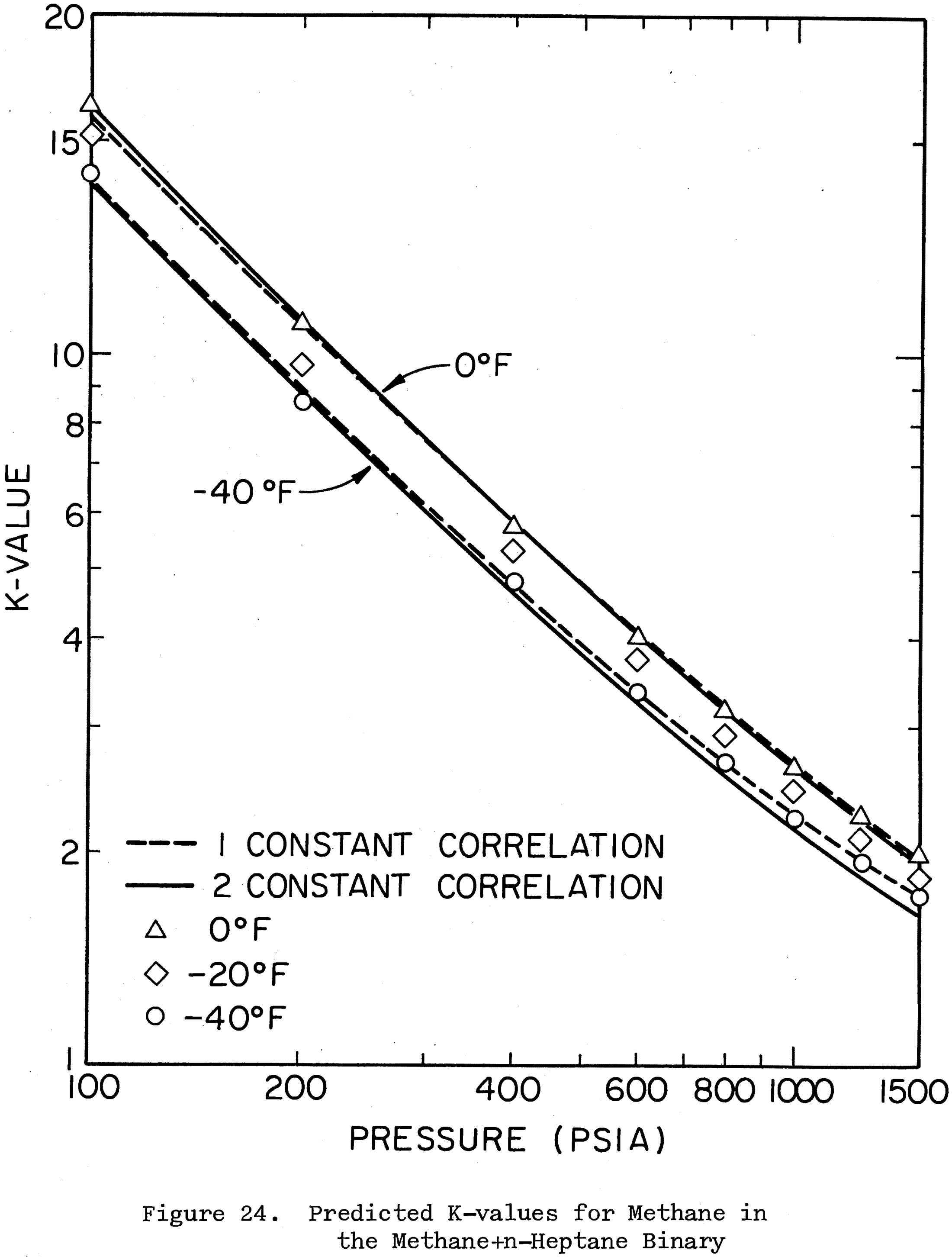

Figure 24. Predicted K-values for Methane in the Methane+n-Heptane Binary System

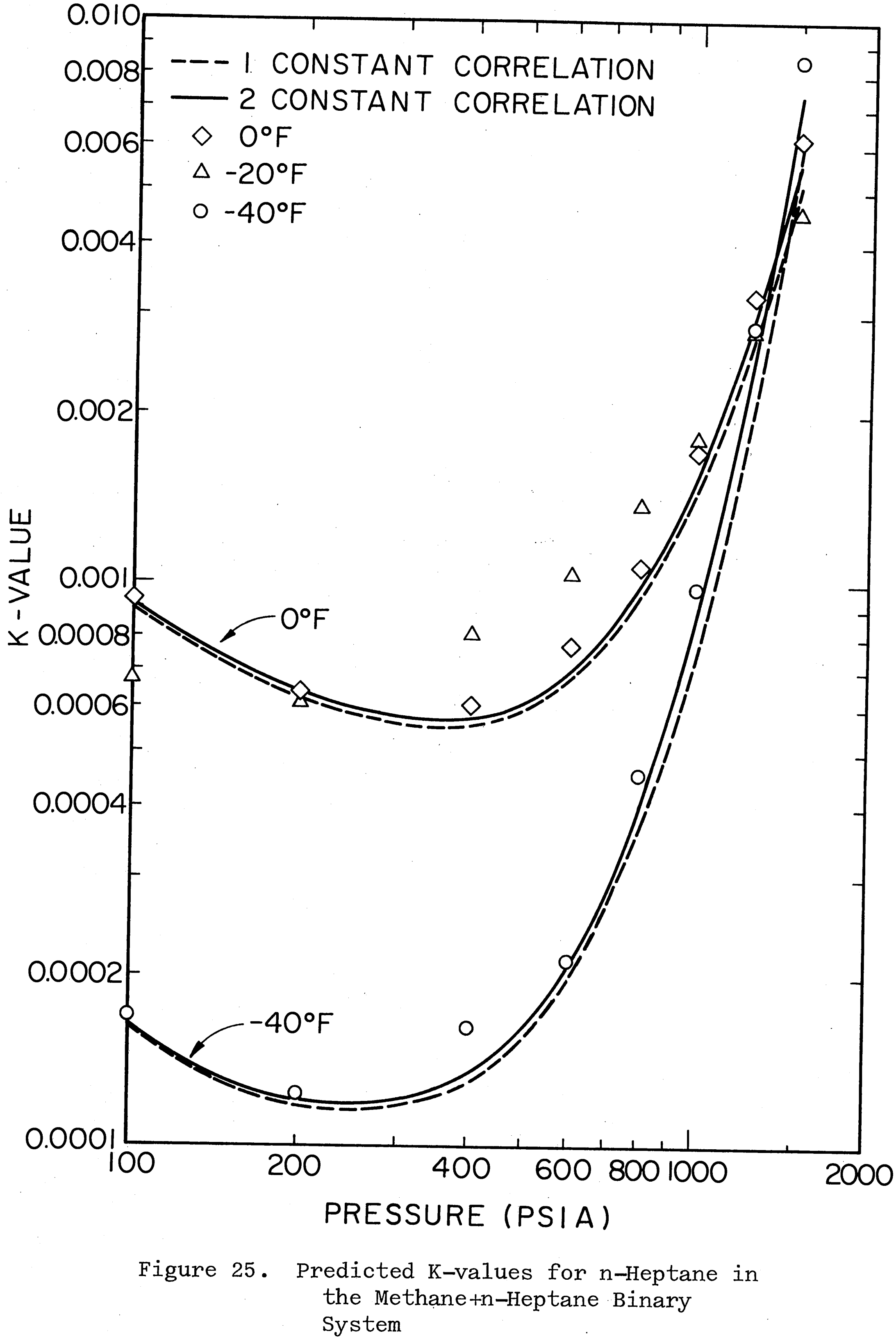

Figure 25. Predicted K-values for n-Heptane in the Methane+n-Heptane Binary System

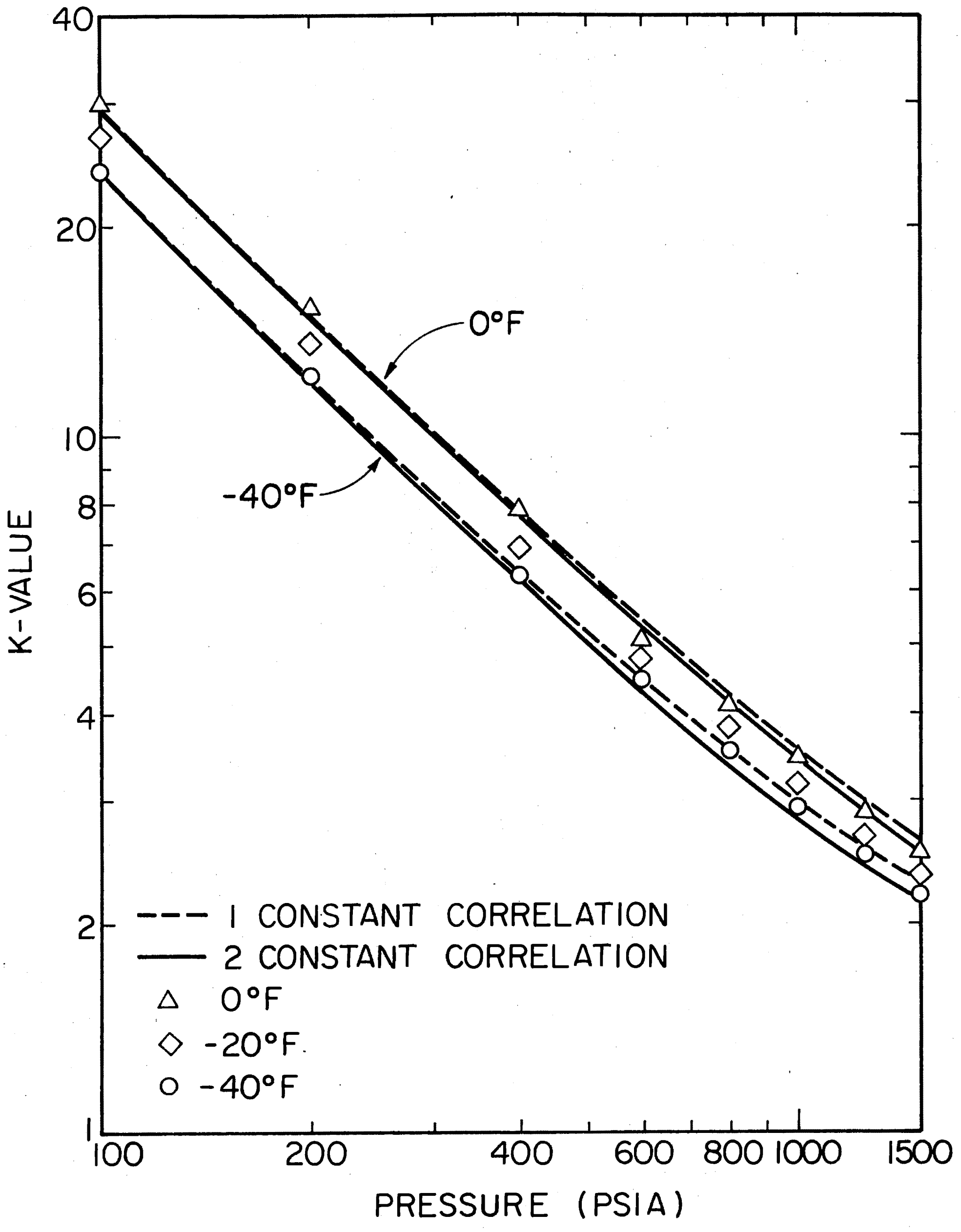

Figure 26. Predicted K-values for Methane in the Methane+Methylcyclohexane Binary System

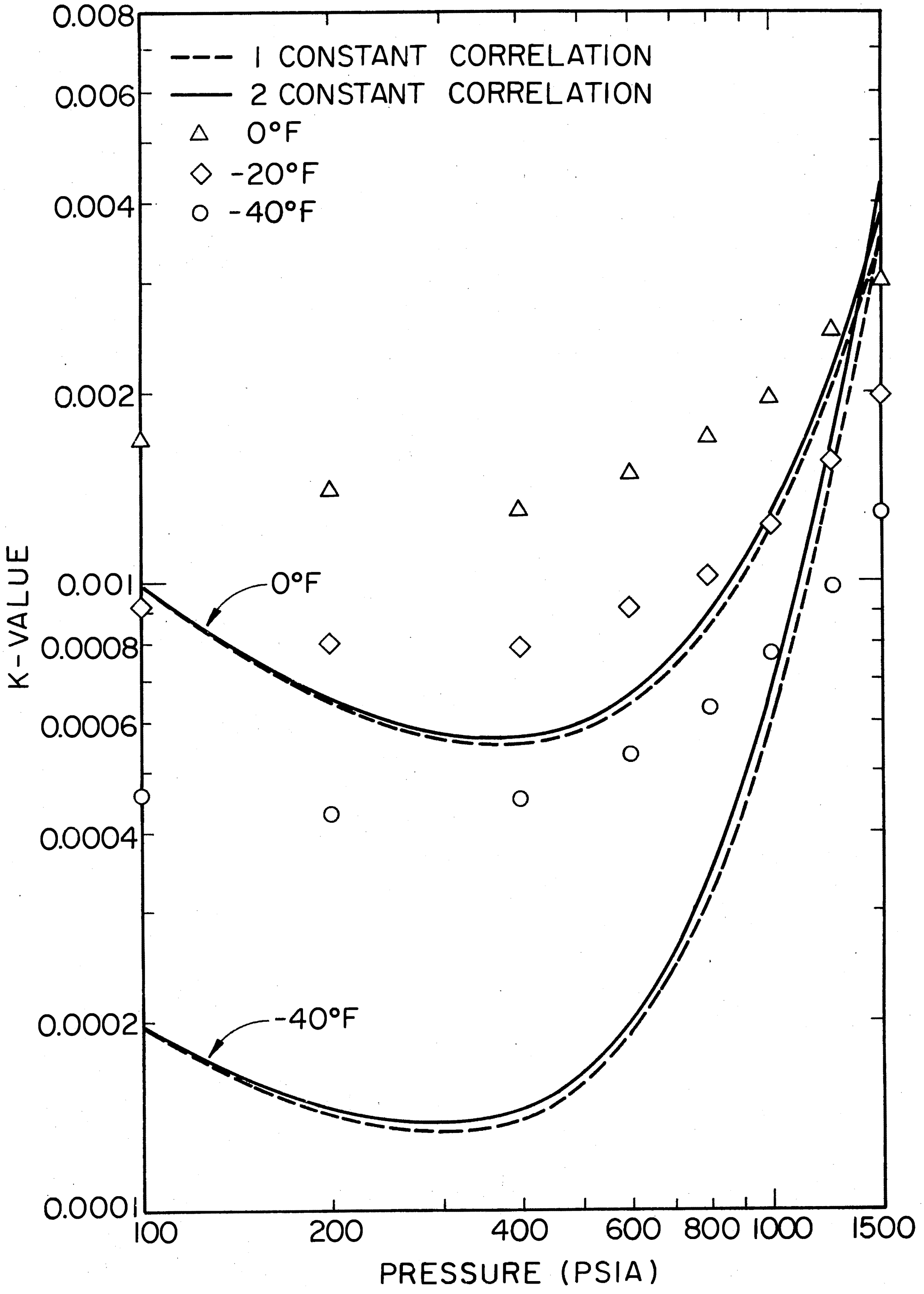

Figure 27. Predicted K-values for Methylcyclohexane in the Methane+ Methylcyclohexane Binary System

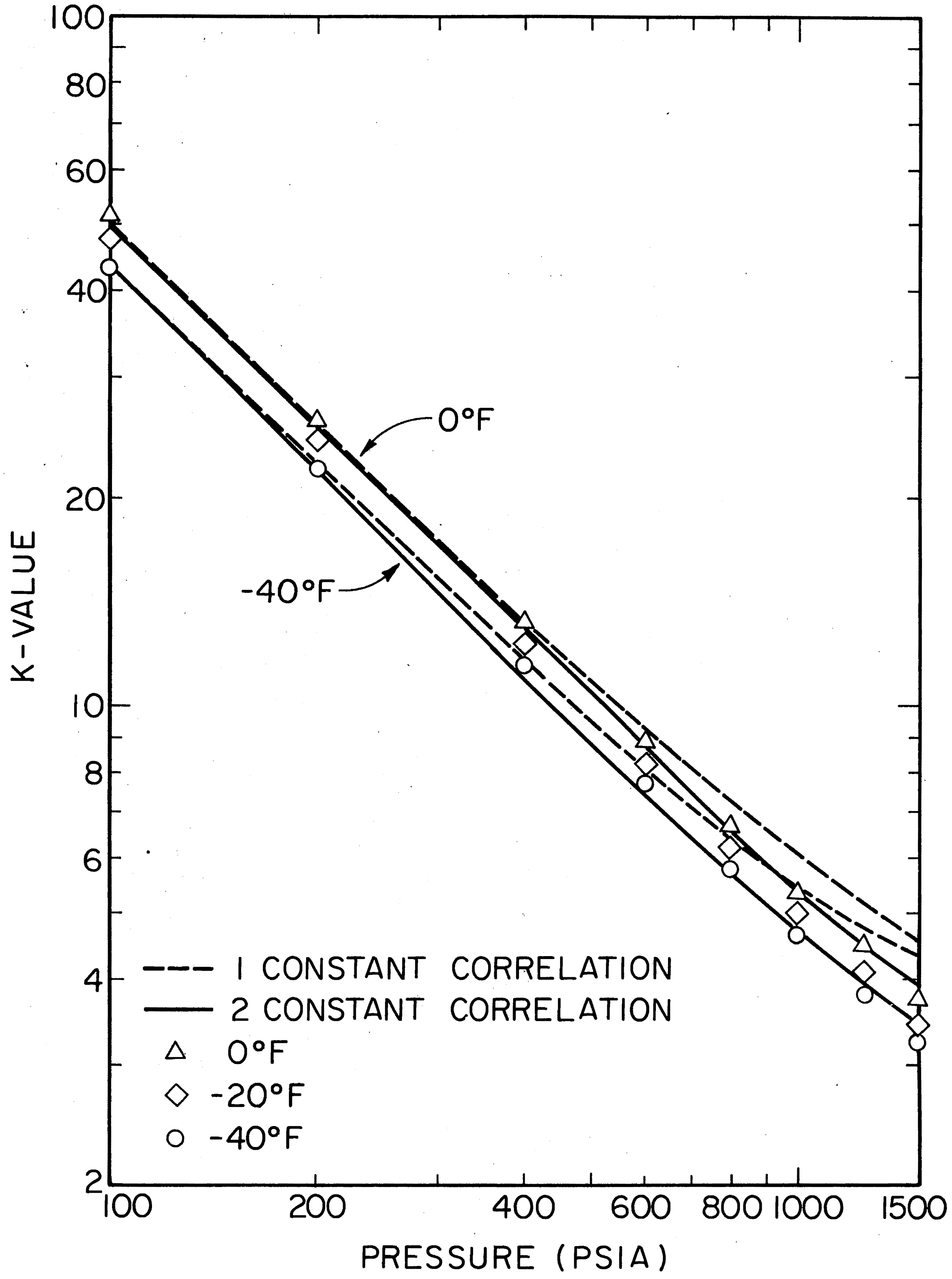

Figure 28. Predicted K-values for Methane in the Methane+Toluene Binary System

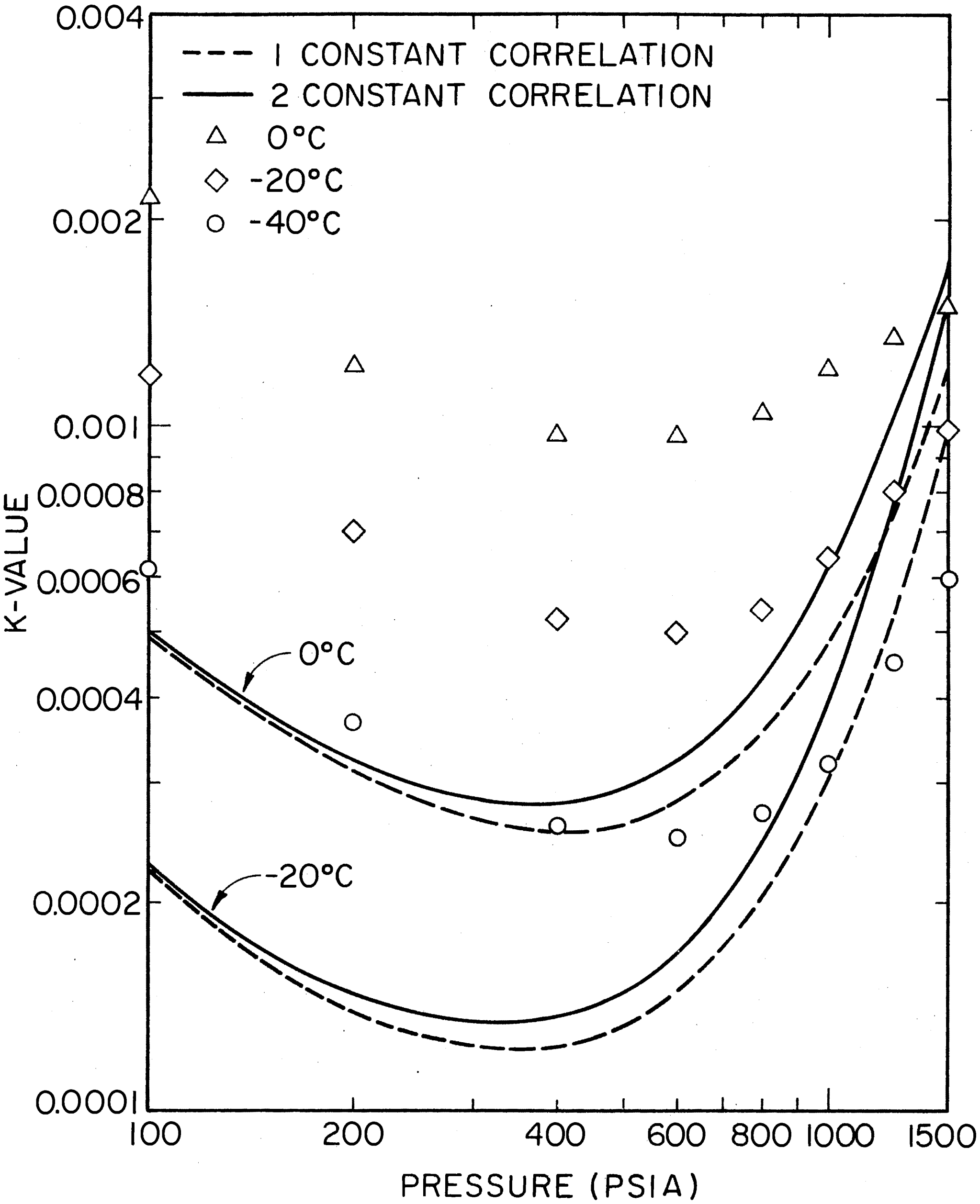

Figure 29. Predicted K-values for Toluene in the Methane+Toluene Binary System

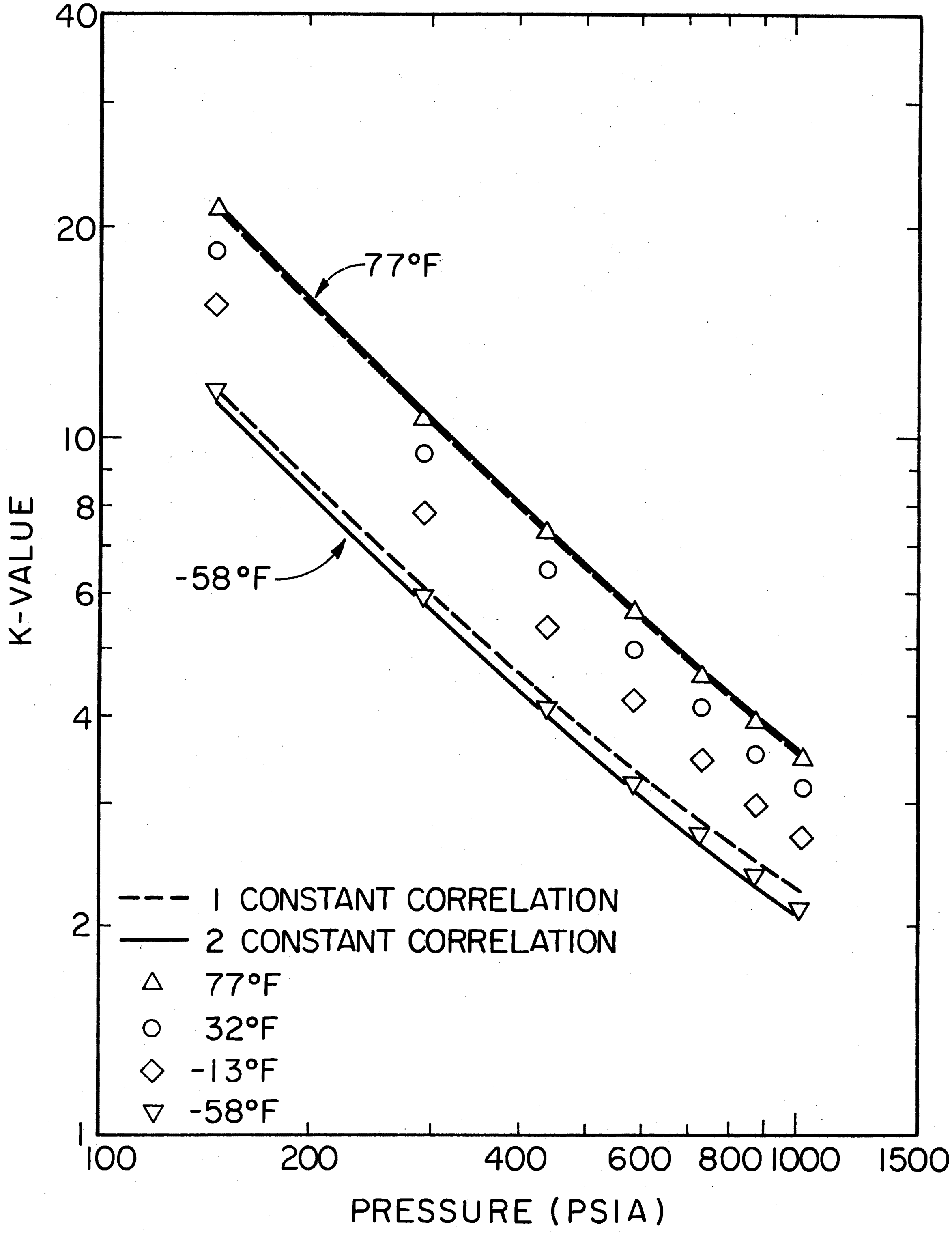

Figure 30. Predicted K-values for Methane in the Methane+n-Octane Binary System

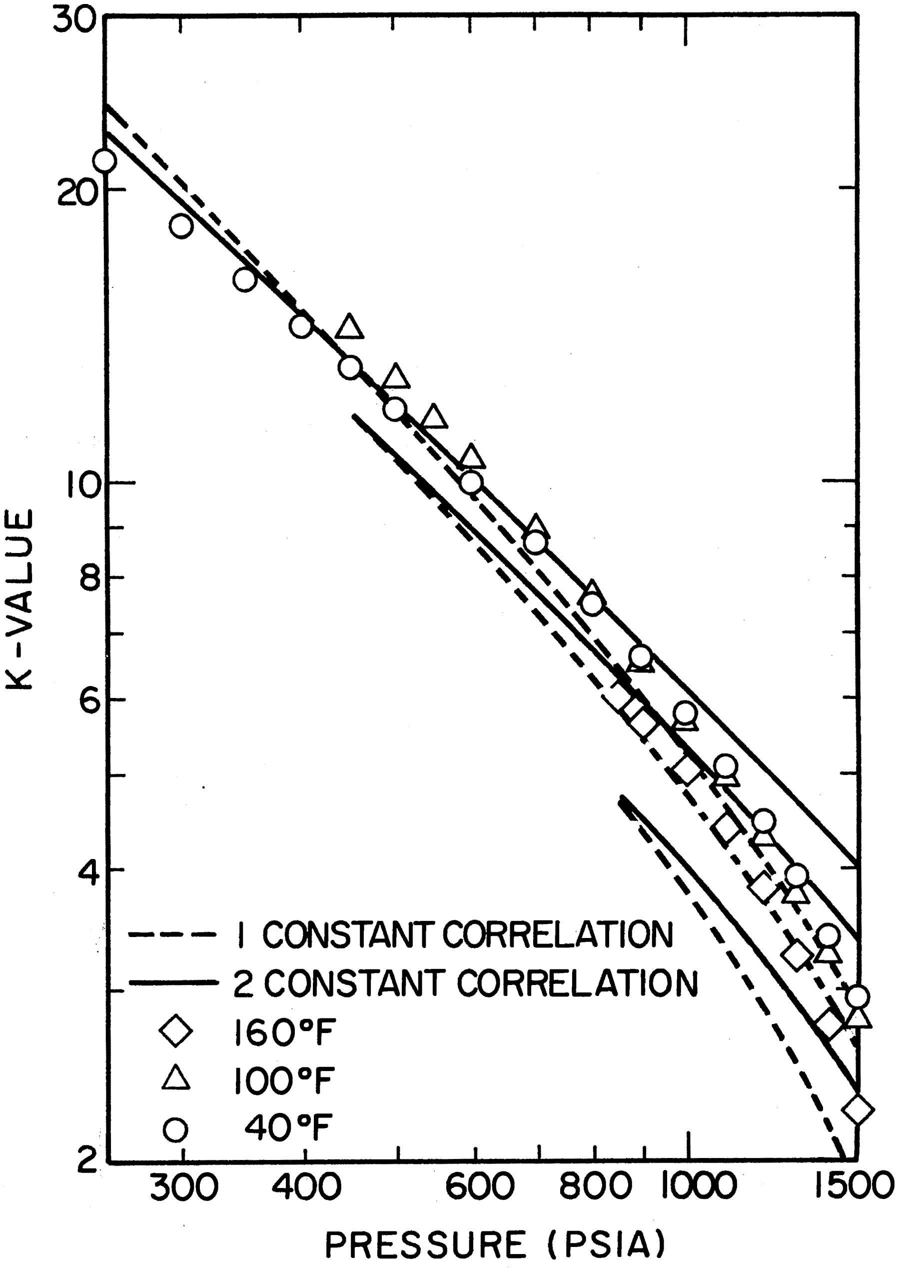

Figure 31. Predicted K-values for Methane in the Methane+Hydrogen Sulfide Binary System

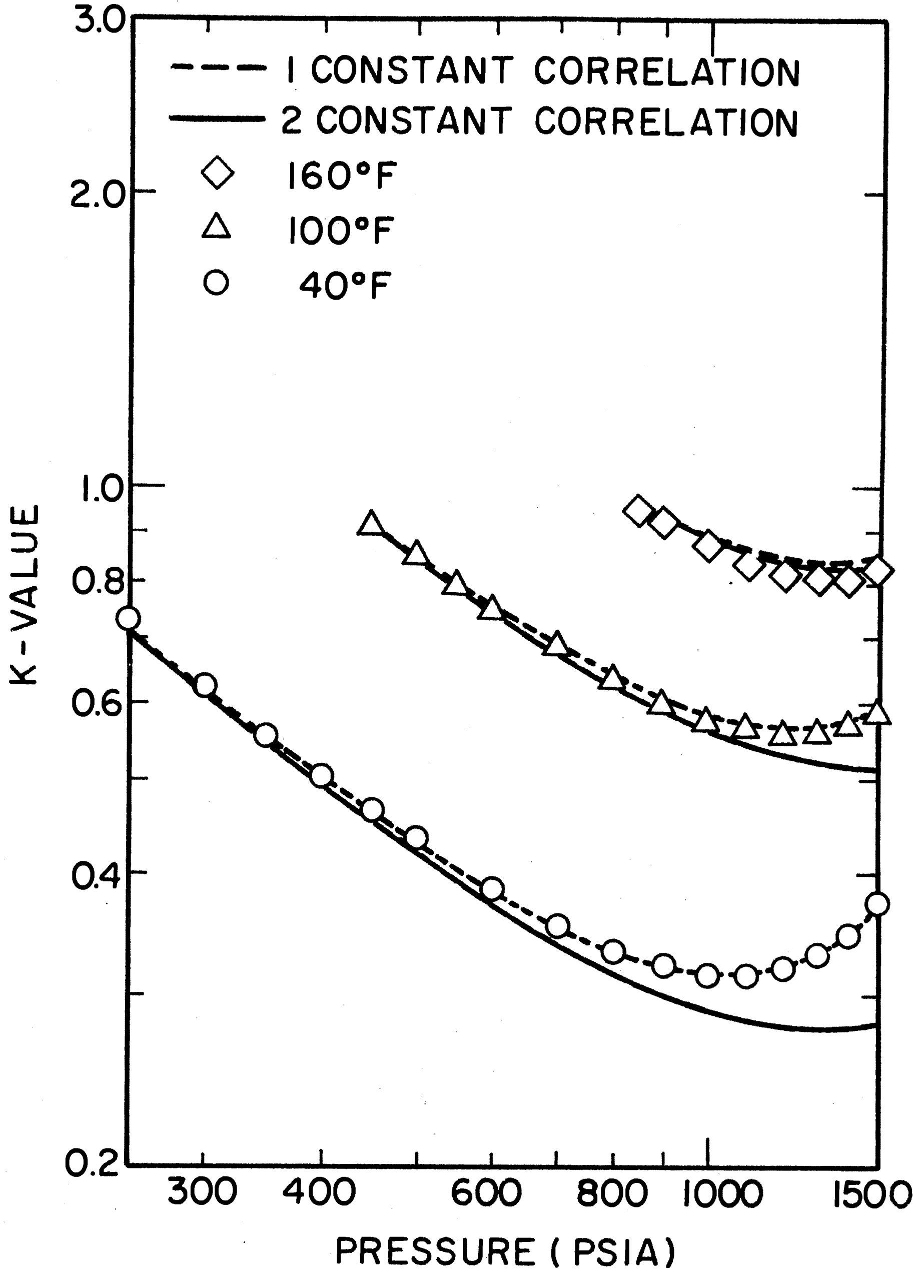

Figure 32. Predicted K-values for Hydrogen Sulfide in the Methane+ Hydrogen Sulfide Binary System

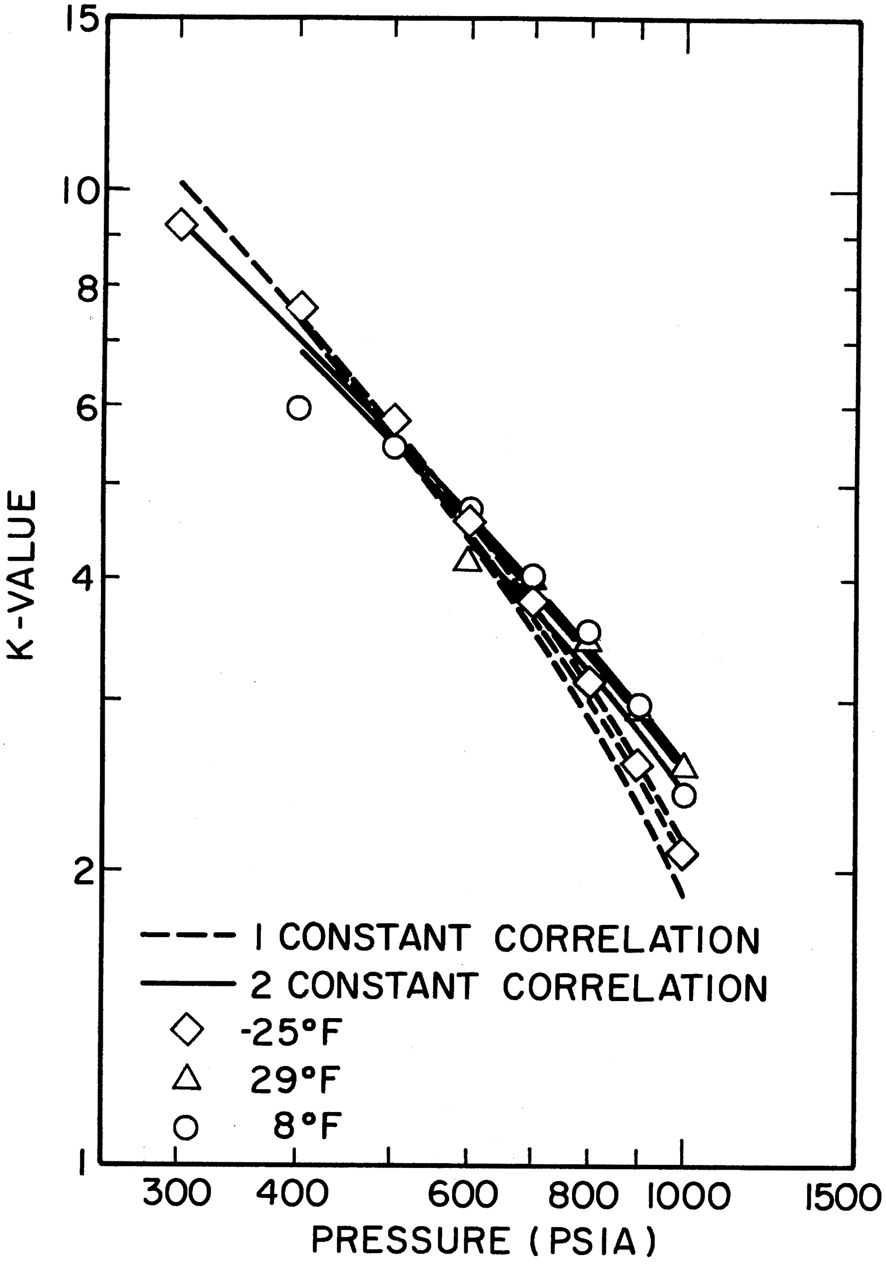

Figure 33. Predicted K-values for Methane in the Methane+Carbon Dioxide Binary System

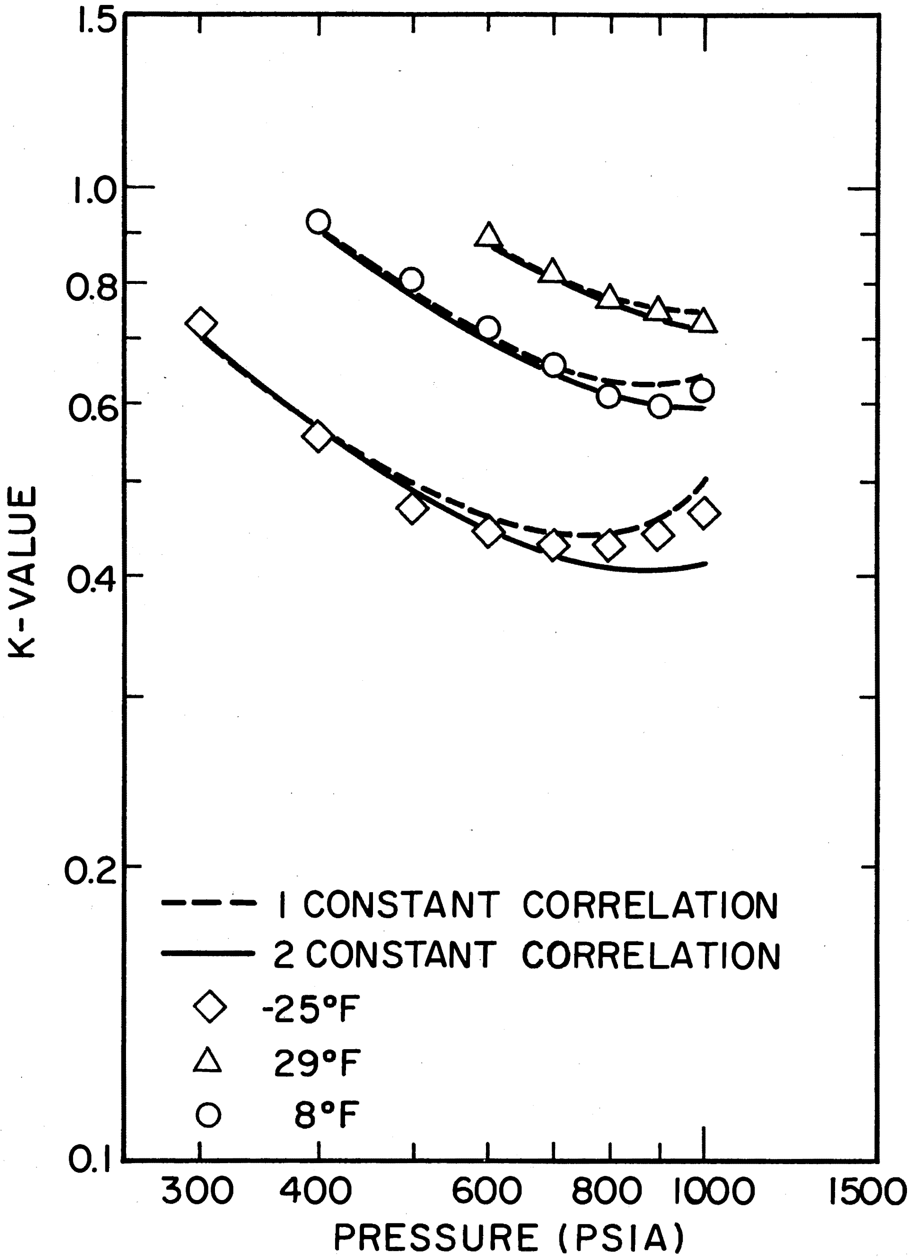

Figure 34. Predicted K-values for Carbon Dioxide in the Methane+ Carbon Dioxide Binary System

The results of the correlational work are given by the dashed lines (one constant correlational method) and the solid lines (two constant method). Some of the predicted isotherms are not shown to prevent cluttering the figures. In general, the highest and lowest temperatures are shown. The intermediate isotherms show similar trends. In Figure 25, which shows heptane K-values for the methane-heptane system, the 0°F and -40°F isotherms are data which were taken much more recently than the -20°F isotherm and were measured using an improved technique. In fact, the heptane, MCH, and toluene K-values of Chang and Kobayoahi are all suspect. The correlation fits the new data quite well while the older data (-20°F) differs greatly from the correlation. Since Kohn and Bradish (22) did not report the octane K-values of their work, no figure is shown illustrating the correlation.

The results shown in Table XI and Figures 24 through 34 show that the two constant correlational method seems to fit the experimental data slightly better than the one constant correlational method.

Table XII lists the results of the correlation of CO_2 and H_2S K-values at infinite dilution from the experimental data of this work. The table gives the average absolute percent deviation between the experimental and predicted K-values. Results are shown for both correlational methods and for the original Soave modification of the R-K equation of state.

The two correlations of this work fit the experimental data much better than the Soave equation. The results indicate that the one constant correlational method fits the experimental data of this work slightly better than the two constant method for all cases except the methane

TABLE XII

RESULTS OF CORRELATION OF CARBON DIOXIDE (HYDROGEN SULFIDE) K-VALUES AT INFINITE DILUTION IN METHANE+SOLVENT BINARY SYSTEMS

			Average Absolute Percentage Deviation In Predicted K-Value			
System	Soave		Two Parameter Method k_{ij}, ℓ_{ij}		One Parameter Method k'_{ij}	
C_1 - C_7	58.5	(37.5)	4.5	(4.4)	4.3	(4.1)
C_1 - C_8	57.4	(33.1)	2.6	(3.4)	1.9	(1.7)
C_1 - MCH	66.54	(45.0)	4.5	(3.6)	3.7	(2.0)
C_1 - TOL	58.57	(69.7)	5.5	(2.2)	7.1	(3.2)

system. Figure 35 through 38 illustrate the fit of the two correlational methods to the experimental data.

The results demonstrate that the two parameter correlation provided in general a better fit to the binary data; however, the one parameter correlation seems to fit the data of this work better. The differences between the two correlations were minor. Both correlation methods fit the experimental data considerably better than the original Soave modification of the R-K equation of state.

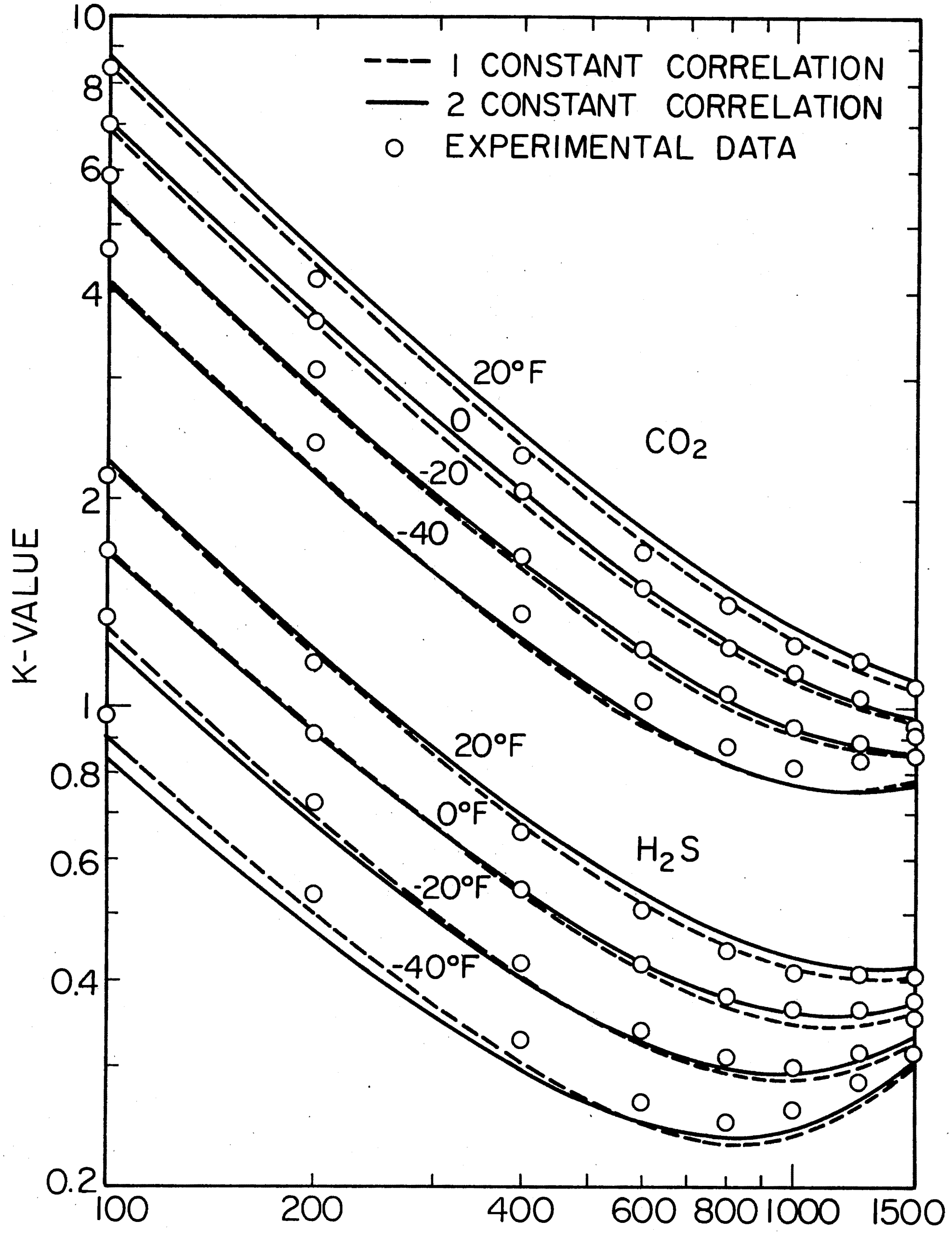

Figure 35. Predicted K-values for Carbon Dioxide and Hydrogen Sulfide at Infinite Dilution in the Methane+ n-Heptane System

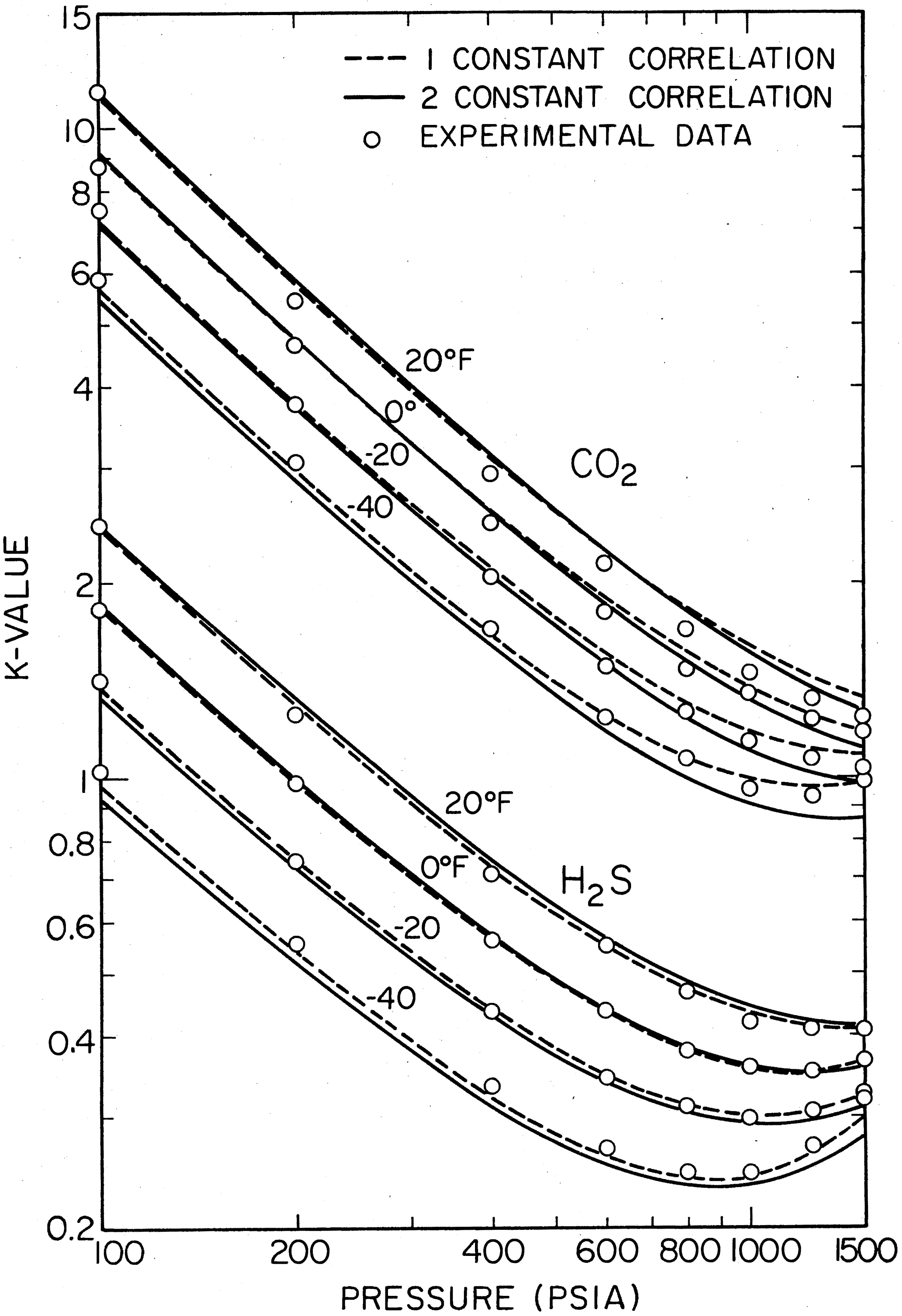

Figure 36. Predicted K-values for Carbon Dioxide and Hydrogen Sulfide at Infinite Dilution in the Methane+Methylcyclohexane System

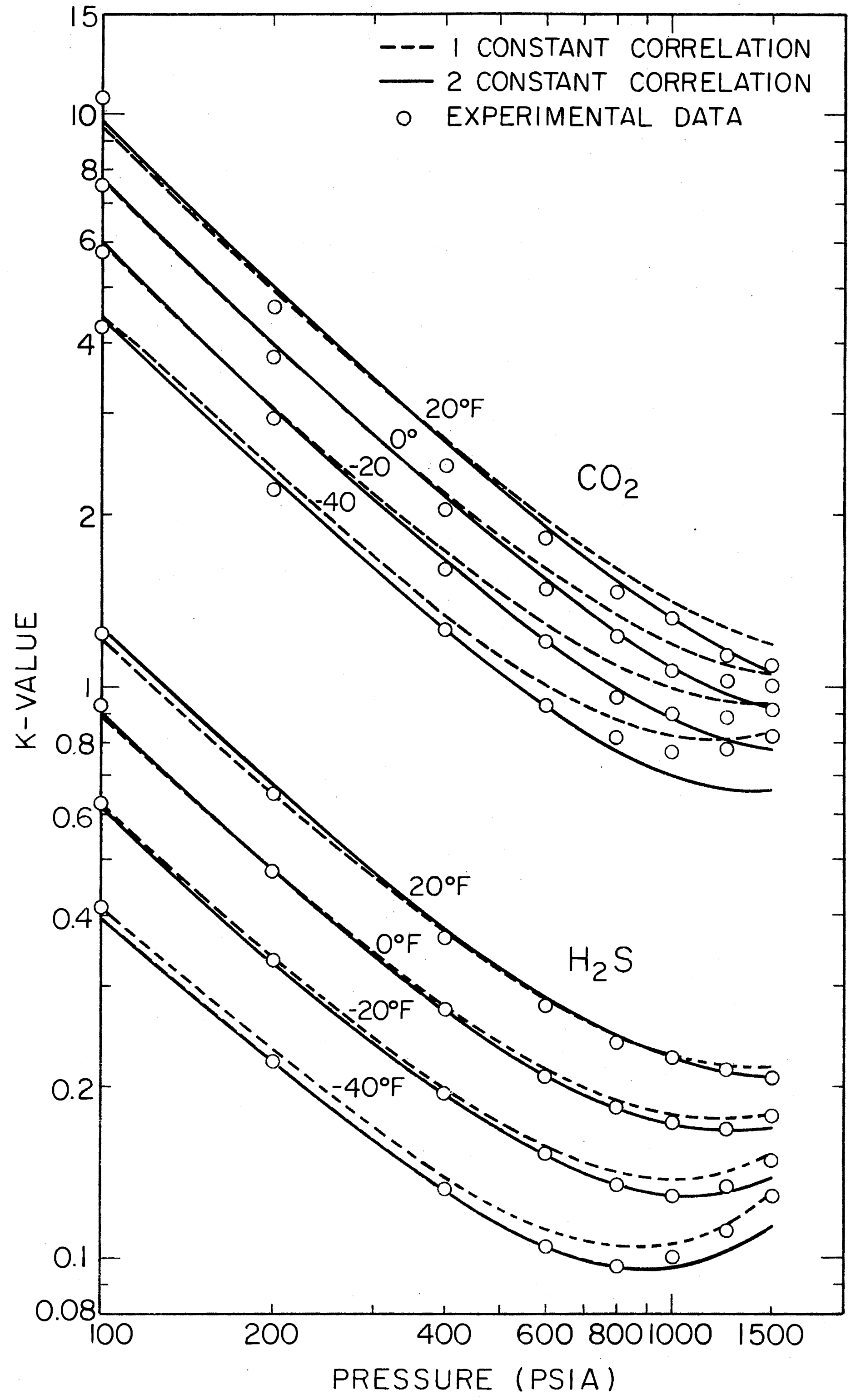

Figure 37. Predicted K-values for Carbon Dioxide and Hydrogen Sulfide at Infinite Dilution in the Methane+Toluene System

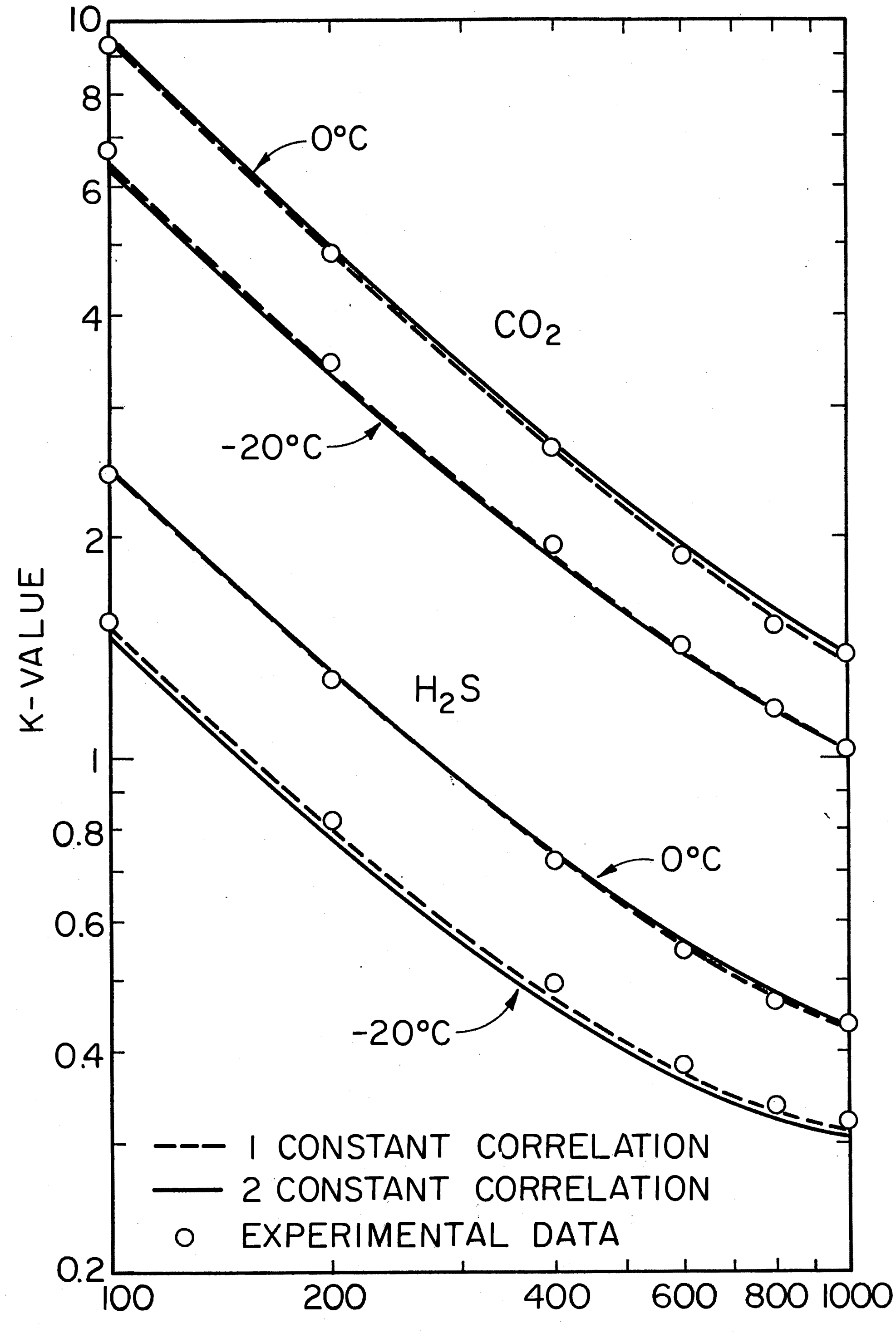

Figure 38. Predicted K-values for Carbon Dioxide and Hydrogen Sulfide at Infinite Dilution in the Methane+n-Octane System

CHAPTER VIII

CONCLUSIONS AND RECOMMENDATIONS

This study consists of an investigation of the vaporization equilibrium ratios of CO_2 and H_2S in aromatic and naphthenic solvents. An apparatus was constructed suitable for determination of chromagographic K-values for the components and conditions of interest in this study. The data of this study were correlated by a modified version of the Redlich-Kwong equation of state.

The following conclusions were made from this study:

(1) The design of the apparatus was sound, as illustrated by the precision and accuracy of the data taken. The apparatus was simple to use and experimental measurements were easy to make.

(2) The chromatographic data of this work and the static cell data of this work for the CO_2 or H_2S in methane-octane system show reasonable agreement. The fact that these two experimental methods are entirely different tends to substantiate the accuracy as well as the precision of the present results.

(3) Error analysis indicates that the maximum expected uncertainty for the chromatographic experiment was less than 2.5%; however, inspection of the experimental results leads to the conclusion that the uncertainty is probably on the order of 3%. Similarly, for the windowed cell experiment, error analysis

predicts an uncertainty of 5.0% while experimental results also demonstrate an uncertainty of 5.0%.

(4) Based on the agreement of the H_2S K-values in octane by the two separate techniques of this work, the H_2S K-values of Asano (1) appear to be somewhat low.

(5) The presence of the aromatic component toluene in a solvent reduces the K-value of H_2S substantially relative to the paraffinic solvents, while the naphthenic component methylcyclohexane (MCH) has only a minor effect relative to the paraffins. These effects are very similar to that seen by Yarborough (49).

(6) The presence of the naphthenic component methylcyclohexane in a solvent enhances the K-values of CO_2 by as much as 30% relative to the paraffinic solvents. The aromatic component toluene has only a minor effect relative to the paraffins on the K-values.

(7) The data of this work have been represented adequately by a modified Redlich-Kwong equation of state. This correlational scheme illustrates the applicability of the modified Soave equation to the representation of the phase behavior of H_2S and CO_2 in various hydrocarbon solvents.

(8) The modified Soave equation of state with one empirical interaction constant fit the ternary data of this work slightly better than the model employing two interaction constants, although the binaries were better represented by a two constant fit. The conclusion was reached that no justification was found for the inclusion of an additional second constant in the correlation framework.

The following recommendations are made from the results of this study for future work in this area of research:

(1) In this work, the detector was downstream of the expansion valve, in a region of near atmospheric pressure. If a detector which could operate at the system pressure could be installed above the expansion valve, the more accurate method for calculating V_g suggested by Yudovich (51) could be employed (on systems for which liquid volumetric data exist for the binary carrier gas-solvent system).

(2) The correlations, in general, predict K-values which are slightly high at the higher temperature and slightly low at the lower temperature than the experimental data. This indicates that an empirical correlation factor which is temperature dependent could be employed to improve the accuracy of the prediction method.

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APPENDIX A

ERROR ANALYSIS

Error analysis was used to establish limits of accuracy for the calculation of K-values and to point out major sources of error present in the experiment. Beers (2) presents a detailed discussion of error analysis. His method for calculation of expected uncertainty was used in this work.

The experimental measurement errors were assumed to be independent and uncorrelated, that is, the accuracy with which the pressure could be measured was independent of the temperature, etc. Beers describes the effects of independent and uncorrelated errors on the dependent variables with the following equation

$$\varepsilon_y^2 = \sum_{i=1}^{n} \left(\frac{\partial y}{\partial x_i} \varepsilon_{xi}\right)^2 \qquad \text{(A-1)}$$

where the equation relating dependent and independent variables is given by

$$y = y(x_1, x_2, \ldots x_n) \qquad \text{(A-2)}$$

Chromatographic Experiment

For this work the equations used in the error analysis were

$$K_i = \frac{W_L^o}{(1-\chi_1)\,\rho_g\,(V_{Ri} - V_g)} \qquad \text{(A-3)}$$

where

$$V_{Ri} = t^c_{Ri}\ f^c - t^B_{Ri}\ f^B \qquad \text{(A-4)}$$

$$f = f_a \frac{P_a}{P} \frac{T}{T_a} Z_g \qquad \text{(A-5)}$$

$$f_a = \frac{V_B}{t_B} \left[\frac{P_{aa} - P_{H_2O}}{P_a}\right] \qquad \text{(A-6)}$$

$$V_g = 1.143\ V_{RHe} - 0.143\ V_{RAr} \qquad \text{(A-7)}$$

$$V_{RHe} = t^c_{R_{He}}\ f^c - t^B_{RHe}\ f^B \qquad \text{(A-8)}$$

$$V_{RAr} = t^c_{RAr}\ f^c - t^B_{RAr}\ f^B \qquad \text{(A-9)}$$

$$P_{H_2O} = 9.412 - 0.266\ T_a + 0.0366\ T_a^2 \qquad \text{(A-10)}$$

$$\rho_g = \frac{n}{V} = \frac{P}{Z_g RT} \qquad \text{(A-11)}$$

Although P_a, T_a, and t_B vary slightly from sample to sample, they were considered to be constant in the error analysis. Equations A-3 through A-11 can be combined to express K_i as

$$K_i = \frac{W_L^o R T_a t_B}{(1-\chi_1)(\ t_{Ri} - 1.143\ t_{RHe} + 0.143\ t_{RAr})V_B(P_a - 9.412 + 0.266T_a - 0.0366T_a^2)} \qquad \text{(A-12)}$$

where

$$t_{Ri} = t^c_{Ri} - t^B_{Ri}$$

Errors arise in the measurement of W_L^o, χ_1, t_{Ri}, t_{RHe}, t_{RAr}, P , T , V_B and t_B. The equation of Beers gives

$$\varepsilon^2_{K_i} = \left(\frac{\partial K_i}{\partial W^o_L}\right)^2 \varepsilon^2_{W^o_L} + \left(\frac{\partial K_i}{\partial \chi_1}\right)^2 \varepsilon^2_{\chi_1} + \left(\frac{\partial K_i}{\partial P_a}\right)^2 \varepsilon^2_{P_a} + \left(\frac{\partial K_i}{\partial t^c_{Ri}}\right)^2 \varepsilon^2_{t^c_{Ri}}$$

$$+ \left(\frac{\partial K_i}{\partial t^c_{RAr}}\right)^2 \varepsilon^2_{t^c_{RAr}} + \left(\frac{\partial K_i}{\partial t^c_{RHe}}\right)^2 \varepsilon^2_{t^c_{RHe}} + \left(\frac{\partial K_i}{\partial t^B_{Ri}}\right)^2 \varepsilon^2_{t^B_{Ri}} + \left(\frac{\partial K_i}{\partial t^B_{RAr}}\right)^2 \varepsilon^2_{t^B_{RAr}}$$

$$+ \left(\frac{\partial K_i}{\partial t^B_{RHe}}\right)^2 \varepsilon^2_{t^B_{RHe}} + \left(\frac{\partial K_i}{\partial T_a}\right)^2 \varepsilon^2_{T_a} + \left(\frac{\partial K_i}{\partial V_B}\right)^2 \varepsilon^2_{V_B} + \left(\frac{\partial K_i}{\partial t_B}\right)^2 \varepsilon^2_{t_B} \qquad \text{(A-13)}$$

An equation for the percent error in the K-value can be obtained by dividing equation (A-13) by K_i^2. Taking the partial derivatives and dividing through by K_i^2, equation (A-13) reduces to

$$\frac{\varepsilon^2_{K_i}}{K_i^2} = \frac{\varepsilon^2_{W^o_L}}{W^{o2}_L} + \frac{\varepsilon^2_{\chi_1}}{(1-\chi_1)^2} + \frac{\varepsilon^2_{P_a}}{[P_a-9.412+0.266T_a-0.0366T_a^2]^2}$$

$$+ \frac{\varepsilon^2_{t^c_{Ri}} + \varepsilon^2_{t^B_{Ri}} + (1.143\varepsilon_{t^c_{RHe}})^2 + (1.143\varepsilon_{t^B_{RHe}})^2}{(\Delta t_{Ri} - 1.143\Delta t_{RHe} + 0.143\Delta t_{RAr})^2}$$

$$+ \frac{(0.143\varepsilon_{t^c_{RAr}})^2 + (0.143\varepsilon_{t^B_{RAr}})^2}{(\Delta t_{Ri} - 1.143\Delta t_{RHe} + 0.143\Delta t_{RAr})^2}$$

$$+ \frac{\varepsilon^2_{t_B}}{t_B^2} + \frac{\varepsilon^2_{V_B}}{V_B^2} + \frac{\varepsilon^2_{T_a}}{\left[\dfrac{T_a(P_a-9.412+0.266T_a-0.0366T_a^2)}{(P_a-9.412+0.0366T_a^2)}\right]^2} \qquad \text{(A-14)}$$

The weight of stationary liquid, W^o_L, is calculated using equations (5-2) and (5-3), that is,

$$W^o_L = \left[\frac{SWW - SWD}{SWW - CW}\right]\left[\frac{PCF - PCE}{LMW}\right] \qquad \text{(A-15)}$$

where SWW-solid weight wet

SWD-solid weight dry

CW - crucible weight

PCF-weight of packed column full

PCE-weight of packed column empty

LMW-liquid molecular weight

using Beers equation to get percent error, we have

$$\frac{\varepsilon^2_{W_L^o}}{W_L^{o2}} = \frac{\varepsilon^2_{SWW}}{\left[\frac{SWW - SWD)(SWW - CW)}{(SWD - CW)}\right]^2} + \frac{\varepsilon^2_{SWD}}{(SWW - SWD)^2}$$

$$+ \frac{\varepsilon^2_{CW}}{(SWW - CW)^2} + \frac{\varepsilon^2_{PCF}}{(PCF - PCE)^2} + \frac{\varepsilon^2_{PCE}}{(PCF - PCE)^2} \qquad \text{(A-16)}$$

The error in the measurement of the variables in equations (A-14) and (A-16) will now be discussed.

(1) SWW, SWD, CW, PCF, PCE - All values are measured on the mettler balance. Expected error is ± 0.00020 gm.

(2) χ_1 - The concentrations of methane in the stationary liquid come from the literature (4, 5, 6, 22) and have an uncertainty of ± 0.2%.

(3) P_a - The ambient pressure was measured with a mercury in glass thermometer with 0.1 mm divisions. Readings were taken once an hour, varying by at most 0.4 mm Hg. Thus ε_{P_a} was equal to ± 0.2 mm Hg.

(4) t_B - The time required for a volume of gas V_B to pass through the bubble meter was measured to the nearest 0.02 seconds. It should be accurate to 0.05 seconds.

(5) V_B - The standard deviation in the calibration of the bubble meter was $\pm$ 0.019 cc.

(6) T_a - The ambient temperature was measured to within 0.1°C.

(7) t_{Ri} - The uncertainty in the solute retention time depended upon the chart speed. For high pressure H_2S samples, $\varepsilon_{t_{Ri}}$ was estimated to be 0.6 seconds, since a chart speed of 2 inch/minute was used. At lower pressures a chart speed of 5 inch/minute was used, leading to an estimated uncertainty of 0.3 seconds.

(8) t_{RHe}, t_{RAr} - The uncertainty in the solute times of He and Ar was 0.3 seconds.

Sample calculations illustrating the use of the above equations are given in Appendix D. The results of the error analysis are discussed in Chapter VII.

Classical Windowed Cell Experiment

This section will describe the derivation of the equations used to calculate the maximum expected uncertainty in the K-values from the windowed cell. The method of Beers (2) was again used, similar to that of the last section.

The K-values were calculated using Equations (3-21), (3-23) and (3-24),

$$\frac{n_{Ci}}{n_{C1}} = [R_{1i}] \left[\frac{\text{counts } C_i}{\text{counts } C1}\right] \tag{3-21}$$

$$x_i = \frac{n_{Ci}/n_{C1}}{\sum_i (n_{Ci}/n_{C1})} \tag{3-23}$$

$$K_i = x_i/y_i \tag{3-24}$$

The ratio of counts (counts C_i/counts Cl) will be abbreviated by "C_i," while R_{1i} will be simply written "R_i." Thus, the mole fraction of component i, x_i, in the liquid or vapor phase can be expressed as

$$x_i = \frac{R_i C_i}{\sum_j R_j C_j} \qquad \text{(A-17)}$$

The expected errors in the measurement of R_j and C_j can be estimated. Applying the equation of Beers to Equation (A-17), and dividing through by x_i^2 to get percent expected uncertainty, the result is

$$\frac{\varepsilon_{x_i}^2}{x_i^2} = \frac{\sum_{j=1}^{n} [(\frac{\partial x_j}{\partial R_j})^2 \varepsilon_{R_j}^2 + (\frac{\partial x_j}{\partial C_j})^2 \varepsilon_{cj}^2]}{x_i^2} \qquad \text{(A-18)}$$

Applying Equation (A-1) to (A-18) gives the following result,

$$\frac{\varepsilon_{x_i}^2}{x_i^2} = (1 - x_i)^2 [(\frac{\varepsilon_{Ri}}{R_i})^2 + (\frac{\varepsilon_{Ci}}{C_i})^2]$$

$$+ \sum_{\substack{j=1 \\ j \neq 1}}^{n} (x_j)^2 [(\frac{\varepsilon_{R_j}}{R_j})^2 + (\frac{\varepsilon_{C_j}}{C_j})^2] \qquad \text{(A-19)}$$

The above equation can be used to calculate the maximum expected error for both the liquid and vapor mole fractions.

Equation (A-1) can be applied to Equation (3-24) to give the expected uncertainty in the calculation of the K-value from the windowed cell experiment, or

$$(\frac{\varepsilon_{Ki}}{K_i})^2 = (\frac{\varepsilon_{xi}}{x_i})^2 + (\frac{\varepsilon_{yi}}{y_i})^2 \qquad \text{(A-20)}$$

APPENDIX B

METHOD FOR CALCULATING EMPIRICAL CORRELATION FACTORS FOR BASIC SOAVE EQUATION

The empirical correlation factors of the methane binaries were determined by fitting the correlation to binary data from the literature. The results were then used along with the data of this work to calculate the empirical correlation factors of the CO_2 and H_2S in solvent binaries. Figure 39 is a flow diagram describing the procedure for calculating the empirical correlation factor k'_{ij} (one constant method). Calculation of k_{ij} and ℓ_{ij} (two constant method) is identical except that the mixing rules differ slightly (as given in Equations (3-54) to (3-57)), and two constants must be adjusted in minimizing the sum of squares. A listing of the subroutines which perform the Soave calculations is given in Appendix H.

The calculation of the best empirical correlation factors consists of two main loops. The innermost loop uses the present correlation factor to calculate K-values for each component at all temperatures and pressures and the outmost loop adjusts the correlation factors until the best fit of the experimental data is achieved.

A description of the procedure follows:

(1) Critical temperatures and pressures, and acentric factors were read in for each component. An initial value for the correlation factor was read in.

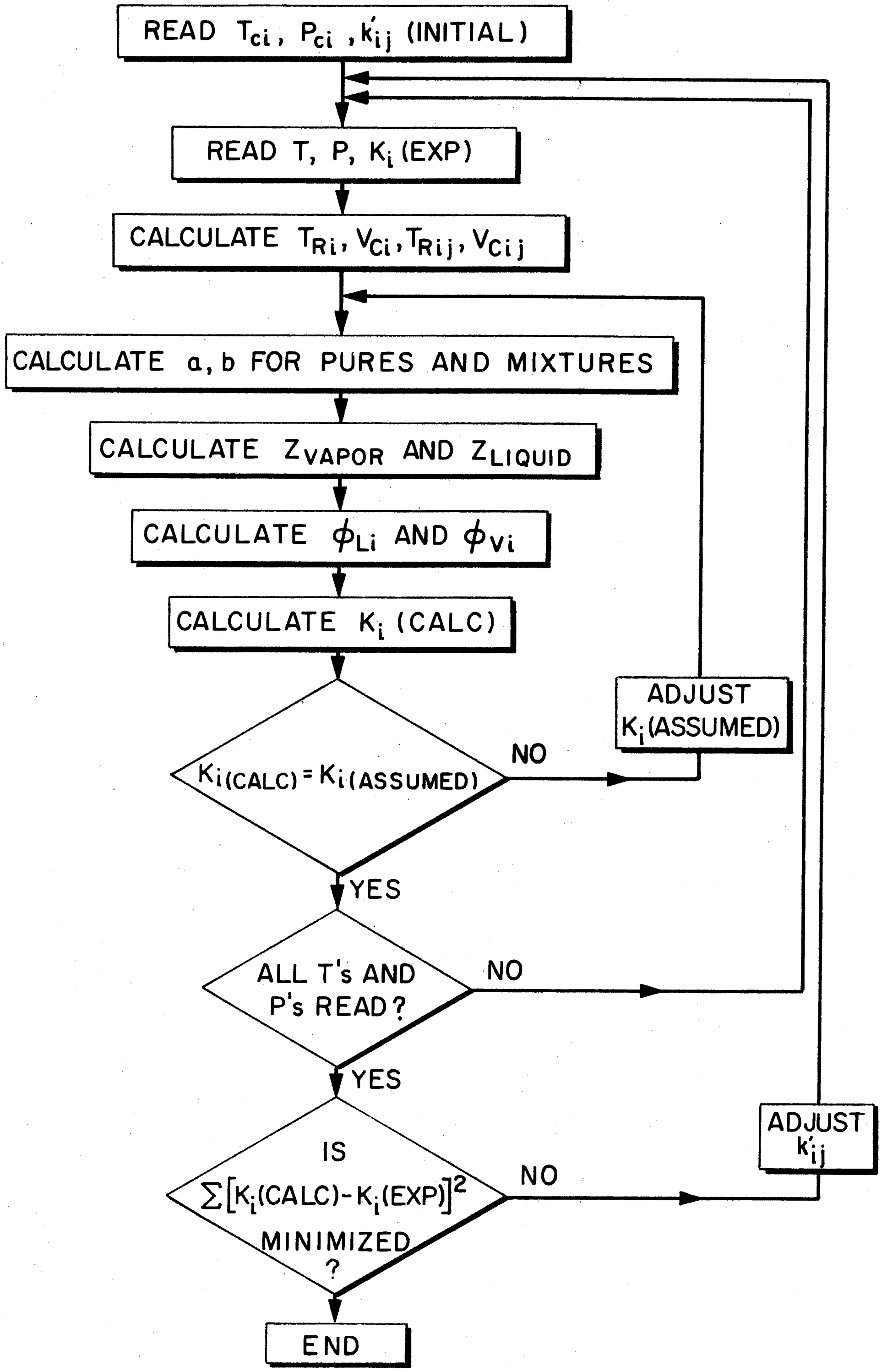

Figure 39. Flow Diagram of Method Used to Calculate Empirical Correlation Factors

(2) The temperature, pressure and corresponding experimental K-values for each component were read in. The experimental K-values were used as initial guesses in the trial and error solution of the K-value predicted by the Soave equation with the present correlation factor.

(3) Reduced temperatures, critical volume and critical temperature for mixtures were calculated.

(4) Liquid and vapor mole fractions were calculated from the K-values.

(5) A, B, and α were calculated for the pure components and then for the binaries.

(6) The liquid and vapor compressibilities were calculated by an interval halving solution of the cubic form of the Soave modification of the R-K equation; i.e., Equation (3-28). Liquid and vapor volumes were calculated with the compressibilities.

(7) Liquid and vapor fugacity coefficients were calculated for each component using equation (3-50). K-values were then calculated for each component using the fugacity coefficients.

(8) If $\left| \frac{K_{calc} - K}{k_{calc}} \right| \not< .001$ for all K_i, then the calculated K_i is used as a new guess for K_i and steps 3 through 7 are required.

(9) If K_{calc} and K_{exp} agree, steps 2 through 8 are repeated for a new temperature and pressure.

(10) When all temperatures and pressures have been run, the sum of the deviations is calculated; i.e., $\sum_{T,P} (K_{calc} - K_{exp})^2$

(11) A regression technique is then used to calculate a new empirical correlation factor. The above steps were repeated and a new sum of squares calculated.

(12) The empirical correlation factor was adjusted until the sum of squares was minimized.

APPENDIX C

DERIVATION OF EQUATION 3-59

The general equation for calculating the fugacity coefficient of component k in a multicomponent system using the Redlich-Kwong equation of state will be developed in this appendix.

The fugacity coefficient of a component is defined (37) as the ratio of that component's fugacity in the mixture to its partial pressure, or

$$\phi_i = \frac{f_i}{y_i P}$$

Prausnitz (33) presents the following equation, which relates ϕ_i to the volumetric properties by

$$\ln \phi_i = \frac{1}{RT} \int_V^\infty \left[\left(\frac{\partial P}{\partial n_i}\right)_{T,\ V,\ n_j} - \frac{RT}{V} \right] dV - \ln Z \tag{3-59}$$

The above equation can be applied to pressure explicit equations of state, thus making it useful for this work.

The Redlich-Kwong equation of state can be written as

$$P = \frac{RT}{(\bar{V}-b)} - \frac{a}{T^{1/2}\ \bar{V}\ (\bar{V}+b)} \tag{3-32}$$

where

$$a = \sum_j \sum_k y_j y_k a_{jk}$$

$$b = \sum_j \sum_k y_j y_k b_{jk}$$

and

$$\bar{V} = V/n \tag{C-1}$$

Since the partial derivative of P with respect to n_K must be taken, a and b must be written as

$$a = \frac{1}{n^2} \sum_j \sum_k n_j n_k a_{jk} = \frac{\tilde{a}}{n^2} \tag{C-2}$$

and

$$b = \frac{1}{n^2} \sum_j \sum_k n_j n_k b_{jk} = \frac{\tilde{b}}{n^2} \tag{C-3}$$

where

$$n = \sum_j n_j = \text{total moles}$$

Substituting Equations (C-1), (C-2), and (C-3) into Equation (3-32) gives

$$P = \frac{RTn^2}{Vn - (\sum_j \sum_k n_j n_k b_{jk})} - \frac{n(\sum\sum_{jk} n_j n_k a_{jk})}{T^{½} V[Vn + (\sum_j \sum_k n_j n_k b_{jk})]} \tag{C-4}$$

The following identities should be noted:

$$\frac{\partial(n)}{\partial(n_i)} = \frac{\partial(\sum_j n_j)}{\partial n_i} = 1 \tag{C-5}$$

$$\frac{\partial n^2}{\partial n_i} = \frac{\partial[(\sum n_j)^2]}{\partial ni} = 2n \tag{C-6}$$

$$\frac{\partial(\sum\sum_{ij} n_i n_j b_{ij})}{\partial n_i} = 2 \sum_i n_i b_{ik} \tag{C-7}$$

$$\frac{\partial[(\sum_i n_i)(\sum\sum_{jk} n_j n_k a_{jk})]}{\partial n_i} = (\sum\sum_{ij} n_i n_j a_{ij}) + 2(\sum_i n_i)(\sum_i n_i a_{ik})$$

$$= \tilde{a} + 2n(\sum_i n_i a_{ik}) \tag{C-8}$$

From the above identities the following can be written

$$\left(\frac{\partial P}{\partial n}\right)_{T,V,n_j} = \frac{(Vn-\tilde{b})2RTn - RTn^2(V-2\sum_i n_i b_{ik})}{(Vn-\tilde{b})^2} \qquad \text{(C-9)}$$

$$-\frac{T^{\frac{1}{2}}V\,[(Vn+\tilde{b})(\tilde{a}+2n\sum_i n_i a_{ik}) - \tilde{n}a(V+2\sum_i n_i b_{ik})]}{TV^2\,(Vn+\tilde{b})^2} \qquad \text{(C-9)}$$

Now the following integral must be evaluated:

$$\int_V^\infty \left[\left(\frac{\partial P}{\partial n}\right)_{T,V,n_k} - \frac{RT}{V}\right] dV$$

Table XIII illustrates the integration. Equation C-9 will be separated into six terms. Column 1 of Table XIII shows each of the six terms as they are in Equations C-9. Column 2 shows each of the terms as they were written before being integrated. The term inside the square brackets is what must be integrated. Column 3 shows the results of integrating each term from V to ∞. Term number 7 is the $(-\frac{RT}{V})$ which is not a part of $(\frac{\partial P}{\partial n_i})$. Term 8 is the $(-\ell n\ z)$ term which is outside the integral sign in Equation (3-51).

The Equations (C-1), (C-2), and (C-3) can be substituted into the terms in column 3 for a, b, and V. The terms can then be summed and rearranged to give

$$\ell n\ \phi_i = -\ell n\ \frac{P(\bar{V}-b)}{RT} + \frac{2\sum_i y_i b_{ik} - b}{(\bar{V}-b)} - \frac{2\sum_i y_i a_{ik}}{RT^{1.5}b}\ \ell n\left(\frac{\bar{V}+b}{\bar{V}}\right)$$

$$-\frac{a(2\sum_i y_i b_{ik} - b)}{RT^{1.5}b}\left\{\frac{1}{\bar{V}+b} - \frac{1}{b}\ \ell n\left(\frac{\bar{V}+b}{\bar{V}}\right)\right\} \qquad \text{(3-59)}$$

TABLE XIII

ITEMIZED LIST OF TERMS IN INTEGRATION OF EQUATION 3-51

	1	2	3
1	$\frac{(Vn-\tilde{b})2RTn}{(Vn-\tilde{b})^2}$	$2RT\ [\frac{1}{(V-\frac{\tilde{b}}{n})}]$	$2RT\ [\ln\infty] - 2RT\ \ln\ (V-\frac{\tilde{b}}{n})$
2	$-\frac{RTn^2V}{(Vn-\tilde{b})^2}$	$-RT\ [\frac{V}{(V-\frac{\tilde{b}}{n})^2}]$	$-RT\ \ln\infty + RT\ \ln\ (V-\frac{\tilde{b}}{n}) - \frac{RT\ \tilde{b}/n}{(V-\frac{\tilde{b}}{n})}$
3	$\frac{2\sum_i n_i b_{ik}}{(Vn-\tilde{b})^2}$	$2RT(\sum_i n_i b_{ik})\ [\frac{1}{(V-\frac{\tilde{b}}{n})^2}]$	$2RT\ (\sum_i n_i b_{ik})\ \frac{1}{(V-\frac{\tilde{b}}{n})}$
4	$\frac{-T^{1/2}V(Vn+\tilde{b})(\tilde{a}+2n\sum_i n_i a_{ik})}{TV^2(Vn+\tilde{b})^2}$	$-\frac{(\frac{\tilde{a}}{n}+2\sum_i n_i a_{ik})}{T^{1/2}}\ [\frac{1}{V(V+\frac{\tilde{b}}{n})}]$	$-\frac{(\frac{\tilde{a}}{n}+2\sum_i n_i a_{ik})}{T^{1/2}(\tilde{b}/n)}\ \ln\ (\frac{(V+\frac{\tilde{b}}{n})}{V})$
5	$\frac{T^{1/2}V^2n\tilde{a}}{TV^2(Vn+\tilde{b})^2}$	$\frac{\tilde{a}/n}{T^{1/2}}\ [\frac{1}{(V+\frac{\tilde{b}}{n})^2}]$	$\frac{\tilde{a}/n}{T^{1/2}}\ (\frac{1}{(V+\frac{\tilde{b}}{n})})$
6	$\frac{T^{1/2}Vn\tilde{a}2\sum_i n_i b_{ik}}{TV^2(Vn+\tilde{b})^2}$	$\frac{2(\frac{\tilde{a}}{n})(\sum_i n_i b_{ik})}{T^{1/2}}\ [\frac{1}{V(V+\frac{\tilde{b}}{n})^2}]$	$\frac{2(\frac{\tilde{a}}{n})(\sum_i n_i b_{ik})}{T^{1/2}}\ [\frac{1}{\frac{\tilde{b}}{n}\ (V+\frac{\tilde{b}}{n})}] + \frac{1}{(\tilde{b}/n)^2}\ \ln\ (\frac{V+\frac{\tilde{b}}{n}}{V})$
7	$\frac{RT}{V}$	$RT\ [\frac{1}{V}]$	$-RT\ \ln\ \infty + RT\ \ln\ V$
8			$-\ln\ Z$

APPENDIX D

SAMPLE CALCULATIONS

The purpose of this appendix is to present examples of all calculations made for the experimental part of this work. Included are the following: (1) error analysis, (2) calculation of response factors for the detector of the windowed cell work, (3) calculation of K-values from equilibrium cell data, and (4) calculation of K-values from the chromatographic apparatus.

Error Analysis of Chromatographic Experiment

This section will illustrate the use of the equations presented in Appendix A. The percent expected uncertainty in the measurement of K-values by the chromatographic technique can be expressed with Equations (A-14) and (A-16). The equations will not be written out in full here. Each term of the equations will be evaluated in this section, and the percent expected uncertainty will be calculated. The example case will be the Cl-H_2S-TOL system at 20°F and 100 psia. The data are the following:

SWW = 14.75050 gm PCF = 67.95506 gm CW = 9.25865 gm

SWD = 13.24605 gm PCE = 65.11584 gm

$\varepsilon_{SWW}, \varepsilon_{SWD}, \varepsilon_{CW}, \varepsilon_{PCF}, \varepsilon_{PCE} = \pm.00020$ gm

$P_a = 740.8$ mmHg $\varepsilon_{Pa} = \pm 0.2$ mmHg

$T_a = 27.8^{\circ}C$ $\varepsilon_{Ta} = \pm 0.1^{\circ}C$

$t_B = 48.65$ sec $\qquad \varepsilon_{t_B} = 0.05$ seconds

$V_B = 45.0993$ $\qquad \varepsilon_{VB} = 0.019$ cc

$t^C_{RHe} = 114.21$ sec $\qquad t^B_{RHe} = 52.57$ sec

$t^C_{RAR} = 115.79$ sec $\qquad t^B_{RAR} = 52.76$ sec

$\varepsilon_{t^C_{RHe}}, \ \varepsilon_{t^B_{RHe}}, \ \varepsilon_{t^C_{RAR}}, \ \varepsilon_{T^B_{RAR}} = 0.3$ sec

$t^C_{RCO_2} = 136.94$ sec $\qquad \varepsilon_{t^C_{RCO_2}} = 0.3$ sec

$t^B_{RCO_2} = 52.69$ sec $\qquad \varepsilon_{t^B_{RCO_2}} = 0.3$ sec

From the above data, numerical solutions for each term are the following:

$$\frac{[\varepsilon_{SWW}]^2}{\left[\frac{(SWW-SWD)(SWW-CW)}{(SWD-CW)}\right]^2} = \frac{(.0002)^2 \quad (13.24605-9.25865)^2}{(14.75050-13.24605)^2 \quad (14.75050-9.25865)^2}$$

$$= \boxed{0.932 \times 10^{-8}}$$

$$\frac{[\varepsilon_{SWD}]^2}{(SWW-SWD)^2} = \frac{(.0002)^2}{(1.50445)^2} = \boxed{1.767 \times 10^{-8}}$$

$$\frac{[\varepsilon_{CW}]^2}{(SWW-CW)^2} = \frac{(.002)^2}{(5.49185)^2} = \boxed{0.1326 \times 10^{-8}}$$

$$\frac{[\varepsilon_{PCF}]^2}{(PCF-PCE)^2} = \frac{[\varepsilon_{PCE}]^2}{(PCF-PCE)^2} = \frac{(.0002)^2}{(67.95506-65.11584)^2} = \boxed{0.496 \times 10^{-8}}$$

$$\frac{[\varepsilon_{\chi_1}]^2}{(1-\chi_1)^2} = (0.002)^2 = \boxed{400. \times 10^{-8}}$$

$$\frac{[\varepsilon_{t_B}]^2}{t_B^2} = \frac{(0.05)^2}{(48.65)^2} = \boxed{105.6 \times 10^{-8}}$$

$$\frac{[\varepsilon_{V_B}]^2}{V_B^{\,2}} = \frac{(.019)^2}{(45.0993)^2} = \boxed{17.7 \text{ x } 10^{-8}}$$

$$\frac{[\varepsilon_{P_a}]^2}{[P_a - 9.412 + .266T_a - .0366T_a^{\,2}]} = \frac{(.2)^2}{[740.8 - 9.412 + .266(27.8) - .0366(27.8)^2]^2}$$

$$= \frac{(.2)^2}{(710.5)^2} = \boxed{7.92 \text{ x } 10^{-8}}$$

$$\frac{[\varepsilon_{T_a}]^2 \; (P_a - 9.412 + .0366T_a^{\,2})^2}{T_a^{\,2} \; (P_a - 9.412 + .266T_a - .0366T_a^{\,2}]^2} = \frac{(.1)^2 \; (740.8 - 9.412 + .0366 \; (27.8)^2]_1^2}{(27.8 + 273.15) \; (710.5)^2}$$

$$= \frac{(.1)^2 \; (759.7)^2}{(301.0)^2 \; (710.5)^2} = \boxed{12.6 \text{ x } 10^{-8}}$$

Since errors in retention times are all equal,

$$\frac{2[\varepsilon_{tRi}] + 2 \; (1.143\varepsilon_{tRHe})^2 + 2 \; (0.143\varepsilon_{tRAr})^2}{(\Delta t_{Ri} - 1.143\Delta t_{RAr} + 0.143\Delta t_{RAr})^2}$$

$$\frac{2\varepsilon_t^2 \; (1 + 1.143^2 + .143^2)}{(136.94 - 52.69) - 1.143 \; (114.21 - 52.57) + 0.143 \; (115.79 - 52.76)}$$

$$= \frac{2 \; (.3)^2 \; (2.327)}{(30.48)^2} = \boxed{45083. \text{ x } 10^{-8}}$$

Summing the terms listed above (in boxes) gives

$$\frac{[\varepsilon_{Ki}]^2}{K_i^{\,2}} = 4.563 \text{ x } 10^{-4}$$

$$\frac{\varepsilon_{Ki}}{K_i} = 2.1361 \text{ x } 10^{-2}$$

Thus, the percent expected uncertainty is equalty to 2.14%.

Investigation of the terms which contribute to $\frac{\varepsilon_{Ki}}{K_i}$ indicate that the errors in the measurement of the bubbletime, the retention times, and the solubility data from the literature make the largest contribution. Errors in retention times are definitely greatest. Results of other runs are given in Table V.

Error Analysis of Windowed Cell

This section illustrates the use of Equations (A-19) and (A-20) to calculate the maximum expected uncertainty in the calculation of K-values from windowed cell data. The data which were taken at 0°C and 1000 psia will be used in the example and are shown below.

	Relative Response and Ratio of Counts			Maximum Expected Uncertainty	
	Liquid	Vapor		Liquid	Vapor
R_{C1}	1.0	1.0	$\varepsilon_{R_{C1}} / R_{C1}$	0.0	0.0
C_{C1}	1.0	1.0	$\varepsilon_{C_{C1}} / C_{C1}$	0.0	0.0
R_{C8}	0.274	0.0805	$\varepsilon_{R_{C8}} / R_{C8}$	0.025	0.025
C_{C8}	5.6504	0.00967	$\varepsilon_{C_{C8}} / C_{C8}$	0.025	0.10
R_{H_2S}	0.739	0.739	$\varepsilon_{R_{H_2S}} / R_{H_2S}$	0.035	0.035
C_{H_2S}	0.1764	0.02902	$\varepsilon_{C_{H_2S}} / C_{H_2S}$	0.022	0.015
R_{CO_2}	0.716	0.716	$\varepsilon_{R_{CO_2}} / R_{CO_2}$	0.024	0.024
C_{CO_2}	0.1204	0.06098	$\varepsilon_{C_{CO_2}} / C_{CO_2}$	0.019	0.002

An explanation of the calculation of the relative response and the ratio of counts shown above can be found in later sections of this appendix, that is, the sections dealing with the "calibration of detectors" and the "calculation of K-values for the windowed cell."

The liquid mole fraction for each component was calculated using Equation (3-23), or

$$S = \sum_j R_j C_j = (1.0)(1.0) + (0.274)(5.6504) + (0.739)(0.1764) + (0.716)(0.1204)$$

$$= (1.0 + 1.5492 + 0.1304 + 0.0862 = 2.7658$$

$$x_{C1} = \frac{R_{C1}\ C_{C1}}{S} = \frac{1.0}{2.7658} = 0.3616$$

$$x_{C8} = \frac{R_{C8}\ C_{C8}}{S} = \frac{1.5492}{2.7658} = 0.5601$$

$$x_{H_2S} = \frac{R_{H_2S}\ C_{H_2S}}{S} = \frac{0.1304}{2.7658} = 0.0471$$

$$x_{CO_2} = \frac{R_{CO_2}\ C_{CO_2}}{S} = \frac{0.0862}{2.7658} = 0.0312$$

Vapor mole fractions were calculated similarly. The results were y_{C1} = 0.9382, y_{C8} = 0.0007, y_{H_2S} = 0.0201, and y_{CO_2} = 0.0410. Equation (A-19) was used to calculate the maximum expected error in mole fractions. For the liquid mole fraction for H_2S, the expected error was

$$\left(\frac{\varepsilon_{H_2S}}{x_{H_2S}}\right)^2 = (1-x_{H_2S})^2\left[\left(\frac{\varepsilon_{R_{H_2S}}}{R_{H_2S}}\right)^2\right] + x_{C1}^2\left[\left(\frac{\varepsilon_{R_{C1}}}{R_{C1}}\right)^2 + \left(\frac{\varepsilon_{C_{C1}}}{C_{C1}}\right)^2\right]$$

$$+ x_{C8}^2\left[\left(\frac{\varepsilon_{R_{C8}}}{R_{C8}}\right)^2 + \left(\frac{\varepsilon_{C_{C8}}}{C_{C8}}\right)^2\right] + x_{CO_2}^2\left[\left(\frac{\varepsilon_{R_{CO_2}}}{R_{CO_2}}\right)^2 + \left(\frac{\varepsilon_{C_{CO_2}}}{C_{CO_2}}\right)^2\right]$$

$$= (1.0 - 0.0471)^2\ [(0.035)^2 + (0.022)^2] + (0.3616)^2\ (0.0^2 + 0.0^2)$$

$$+ (0.5601)^2\ [(0.025)^2 + (0.025)^2] + (0.0312)^2\ [(0.024)^2 + (0.019)^2]$$

$$= 0.001552 + 0.0 + 0.000392 + 0.000001$$

$$= 0.001945$$

A similar calculation for the vapor phase gave

$$\left(\frac{\varepsilon_{y_{H_2S}}}{y_{H_2S}}\right)^2 = 0.001393$$

Thus the maximum expected error in the K-value was

$$\left(\frac{\varepsilon_{K_{H_2S}}}{K_{H_2S}}\right)^2 = \left[\left(\frac{\varepsilon_{x_{H_2S}}}{x_{H_2S}}\right)^2 + \left(\frac{\varepsilon_{y_{H_2S}}}{y_{H_2S}}\right)^2\right]^{1/2}$$

$$= (0.001945 + 0.001393)^{1/2}$$

$$= (0.0578)$$

The percent error was

$$\left(\frac{\varepsilon_{K_{H_2S}}}{K_{H_2S}}\right) \times 100 = 5.8\%$$

Similar calculations for CO_2, methane, and octane gave the following results:

$$\frac{\varepsilon_{K_{CO_2}}}{K_{CO_2}} = 4.3\%$$

$$\frac{\varepsilon_{K_{C8}}}{K_{C8}} = 10.4\%$$

$$\frac{\varepsilon_{K_{C1}}}{K_{C1}} = 2.0\%$$

For the data at $0^{\circ}C$ and 200 psia, the results were

$$\frac{\varepsilon K_{H_2S}}{K_{H_2S}} = 6.3\%$$

$$\frac{\varepsilon K_{CO_2}}{K_{CO_2}} = 4.9\%$$

$$\frac{\varepsilon K_{C8}}{K_{C8}} = 10.3\%$$

$$\frac{\varepsilon K_{C1}}{K_{C1}} = 3.2\%$$

Calculation of Response Factors for Windowed Cell Work

This section will illustrate the method used in calculating the number of moles of each component in the detector calibration mixture and the method used in calculating the response factors.

In making up the calibration mixture, preliminary calculations were made to find approximately the amount of each component which must be injected into the windowed cell. The approximate desired composition was the following: C1 -0.55, C8 -0.25, H_2S -0.10, CO_2 -0.10. The following table gives the amounts of each component which were injected into the cell (and the conditions).

Comp.	Temp. (^{o}F)	Pressure (psia)	Vol (cc)
C1	74.3	990.	1049.2
C8	72.0	1000.	241.74
H_2S	72.0	1000.	25.67
CO_2	77.4	1500.	31.89

The following physical property data were taken from the literature (39, 40, 45) at the conditions that each sample was injected: C1, Z = 0.879; C8, ρ_L = 161.17 cc/mole; CO_2, Z = 0.225; H_2S, ρ_L = 42.77 cc/mole. The moles of each component in the mixture can be calculated in the following way (R = 669.97 $\frac{\text{psia cc}}{\text{gm mol } ^{o}\text{R}}$):

$$\text{C1:}\quad n = \frac{PV}{ZRT} = \frac{(990.)\ (1049.2)}{(0.879)\ (669.97)\ (459.7 + 74.0)} = 3.305 \text{ gm mol}$$

$$CO_2\text{:}\quad n = \frac{PV}{ZRT} = \frac{(1500.)\ (31.89)}{(0.225)\ (669.97)\ (459.7 + 77.4)} = 0.591 \text{ gm mol}$$

$$\text{C8:}\quad n = \frac{V_L}{\rho_L} = \frac{241.74}{161.17} = 1.500 \text{ gm mol}$$

$$H_2S\text{:}\quad n = \frac{V_L}{\rho_L} = \frac{25.67}{42.77} = 0.600 \text{ gm mol}$$

The mixture was pressured and shaken until it existed in single phase in the windowed cell. Four samples were taken from the windowed cell and injected into the chromatograph system. The results from the digital integrator are given below, followed by a table showing counts C_i/counts C1, calculated from the first table.

COUNTS

Sample	TC				HF	
Number	C1	CO_2	H_2S	C8	C1	C8
1	235414	61002	57501	399780	566853	3169290
2	388016	98967	94675	630556	929611	5282490
3	236444	61172	58301	399318	580005	3181920
4	389773	99648	94523	629299	914235	5285040

COUNTS C_i/COUNTS C1

1	1.0	0.25913	0.24425	1.6982	1.0	5.5910
2	1.0	0.25506	0.24400	1.6251	1.0	5.6825
3	1.0	0.25872	0.24657	1.6888	1.0	5.4860
4	1.0	0.25566	0.24251	1.6143	1.0	5.7808
AVG	1.0	0.25714	0.24433	1.6566	1.0	5.6351

The relative response factor, R_{1i}, of component i can now be calculated using Equation (3-20), or

$$R_{1H_2S} = \frac{\text{moles } C_{H_2S}/\text{moles C1}}{\text{counts } C_{H_2S}/\text{counts C1}} = \frac{0.600/3.305}{0.24433} = 0.7430$$

$$R_{1CO_2} = \frac{0.591/3.305}{0.25714} = 0.6954$$

$$R_{1\ C8}\ (\text{TC}) = \frac{1.500/3.305}{1.6566} = 0.2740$$

$$R_{1\ C8}\ (\text{HF}) = \frac{1.500/3.305}{5.6351} = 0.0805$$

Seven mixtures were run. The resulting relative response factors of each are given below. The values marked by an asterick appear to be in error, thus they were not used in the calculation of the average response factor. Two of the mixtures only contained three components.

Mixture	CO_2	H_2S	C8 (TC)	C8 (HF)
1	0.562*	0.701	0.253*	0.0782
2	0.701	0.719	0.268	0.0810
3	0.735	---	0.277	0.0973*
4	---	0.800	0.287	0.1008*
5	0.715	0.734	0.278	0.0812
6	0.735	0.994*	0.262	0.0818
7	0.695	0.743	0.274	0.0805
AVG	0.716	0.739	0.274	0.0805

The response factors for the seven mixtures were averaged arithmetically to give the factors which were used in the calculation of K-values.

Calculation of K-Values from Windowed Cell Data

This section will show the method used to calculate K-values from the relative response factors of the last section and the raw data from the digital integrator.

For the K-values of CO_2 and H_2S at $0^\circ C$ and 1000 psia, the results from the digital integrator are given below.

Sample Type	TC				HF	
	C1	CO_2	H_2S	C8	C1	C8
LIQ	195419	22873	32601	1037558	287325	5750030
VAP	136253	8340	3976	----	202934	1955.3
VAP	130496	7927	3766	----	201719	1959.5
LIQ	193952	24008	36070	1123242	283791	6237460

The following table shows "counts Ci/counts C1," calculated from the above table. The second table below gives the average value of "counts Ci/counts C1" for the two liquid and two vapor samples. The average value is simply an arithmetic average.

COUNTS Ci/COUNTS C1

	TC				HF	
	C1	CO_2	H_2S	C8	C1	C8
LIQ	1.0	0.11705	0.16683	5.3094	1.0	20.012
VAP	1.0	0.06121	0.02918	---	1.0	0.009635
VAP	1.0	0.06075	0.02886	---	1.0	0.009714
LIQ	1.0	0.12378	0.1860	5.9913	1.0	21.979

AVERAGE VALUES

VAP	1.0	0.06098	0.02902	---	1.0	0.009674
LIQ	1.0	0.12041	0.17641	5.6504	1.0	20.995

The ratio of moles of each component to the moles of C1 were calculated using Equation (3-21). The sum of the ratios gives the ratio of the total moles to the moles of C1 in that phase, or

	C1	CO_2	H_2S	C8
LIQUID:	1.0 +	(0.12041) (0.716) +	(0.17641) (0.739) +	(5.6504) (0.274)
	1.0 +	0.0862 +	0.1304 +	1.5482 = 2.7648
VAPOR:	1.0 +	(0.06098) (0.716) +	(0.02902) (0.739) +	(0.009674) (0.0805)
	1.0 +	0.0437 +	0.0215 +	0.00078 = 1.0660

The liquid mole fraction, $_{CO_2}$, for CO_2 is

$$x_{CO_2} = \frac{n_{CO_2}/nC1}{n_T/nC1} = \frac{0.0862}{2.7648} = 0.0312$$

while the vapor mole fraction is

$$y_{CO_2} = \frac{n_{CO_2}/nC1}{n_T/nC1} = \frac{0.0437}{1.0660} = 0.0410$$

The K-values of CO_2 at 0°C and 1000 psia can be calculated using

$$K_{CO_2} = \frac{y_{CO_2}}{x_{CO_2}} = \frac{0.0410}{0.0312} = 1.31$$

The K-value of H_2S, C8, and C1 would be

$$K_{H_2S} = \frac{y_{H_2S}}{x_{H_2S}} = \frac{0.0215/1.0660}{0.1304/2.7648} = 0.427$$

$$K_{C1} = \frac{y_{C1}}{x_{C1}} = \frac{1.0/1.0660}{1.0/2.7648} = 2.594$$

$$K_{C8} = \frac{y_{C8}}{x_{C8}} = \frac{0.00078/1.0660}{1.5482/2.7648} = 0.00131$$

Calculation of K-Values from Chromatographic Data

This section shows the method used to calculate the K-values of CO_2 and H_2S from the chromatographic data. The raw data for the run at 20^oF and 100 psia for the methane-toluene system are given below.

$T = 20.0^oF = -6.67^oC$ SWW = 14.75050 gms

P = 101.5 psia SWD = 13.24605 gms

PCF = 67.95506 gms CW = 9.25865 gms

PCE = 65.11584 gms

		t_B	t_{Ri}	P_A	T_A
He	Blank	0:48.75	0:52.57	740.8	27.7
	Column	0:48.70	1:54.21	740.8	27.9
Ar	Blank	0:48.75	0:52.76	740.8	27.7
	Column	0:48.65	1:55.79	740.8	27.9
CO_2	Blank	0:47.75	0:52.69	740.8	27.8
	Column	0:48.65	2:16.94	740.8	28.0
H_2S	Blank	0:48.76	0:52.12	740.8	27.8
	Column	0:48.60	5:10.00	740.8	28.0

Data from the literature which were used in the calculations were LMW (TOL) = 92.13, Z = 0.9821 and $\chi_1 = 0.0180$.

The weight of liquid in the column, W_L^o, was calculated with Equations (4-1) and (4-2), or

$$W_L^o = [\frac{SWW - SWD}{SWW - CW}] [\frac{PCF - PCE}{LMW}]$$

$$W_L^o = [\frac{14.75050 - 13.24605}{14.75050 - 9.25865}] \quad [\frac{67.95506 - 65.11584}{92.13}]$$

$$W_L^o = 0.008442 \text{ gm mols}$$

The retention volumes for each of the four components for both bypass and column runs were calculated, that is, eight values. The calculation of the retention volume for CO_2 will be shown here. Equations (3-17), (3-18), and (3-18a) can be combined to give

$$f = \frac{V_B}{t_B} [\frac{P_a - P_{H_2O}}{P_a}] \frac{P_a}{P} \frac{T}{T_a} Z_g$$

where $P_{H_2O} = 9.412 - 0.266\ T_a + 0.0366\ T_a^2$

The water vapor pressures for the CO_2 runs were

$$P_{H_2O}(27.8) = 9.412 - 0.266(27.8) + 0.0366(27.8)^2$$

$$= 30.30 \text{ mm Hg}$$

$$P_{H_2O}(28.0) = 30.66 \text{ mm Hg}$$

The carrier gas flow rates for the two runs were

$$f_{CO_2}^B = \frac{45.0993}{48.75} [\frac{740.8 - 30.30}{740.8}] \frac{(740.8/760.)}{\frac{(101.5)}{(14.696)}} \frac{(-6.67 + 273.15)}{(27.8 + 273.15)} (0.9821)$$

$$= 0.1089 \frac{cc}{sec}$$

$$f_{CO_2}^C = \frac{45.0993}{48.65} [\frac{740.8 - 30.66}{740.8}] [\frac{740.8/760.}{\frac{101.5}{14.696}}] [\frac{-6.67 + 273.15}{28.0 + 273.15}] (0.9821)$$

$$= 0.1090 \frac{cc}{se}$$

The retention volume for CO_2 was calculated using Equation (3-16), or

$$V_{RCO_2} = t^C_{RCO_2}\ f^C_{CO_2} - t^B_{RCO_2}\ f^B_{CO_2}$$

$$= [2\ (60.) + 16.94]\ (0.1090) - (52.69)\ (0.1089)$$

$$= 14.926 - 5.738 = 9.188 \text{ cc}$$

Similar calculations for the other three components gave the following results:

$V_{RHe} = 6.714$ cc; $V_{RAr} = 6.879$ cc; $V_{RH_2S} = 28.147$ cc

The free gas volume, V_g, was calculated using Equation (3-19), or

$$V_g = 1.143\ V_{RHe} - 0.143\ V_{RAr}$$

$$V_g = (1.143)\ (6.714) - (0.143)\ (6.879)$$

$$V_g = 6.690 \text{ cc}$$

The density of the carrier gas ρ_g was calculated using

$$\rho_g = \frac{n}{V} = \frac{P}{ZRT} = \frac{101.5/14.696}{(0.9821)(82.07)\ (-6.67 + 273.15)}$$

$$\rho_g = 0.0003216\ \frac{\text{moles}}{\text{cc}}$$

Finally, the K-values of CO_2 and H_2S were calculated using Equation (3-15), or

$$K_{CO_2} = \frac{W^o_L}{(1-\chi_1)\ \rho_g\ (V_{RCO_2} - V_g)}$$

$$= \frac{0.008442}{(1.-0.018)(0.0003216)\ (9.188 - 6.690)} = 10.71$$

$$K_{H_2S} = \frac{0.008442}{(1.-0.018)(0.0003216)\ (28.147-6.690)} = 1.246$$

APPENDIX E

CALIBRATION OF THERMOPILE

A copper-constantan thermopile was used to measure the system termperature for the chromatographic experiment. The thermopile consisted of eight thermocouples connected in series. The thermopile was used because it provided eight times the emf for a given temperature, thus allowing more accurate temperature measurement.

The thermopile was calibrated in the Ladau constant temperature bath. An NBS platinum resistance thermometer was used to measure the temperature of the bath. The calibration of the platinum resistance thermometer was tested by use of a triple point cell. At the water triple point, the platinum resistance thermometer proved to be accurate within 0.01°C.

The thermopile was calibrated by recording the temperature from the platinum resistance thermometer and reading the emf of the thermopile. Figure 40 shows a plot of the difference between the thermopile emf reading and the emf reading which corresponded to the temperature measured with the platinum resistance thermometer, as a function of temperature. The solid line of the figure shows the emf correction used at a given temperature. From this figure, the emf corresponding to the temperatures at which data were to be taken were calculated. The following table shows the emf values which were used for the temperatures used in this work.

Temperature	Thermocouple Table Reading (E_T) (52) (millivolts)	Correction (C)	EMF For This Work ($8E_T + C$)
-40°F	-1.463	.032	-11.672
-20°F	-1.072	.021	- 8.555
0°F	-0.670	.011	- 5.349
20°F	-0.254	.002	- 2.030
-20°C	-0.751	.013	- 5.995
0°C	0.00	-.003	- .003

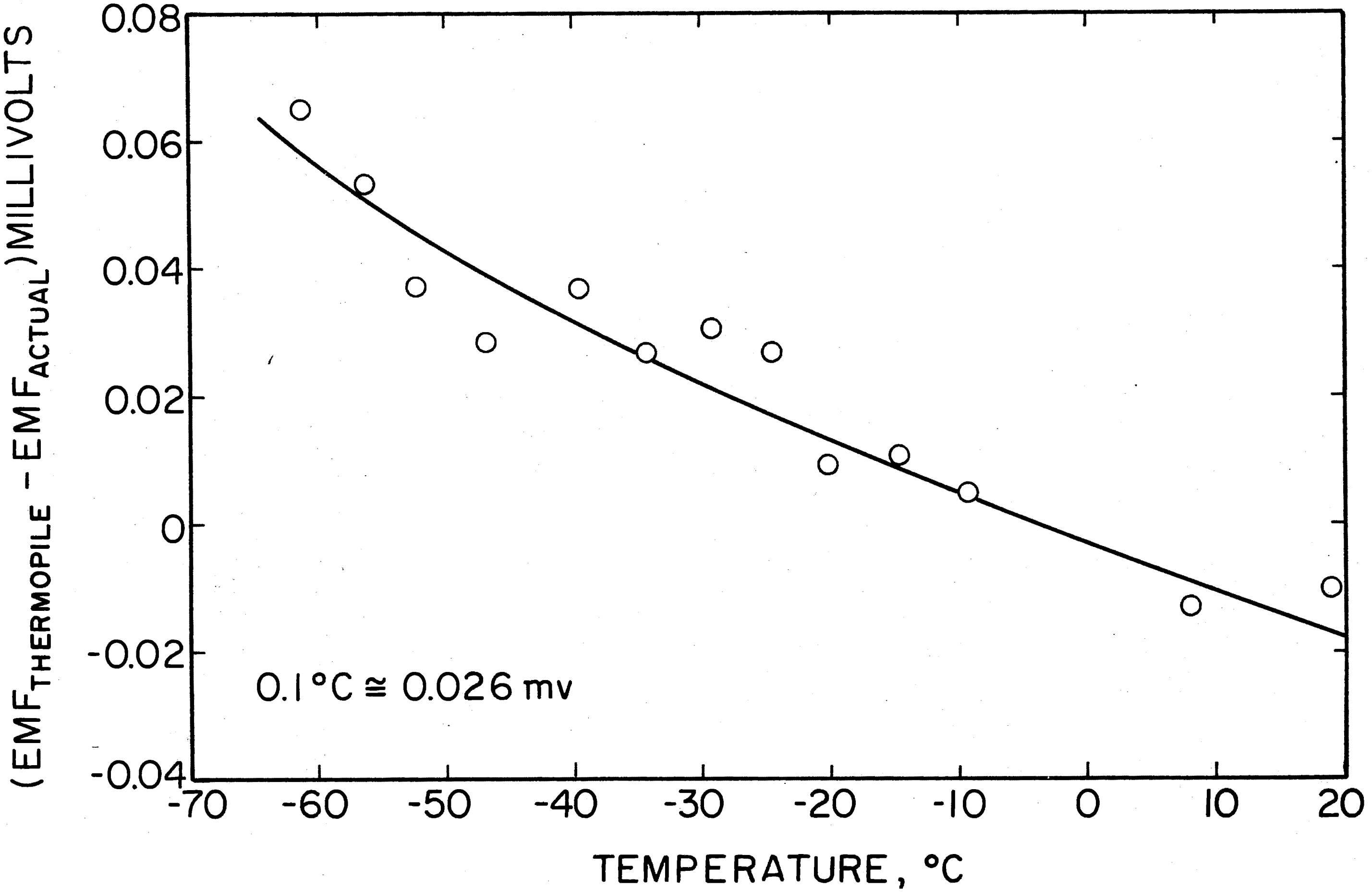

Figure 40. Deviation of Thermopile Readings from Thermocouple Table Readings (emf) as a Function of Temperature

APPENDIX F

DISCUSSION OF EXPERIMENTAL WORK - DIFFICULTIES, TESTS, AND COMMENTS

The purpose of this appendix is to discuss the chromatographic experimental work. Difficulties which were encountered are discussed. Several tests were run to see if any of several experimental variables would cause a change in K-values. This section contains a discussion of the experimental difficulties, the sensitivity tests, and other factors concerning the operating procedures. Hopefully, this section will aid some future investigator in avoiding some of the problems encountered in this work.

Difficulties

Two major difficulties were encountered during the work. At high pressures the sample stream flow rate would begin to drop although the system pressure remained constant. The reference stream was not affected. If the needle valve was heated with a heat gun, the flow rate would increase. Of course, the flow rate would not become steady until the valve had cooled to room temperature. This sometimes took 30 minutes to an hour. Thus, a heating tape was attached to the valves and they were heated constantly. This problem was most often encountered when running with toluene as the solvent. Even when the valves were heated, the problem would occasionally occur.

Before the GLC column bypass was installed, liquid loss of the GLC column was a problem. Some of the very first runs were made with decane as a solvent. After taking data for 12 hours, at 25°C, liquid losses were as much as 5-7% of the total liquid of the column. Since the vapor pressures of heptane, MCH, and toluene are considerably greater than decane, a problem could be foreseen. Thus, the bypass was installed and liquid losses for a 16 hour run were less than 1% of the total liquid.

A few precautions which were taken to help insure more consistant data are given below.

(1) When blank, or bypass, runs were being made, the flow rates were measured with the GLC column being bypassed. When column runs were made, flow rates were measured with the GLC column in the stream. In general, flow rates were not measured while the sample was in the stream.

(2) The valves in the flow stream between the sample valve and detector were always turned the same number of turns to insure identical free gas volumes for each run.

(3) When all data for a given pressure were complete and the system was pressured to a higher pressure, the pressure on the GLC column was raised at that time. Thus, while the bypass runs were being made, the GLC column solvent had time to become saturated with carrier gas.

(4) When an isotherm was completed, the GLC column was closed off (bypass opened) and the constant temperature bath was lowered away from the GLC column. The column was then left connected to the system overnight so that it would dry and come to room temperature.

In general, the equipment was easy to use. Many minor difficulties were corrected with improved and more experienced operating procedures.

Tests

This section describes several tests that were made to see if any parameters affected the experimental K-values obtained in this work. The majority of the tests were run because of the difference in results between this work and Asano (1). These tests were made to be sure that the procedures used in this work were not causing the differences. These tests were run before the classical windowed cell data were taken.

Almost all tests were run by measuring CO_2 K-values in the methane-octane system at -20^oC or 0^oC. The tests are listed below:

(1) Effect of flow rate on K-value was tested. Flow rates were varied by as much as a factor of 10, that is from 18 to 180 cc/min. The K-values varied by at most 5% and only an average of 2.5%. Lower flow rates gave higher K-values.

(2) Sample sizes were varied by a factor of ten by varying the pressure at which the samples were trapped. The average percent error was 3.0%. Larger samples had lower K-values. The tailing was somewhat worse for large samples, as would be expected.

(3) Runs were made with varying amounts of liquid loading, that is, the percent liquid on the solid support. Runs were made with 15, 25, 30 and 35% loading. Again the results varied 3 to 5%, with no general trends being observed.

(4) Presaturator length was increased from 48 inches to 80 inches to insure that the carrier gas was saturated. No appreciable changes in results were noticed.

(5) Seven feet of 1/8" O.D. tubing was put in the sample stream directly before the GLC column and submerged in the constant temperature bath. The tubing was to insure that the carrier gas was at system temperature when it entered the column. No effect on K-values was noticed.

(6) A modified version of the system was built such that the void tubing between the sample valve and the detector was minimized (ten to fifteen inches) to see if excessive void volume affected results. No effect was noted.

(7) The sample valve was replaced by one used in the work of Yudovich (51). No effect was noted.

(8) Elution times were measured to the centroid of the peak (center of area) rather than by measuring horizontally across the peaks. A planimeter was used to calculate the areas. Elution times were increased slightly due to slight tailing, but that was the case for all samples and the differences canceled each other out. No effect was noted.

(9) Data were taken by starting at 1500 psia and decreasing the pressure continuously to 100 psia. No effects were noted.

(10) The solid support-solvent mixture was prepared by placing approximately 40% liquid on the solid support and then slowly evaporating the solvent while tumbling the mixture until the loading was 30%. Results from this method were compared to the method used in this work. No effect was noted.

None of the above-mentioned tests had any appreciable effect on the measured K-values. These results illustrate the simplicity of the chromatographic technique and show the soundness of the apparatus and experimental procedure used in this work.

APPENDIX G

PHYSICAL PROPERTIES

The purpose of the appendix is to list in tabular form the physical properties from the literature that were used in the calculation of chromatographic K-values in this work. The data consist of the compressibility factors of methane and the solubility of methane in the solvents heptane, toluene, methylcyclohexane, and n-octane. Table XIV lists the methane compressibility factors which were used in this work. They were calculated using the equation of Vennix (47). Table XV lists the methane solubilities. The source of the solubility data for each system is listed in the table. Plots of methane mole fractions in the liquid as a function of reciprocal temperature were used to interpolate the data to temperatures at which the data were not listed.

TABLE XIV

COMPRESSIBILITY FACTORS, Z, OF METHANE

Pressure (psia)	-40°F	-20°F	0°F	20°F	-20°C	0°C
100	0.9725	0.9763	0.9794	0.9821	0.9788	0.9835
200	0.9443	0.9521	0.9587	0.9641	0.9575	0.9671
400	0.8857	0.9028	0.9167	0.9283	0.9141	0.9344
600	0.8242	0.8522	0.8745	0.8928	0.8704	0.9023
800	0.7600	0.8010	0.8327	0.8581	0.8269	0.8711
1000	0.6948	0.7503	0.7920	0.8249	0.7846	0.8415
1250	0.6198	0.6919	0.7454	0.7868	—	—
1500	0.5690	0.6460	0.7068	0.7549	—	—

TABLE XV

METHANE SOLUBILITIES, χ_1, IN SOLVENTS

		Pressure (psia)							
Solvent	Temp.	100	200	400	600	800	1000	1250	1500
C8 (22)	0°C	0.038	0.073	0.141	0.205	0.263	0.314	--	--
	-20°C	0.043	0.083	0.163	0.237	0.300	0.353	--	--
C7 (4)	20°F	0.0400	0.0815	0.161	0.230	0.301	0.354	0.4190	0.470
	0°F	0.0445	0.0901	0.1744	0.2490	0.3160	0.3772	0.4452	0.4966
	-20°F	0.0490	0.1033	0.1883	0.2668	0.3412	0.4078	0.4784	0.5388
	-40°F	0.0556	0.1163	0.2081	0.2990	0.3728	0.4481	0.5160	0.5789
MCH (5)	20°F	0.0305	0.0595	0.1155	0.1845	0.229	0.271	0.325	0.376
	0°F	0.0333	0.0655	0.1274	0.1961	0.2439	0.2899	0.3470	0.3984
	-20°F	0.0377	0.0737	0.1447	0.2088	0.2631	0.3165	0.3749	0.4274
	-40°F	0.0417	0.0820	0.1588	0.2227	0.2831	0.3406	0.3975	0.4545
TOL (6)	20°F	0.0180	0.0360	0.0688	0.1060	0.140	0.176	0.210	0.2520
	0°F	0.0193	0.0390	0.0740	0.1120	0.1495	0.1861	0.2230	0.2660
	-20°F	0.0209	0.0410	0.0815	0.1211	0.1609	0.1989	0.2465	0.2900
	-40°F	0.0230	0.0452	0.0867	0.1296	0.1729	0.2150	0.2626	0.3099

APPENDIX H

COMPUTER PROGRAMS

This appendix lists the computer programs or subroutines of programs which were most pertinent to this work. The listings include (1) calculation of K-values for chromatographic experiment, (2) calculation of K-values for windowed cell experiment, and calculation of K-values using the two modifications of the Soave equation for the (3) binary data from the literature and (4) the ternary data of this work.

A short documentation is given at the first of each listing to explain the program nomenclature. The first two programs are self explanatory. The third and fourth listings are from subroutines from the the non-linear regression decks which were used to calculate the empirical correlation factors which best fit the data. These subroutines calculate K-values using the modifications of the mixing rules of Soave which were used in this work. In each of the two subroutines, cards marked with "**1**" were used in the one parameter correlation method while cards marked with "**2**" were used in the two parameter correlation method. The equations used in the two programs and two subroutines are explained in detail in Chapter III.

```
C       THIS PROGRAM CALCULATES THE K-VALUES OF CO2 AND H2S AT INFINITE
C       DILUTION FROM DATA TAKEN WITH THE CHROMAGRAPHIC TECHNIQUE.
C
C      COMPONENT NUMBERS  =  HE = 1,  AR = 2,  CO2 = 3,  H2S = 4  .
C       TERMS TO DETERMINE WEIGHT OF LIQUID ON COLUMN
C       SWW = WEIGHT OF LIQUID+SOLID+CRUCIBLE
C       SWD = WEIGHT OF SOLID+CRUCIBLE
C       BWE = WEIGHT OF CRUCIBLE
C       CWP = GLC COLUMN WEIGHT PACKED
C       CWE = GLC COLUMN WEIGHT EMPTY
C       WTMW = MOLECULAR WEIGHT OF SOLVENT
C       WFL = FRACTION LIQUID ON GLC COLUMN
C       WL = WEIGHT OF LIQUID ON GLC COLUMN (GMS)
C
C       T = SYSTEM TEMPERATURE (DEG C)
C       P = SYSTEM PRESSURE (PSI)
C       Z = METHANE COMPRESSIBILITY FACTOR
C       X = SOLUBILITY OF METHANE IN SOLVENT
C        RHO = METHANE DENSITY AT T AND P
C
C   THE FOLLOWING TERMS APPLY TO RUNS MADE WITH THE GLC COLUMN IN STREAM
C       A,B = TIME MEASURED ON BUBBLEMETER TO CALCULATE FLOW RATE.A=MIN,B=SEC.
C       C,D = RETENTION TIMES. C=MIN,D=SEC
C       PA = AMBIENT PRESSURE (MM HG)
C       TA = AMBIENT TEMPERATURE (DEG C)
C       TR = RETENTION TIME
C       VPT = VAPOR PRESSURE OF WATER AT TA
C       F = CARRIER GAS FLOW RATE
C       VRP = RETENTION VOLUME FOR GLC COLUMN RUN
C
C   THE FOLLOWING TERMS ARE SIMILAR TO THE ABOVE EXCEPT THAT THE GLC
C   COLUMN WAS BYPASSED FOR THESE TERMS
C       AB,BB,CB,DB,PAB,TAB,TRB,VPTB,FB,VRB
C
C       VR = VRP-VRB = RETENTION VOLUME USED IN CALCULATION OF K-VALUE
C       EXK = K-VALUE FROM LITERATURE
C       VG = FREE GAS VOLUME
C       EK1(J)  = K-VALUE OF COMPONENT J
C       PCT = PERCENT DEVIATION BETWEEN EXPERIMENTAL K-VALUE AND LITERATURE DATA
C
      DIMENSION CK(8,15),A(10),B(10),C(10),D(10),PA(10),TA(10),L(10),
     1TR(10),F(10),VR(10),EK(10),EKO(10),CKLN(8,15),EKLN(10),EKOLN(10),
     2 DIF(10),DIFO(20),TITLE(20),
     3TRB(10),AB(10),BB(10),CB(10),DB(10),PAB(10),TAB(10),VRB(10),
     4VRP(10),EK1(10),EK2(10),EK3(10),EK4(10),FB(10),EXK(10),PCT(10),
     5PCTI(10)
      MU=0
    1 READ (5,11)  (TITLE(I),I=1,20)
      IF(MU.NE.0) WRITE(6,57)
      WRITE(6,11)  (TITLE(I),I=1,20)
   11 FORMAT (20A4)
      READ(5,2) CP
    2 FORMAT(A3)
    5 READ (5,15) SWW,SWD,BWE,CWP,CWE,WTMW
   15 FORMAT (6F12.5)
      WFL = (SWW-SWD)/(SWW-BWE)
      WL = (CWP-CWE)*WFL/WTMW
      WRITE(6,9889)
      WRITE(6,12) T,SWW,WTMW,CWP,SWD,WFL,CWE,BWE,WL
   12 FORMAT(1H0,12X,3HT =,F10.5,7X,5HSWW =,F10.5,6X,6HWTMW =,F10.5/
     111X,5HCWP =,F10.5,7X,5HSWD =,F10.5,7X,5HWFL =,F10.5/
     211X,5HCWE =,F10.5,7X,5HBWE =,F10.5,8X,4HWL =,F10.5//)
      WRITE (6,57)
   57 FORMAT (1H1)
   18 READ (5,20) T,P,Z,X,M
   20 FORMAT (4F12.5,I2)
      IF(Z.EQ.0.0) GO TO 1
   16 P=P+14.5
      WRITE(6,57)
      T1=T+273.15
      T2=(T*1.8)+32.
      RHO = P/(T1*82.07*14.696*Z)
      DO 30  I=1,10
      READ(5,25)AB(I),BB(I),CB(I),DB(I),PAB(I),TAB(I),L(I)
      IF(PAB(I).EQ.0.0) GO TO 33
      READ (5,25) A(I),B(I),C(I),D(I),PA(I),TA(I),L(I)
   25 FORMAT (4F5.0,2F10.0,I5)
      MU=I
   30 CONTINUE
   33 DO 38 I=1,MU
   26 TRB(I)=CB(I)+(DB(I)/60.)
      VPTB= 9.412 +TAB(I)*(-.266) +TAB(I)*TAB(I) *.0366
      FB(I)=45.0993/(AB(I)+(BB(I)/60.)) *(PAB(I)-VPTB)/PAB(I)
      VRB(I) = TRB(I)*FB(I)*PAB(I)*14.696*T1*Z/(P*760.*(TAB(I)+273.15))
   27 TR(I)=C(I)+(D(I)/60.)
      VPT = 9.412 + TA(I)*(-.266) + TA(I) *TA(I) *.0366
      F(I)=45.0993/(A(I)+(B(I)/60.)) *(PA(I)-VPT)/PA(I)
      VRP(I)=TR(I)*F(I)*PA(I)*14.696*T1*Z/(P*760.*(TA(I)+273.15))
      VR(I) = VRP(I)-VRB(I)
   38 CONTINUE
      WRITE(6,9889)
 9889 FORMAT(/////////)
      DO 126 J=1,4
      WRITE(6,124) AB(J),BB(J),CB(J),DB(J),PAB(J),TAB(J),VRB(J)
      WRITE(6,128) A(J),B(J),C(J),D(J),PA(J),TA(J),VRP(J),VR(J)
  124 FORMAT(5X,6HBYPASS,1X,F3.0,F5.2,F5.0,F5.2,F7.1,F6.1,F8.3,F8.3)
  128 FORMAT(5X,6HCOLUMN,1X,F3.0,F5.2,F5.0,F5.2,F7.1,F6.1,F8.3,F8.3)
  126 CONTINUE
      VG=VR(1)-((VR(2)-VR(1))/7.)
      VG1=VRP(1)-((VRP(2)-VRP(1))/7.)
      DO 40 I=2,MU
   35 EK1(I)=WL/((1.-X)*RHO*(VR (I)-VG))
      EK2(I) = WL/((1.-X)*RHO*(VRP(I)-VG1))
      EK3(I) = WL/((1.-X)*RHO*(VR(I)-VR(1)))
      EK4(I) = WL/((1.-X)*RHO*(VRP(I)-VRP(1)))
   40 CONTINUE
      DO 60 I=2,MU
      EXK(I)=1.
C     EXK(I)=1.  FOR C7,TOL,MCH
C     READ(5,15) EXK(I)  FOR C8
      PCT(I)=(EK1(I)-EXK(I))*100./EXK(I)
      PCTI(I)=(EK2(I)-EXK(I))*100./EXK(I)
   60 CONTINUE
      WRITE(6,127) CP,T2,P,Z,X,VG,EK1(3),EK1(4)
  127 FORMAT(///72X,3HC1-,A3,8H-CO2-H2S /
     1/70X,8H      T =,F10.5
     2/70X,8H      P =,F10.5
     3/70X,8H      Z =,F10.5
     4/70X,8H      X =,F10.5
     5/70X,8H     VG =,F10.5
     6/70X,8HK(CO2) =,F10.5
     7/70X,8HK(H2S) =,F10.5)
   90 GO TO 18
   91 CALL EXIT
      END
```

```
C
C       THIS PROGRAM CALCULATES KVALUES FROM CLASSICAL WINDOWED CELL DATA.
C
C       COMPONENT NUMBER.   1 = C8 (HF),  2 = C8 (TC),  3 = CO2,  4 = H2S.
C     HF = HYDROGEN FLAME DETECTOR,  TC = THERMAL CONDUCTIVITY DETECTOR
C       RH,RCO,RCF,RCT = RESPONSE FACTORS FOR H2S, CO2, C8(HF), C8(TC)
C       AS(J) = ARRAY OF ASANO'S EXPERIMENTAL RESULTS.  J=COMP NUMBER
C       CM(J) = ARRAY OF MUNDIS' EXPERIMENTAL RESULTS.  (CHROMATOGR)
C       ARV(J) = # COUNTS COMP J / # COUNTS C1    FOR VAPOR
C       ARL(J) = # COUNTS COMP J / # COUNTS C1    FOR LIQUID
C       YH,YCO,YC8,YC1 = VAPOR MOLE FRACTIONS FOR H2S, CO2,C8, C1
C       XHF, XCOF, XC8F, XC1F = LIQUID MOLE FRACTIONS FOR H2S, CO2, C8, C1
C                               USING HF RESULTS FOR C8
C       XHT, XCOT, XC8T, XC1T = LIQUID MOLE FRACTIONS FOR H2S, CO2, C8, C1
C                               USING TC RESULTS FOR C8
C       VKC8F = K=VALUE OF C8 USING HF RESULTS
C       VKC8T,VKHF,VKHT,VKCOF,VKCOT,VKC1F,VKC1T = K=VALUES OF OTHER COMPONENTS
C                                                 FROM HF OR TC RESULTS
C       DMCOF = PERCENT DEVIATION OF CO2(CO) MEASURED WITH THE HF(F) FROM
C                MUNDIS' (M) EXPERIMENTAL DATA
C       DAHT = PERCENT DEVIATION OF H2S(H) MEASURED WITH THE TC(T) FROM
C               ASANO'S (A) EXPERIMENTAL DATA.
C       DMHF,DAHF,DACOF,DMHT,DMCOT,DACOT = SIMILAR TO DMCOF AND DAHT WHERE
C                                          A=ASANO, M=MUNDIS,CO=CO2,H=H2S,
C                                          T=TC, AND H=HF.
C
      DIMENSION TITLE(10),ARV(5),ARL(5),AS(5),CM(5)
      DIMENSIONA(30,30),B(3C,3C)
C  3=CO2, 4=H2S, 1=HF,2=TC
C          MU=0 PRINT X,Y,K,EXP,ASANO,MUNG,PCT DEV
C          MU=1 PRINT K,PCT DEV
C          MU=2 PRINT K
 5694 SUMRFT=0.0
      READ(5,3,END=666) ML
    3 FORMAT(I2)
      READ(5,5695) RH,RCO,RCF,RCT
      WRITE(6,5695)RH,RCO,RCF,RCT
 5695 FORMAT(8F10.4)
      DO 6 N=1,500
    2 READ(5,11) (TITLE(J),J=1,10), AS(3),CM(3),AS(4),CM(4)
   11 FORMAT(10A4,4F10.0)
      IF(CM(3).EQ.0.0) GO TO 7
      MUN=N
      READ(5,12) ARV(3),ARV(4),ARV(1),ARL(3),ARL(4),ARL(2),ARL(1)
   12 FORMAT(7F10.0)
      RFT=ARL(1)/ARL(2)
      SUMRFT=SUMRFT+RFT
      AV=RH*ARV(4)+RCO*ARV(3)+RCF*ARV(1)+1.
      YH=RH*ARV(4)/AV
      YCO=RCO*ARV(3)/AV
```

```
      YC8=RCF*ARV(1)/AV
      YC1=1./AV
      ALF=RH*ARL(4)+RCO*ARL(3)+RCF*ARL(1)+1.
      XHF=RH*ARL(4)/ALF
      XCOF=RCO*ARL(3)/ALF
      XC8F=RCF*ARL(1)/ALF
      XC1F=1./ALF
      ALT=RH*ARL(4)+RCO*ARL(3)+RCT*ARL(2)+1.
      XHT=RH*ARL(4)/ALT
      XCOT=RCO*ARL(3)/ALT
      XC8T=RCT*ARL(2)/ALT
      XC1T=1./ALT
      IF(XHF.NE.0.0) GO TO 21
      VKHF=0.0
      GO TO 22
   21 VKHF=YH/XHF
   22 IF(XCOF.NE.0.0) GO TO 23
      VKCOF=0.0
      GO TO 24
   23 VKCOF=YCO/XCOF
   24 IF(XHT.NE.0.0) GO TO 25
      VKHT=0.0
      GO TO 26
   25 VKHT=YH/XHT
   26 IF (XCOT.NE.0.0) GO TO 27
      VKCOT=0.0
      GO TO 28
   27 VKCOT=YCO/XCOT
   28 CONTINUE
      VKC8F=YC8/XC8F
      VKC1F=YC1/XC1F
      VKC8T=YC8/XC8T
      VKC1T=YC1/XC1T
      DMHF=(VKHF-CM(4))/CM(4)*1C0.
      DMCOF=(VKCOF-CM(3))/CM(3)*100.
      DAHF=(VKHF-AS(4))/AS(4)*1C0.
      DACOF=(VKCOF-AS(3))/AS(3)*100.
      DMHT=(VKHT-CM(4))/CM(4)*1C0.
      DMCOT=(VKCOT-CM(3))/CM(3)*100.
      DAHT=(VKHT-AS(4))/AS(4)*1C0.
      DACOT=(VKCOT-AS(3))/AS(3)*100.
      DO 40 L=1,10
   40 B(N,L)=TITLE(L)
      A(N, 1)=VKCOF
      A(N, 2)=VKCOT
      A(N, 3)=VKHF
      A(N, 4)=VKHT
      A(N, 5)=AS(3)
      A(N, 6)=AS(3)
      A(N, 7)=AS(4)
```

```
      A(N, 8)=AS(4)
      A(N, 9)=CM(3)
      A(N,10)=CM(3)
      A(N,11)=CM(4)
      A(N,12)=CM(4)
      A(N,13)=DACØF
      A(N,14)=DACØT
      A(N,15)=DAHF
      A(N,16)=DAHT
      A(N,17)=DMCØF
      A(N,18)=DMCØT
      A(N,19)=DMHF
      A(N,20)=DMHT
      A(N,21)=VKC1F
      A(N,22)=VKC1T
      A(N,23)=VKC8F
      A(N,24)=VKC8T
      IF(MU.NE.0)GØ TØ 6
      WRITE(6,101) (TITLE(J),J=1,10)
      WRITE(6,102)YH,YCØ,YC8,YC1,XHF,XCØF,XC8F,XC1F,VKHF,VKCØF,VKC8F,
     1VKC1F
      WRITE(6,103)VKHF,AS(4),DAHF,VKHF,CM(4),DMHF
      WRITE(6,104) VKCØF,AS(3),DACØF,VKCØF,CM(3),DMCØF
      WRITE(6,105) (TITLE(J),J=1,10)
      WRITE(6,102)YH,YCØ,YC8,YC1,XHT,XCØT,XC8T,XC1T,VKHT,VKCØT,VKC8T,
     1VKC1F,RFT,SUMRFT
      WRITE(6,103) VKHT,AS(4),DAHT,VKHT,CM(4),DMHT
      WRITE(6,104)VKCØT,AS(3),DACØT,VKCØT,CM(3),DMCØT
  101 FØRMAT(10A4,14HHYDRØGEN FLAME    ///)
  102 FØRMAT(10X,3HH2S,17X,3HCØ2,17X,2HC8,18X,2HC1//3X,3HY   ,4(F10.6,10X
     1),//3X,3HX   ,4(F10.6,10X)//3X,3HK   ,6(F10.6,10X)///)
  103 FØRMAT(10X,3HH2S,10X,5HEXP =,F10.6,5X,7HASANØ =,F10.6,5X,11HPCT. D
     1EV. =,F10.6//23X,5HEXP =,F10.6,5X,7HMUNG  =,F10.6,5X,11HPCT. DEV.
     2=,F10.6//)
  104 FØRMAT(10X,3HCØ2,10X,5HEXP =,F10.6,5X,7HASANØ =,F10.6,5X,11HPCT. D
     1EV. =,F10.6//23X,5HEXP =,F10.6,5X,7HMUNG  =,F10.6,5X,11HPCT. DEV.
     2=,F10.6//)
  105 FØRMAT(10A4,20HTHERMAL CØNDUCTIVITY    ///)
    6 CØNTINUE
    7 CØNTINUE
      IF(MU.NE.1.0) GØ TØ 8
      DØ 250 N=1,MUN
      WRITE(6,200) (B(N,L),L=1,10)
  200 FØRMAT(10A4)
      WRITE(6,201) (A(N,L),L=1,20)
  201 FØRMAT (14X,17HHF      CØ2      TC  ,18X,17HHF      H2S      TC  /
     15(10X,F10.6,5X,F10.6,10X,F10.6,5X,F10.6/)///)
  250 CØNTINUE
    8 CØNTINUE
      IF(MU.NE.2) GØ TØ 74
```

```
      DØ 9 N=1,MUN
      WRITE(6,2252)
 2252 FØRMAT(42X,19HCØ2F,CØ2T,H2SF,H2ST/42X,19HC1 F,C1 T,C8 F,C8 T/)
      WRITE(6,251) (B(N,L),L=1,10),(A(N,L),L=1,4),(A(N,L),L=21,24)
  251 FØRMAT (10A4,2F12.6,5X,2F12.6/40X,2F12.6,5X,2F12.6)
    9 CØNTINUE
   74 CØNTINUE
      GØ TØ 5694
  666 CALL EXIT
      END
```

```
      SUBROUTINE FOFX (N,I,XX,B,ZZ,ZY)
C
C      THIS PROGRAM CALCULATES EMPIRICAL CORRELATION FACTORS FROM THE
C      BINARY DATA OF THE LITERATURE.
C
C        COMPONENT NUMBERS:
C        1=     COMPONENT 1
C        2=     COMPONENT 2
C        12=    MIXTURE OF 1 AND 2.
C
C        R=               GAS CONSTANT
C        T=               SYSTEM TEMPERATURE (DEGREES-K)
C        P=               SYSTEM PRESSURE (ATM)
C        TR1,TR2,TR12=    REDUCED TEMPERATURE
C        TC1,TC2,TC12=    CRITICAL TEMPERATURE
C        PC1,PC2=         CRITICAL PRESSURE
C        VC1,VC2,VC12=    IDEAL CRITICAL VOLUME
C        EK1,EK2=         K VALUE
C        X1,X2=           LIQUID MOLE FRACTIONS
C        Y1,Y2=           VAPOR MOLE FRACTIONS
C        A1,A2,A12=       PARAMETER A OF SOAVE EQUATION
C        B1,B2,B12=       PARAMETER B OF SOAVE EQUATION
C        ALPHA1=          PARAMETER ALPHA OF SOAVE EQUATION
C        ALPHA2=          PARAMETER ALPHA OF SOAVE EQUATION
C        ALPHA12=         PARAMETER ALPHA OF SOAVE EQUATION
C        AX,AY=           A FOR LIQUID AND VAPOR FROM MIXING RULES
C        BX,BY=           B FOR LIQUID AND VAPOR FROM MIXING RULES
C        ZV,ZL=           VAPOR AND LIQUID COMPRESSIBILITY FACTORS
C        VV,VL=           VAPOR AND LIQUID MOLAR VOLUMES
C        PHI1L,PHI2L=     LIQUID FUGACITY COEFFICIENTS
C        PHI1V,PHI2V=     VAPOR FUGACITY COEFFICIENTS
C        EK1C,EK2C=       CALCULATED K-VALUES
C        ER1,ER2=         PERCENT DEVIATION BETWEEN EXPERIMENTAL
C                         AND CALCULATED K VALUES
C        B(1),B(2)=       EMPIRICAL CORRELATION FACTORS
C
C
      DOUBLE PRECISION B,XX,ZZ
      DOUBLE PRECISION ER1,ER2
      COMMON/ROMA/PC1,TC1,PC2,TC2,W1,W2
      COMMON/GEORG/MNGRL
      COMMON/CJMU/ZWTF
      DIMENSION B(30),XX(10),VLE(200)
      IF (I-1) 10,50,10
   10 IF (MUNG4) 50, 51,50
   50 LMN=50
      NCOUNT = 0
      R = 0.082054
      T=(XX(1)+459.6)*5./9.
      P=XX(2)/14.696
      TR1=T/TC1
      TR2=T/TC2
      VC1 = R*TC1/PC1
      VC2 = R*TC2/PC2
      TC12 = ((TC1*TC2)**0.5)*(1.-B(1))
      VC12 =  ((VC1**.33333333+VC2**.33333333)           /2.)**3        **1**
      VC12 = (((VC1**.33333333+VC2**.33333333)*(1.+B(2)))/2.)**3        **2**
      EK1=ZY
      EK2=XX(3)
   60 NCOUNT = NCOUNT+1
      X1 = (EK2-1.)/(EK2-EK1)
      X2 = (1.-EK1)/(EK2-EK1)
      Y1 = X1*EK1
      Y2 = X2*EK2
      ALPHA1=(1.+(0.480+1.574*W1-0.176*W1**2)*(1.-TR1**.5))**2
      A1=ALPHA1*0.42747*VC1*R*TC1**1.5*TR1**.5
      B1=0.08664*VC1
      ALPHA2=(1.+(0.480+1.574*W2-0.176*W2**2)*(1.-TR2**.5))**2
      A2=ALPHA2*0.42747*VC2*R*TC2**1.5*TR2**.5
      B2=0.08664*VC2
      TR12=T/TC12
      W12=(W1*W2)**0.5
      ALPH12=(1.+(0.480+1.574*W12-0.176*W12**2)*(1.-TR12**.5))**2
      A12=ALPH12*0.42747*VC12*R*TC12**1.5 *TR12**0.5
      B12=(B1+B2)/2.*(1.+B(2))                                          **1**
      B12=0.08664*VC12                                                  **2**
      BX=B1*X1**2+B2*X2**2+2.*X1*X2*B12
      BY=B1*Y1**2+B2*Y2**2+2.*Y1*Y2*B12
      AX=A1*X1**2+A2*X2**2+2.*X1*X2*A12
      AY=A1*Y1**2+A2*Y2**2+2.*Y1*Y2*A12
C
C     CALCULATE LIQUID COMPRESSIBILITY FACTOR
      AC=(AX*P)/(R**2*T**2.5)
      BC=BX*P/(R*T)
      PL=-1.
      QL=AC-BC-BC**2
      RL=-(AC*BC)
C     CALL CUBIC (PL,QL,RL,ZCLM,ZL)
      CALL ZSOL (PL,QL,RL,ZCLM,ZL)
      VL=ZL*R*T/P
C
C     CALCULATE VAPOR  COMPRESSIBILITY FACTOR
      AC=(AY*P)/(R**2*T**2.5)
      BC=BY*P/(R*T)
      PL=-1.
      QL=AC-BC-BC**2
      RL=-(AC*BC)
C     CALL CUBIC (PL,QL,RL,ZV,ZCAM)
      CALL ZSOL (PL,QL,RL,ZV,ZCAM)
C
      VV=ZV*R*T/P
      IF((VL-BX).LE.0.0) GO TO 210
      IF((VL-BX).LE.0.0) GO TO 210
      CALL FUGA(VL,BX,B2,R,T,P,X2,A2,X1,A12,AX,B12,PHI2L)
      CALL FUGA(VV,BY,B2,R,T,P,Y2,A2,Y1,A12,AY,B12,PHI2V)
      CALL FUGA(VV,BY,B1,R,T,P,Y1,A1,Y2,A12,AY,B12,PHI1V)
      CALL FUGA(VL,BX,B1,R,T,P,X1,A1,X2,A12,AX,B12,PHI1L)
      EK2C = PHI2L/PHI2V
      EK1C = PHI1L/PHI1V
      ER1 = (EK1C-EK1)/EK1C
      ER2 = (EK2C-EK2)/EK2C
      IF((LMN-NCOUNT).GT.0) GO TO 190
      MNGRL=MNGRL+1
      GO TO 210
  190 IF (DABS(ER1)-0.001000) 200,200,220
  200 IF (DABS(ER2)-0.001000) 210,210,220
  220 CONTINUE
      EK1=EK1+(EK1C-EK1)*.5
      EK2=EK2+(EK2C-EK2)*.5
      GO TO 60
  210 ZZ = EK1
      MUNG4 = 0
      GO TO 330
   51 ZZ = EK2
      MUNG4 = 1
      GO TO 330
  330 CONTINUE
      RETURN
      END
```

```
      SUBROUTINE FOFX (N,I,XX,B,ZZ,ZY)
C
C      THIS PROGRAM CALCULATES EMPIRICAL CORRELATION FACTORS FROM THE
C      TERNARY K-VALUE DATA OF THIS WORK.
C
C        COMPONENT NUMBERS:
C                          1=(H2S,CO2),
C                          2=(C1),
C                          3=(SOLVENT)
C        R=                GAS CONSTANT
C        T=                SYSTEM TEMPERATURE (DEGREES-K)
C        P=                SYSTEM PRESSURE (ATM)
C        TC=               CRITICAL TEMPERATURE
C        PC=               CRITICAL PRESSURE
C        VC=               IDEAL CRITICAL VOLUME
C        EK=               K VALUE
C        XF=               LIQUID MOLE FRACTIONS
C        YF=               VAPOR MOLE FRACTIONS
C        BXM,BYM=          LIQUID AND VAPOR B FROM MIXING RULES
C        AXM,AYM=          LIQUID AND VAPOR A FROM MIXING RULES
C        TCM=              CRITICAL TEMPERATURE OF MIXTURE
C        VCM=              CRITICAL VOLUME OF MIXTURE
C        TRM=              REDUCED TEMPERATURE OF MIXTURE
C        W=                ACCENTRIC FACTOR
C        WM=               ACCENTRIC FACTOR OF MIXTURE
C        ALPHAM=           PARAMETER ALPHA OF SOAVE FOR MIXTURE
C        AM=               PARAMETER A OF SOAVE FOR MIXTURE
C        BM=               PARAMETER B OF SOAVE FOR MIXTURE
C        AL,AV=            LIQUID AND VAPOR COMPRESSIBILITY FACTORS
C        VL,VV=            LIQUID AND VAPOR MOLAR VOLUMES
C        PHIL,PHIV=        LIQUID AND VAPOR FUGACITY COEFFICIENTS
C        EKC=              CALCULATED K VALUE
C        ER=               PERCENT DEVIATION BETWEEN EXPERIMENTAL
C                          AND CALCULATED K VALUES.
C
      IMPLICIT REAL*8(A-H,O-Z)
      DOUBLE PRECISION B,XX,ZZ,ER
      DIMENSION B(30),XX(10)
      DIMENSIONVC(6),VCM(6,6),TCM(6,6),TRM(6,6),WM(6,6),AM(6,6),BM(6,6),
     1ALPHAM(6,6),ER(6),EK(6),EKC(6),PHIL(6),PHIV(6),XF(6),YF(6)
      DIMENSION TR(5),A(5),ALPHA(5),BA(5)
      COMMON X(100,7),TC(6),PC(6),W(6),CB1(8,8),CB2(8,8),CB3(8,8),
     1YY(400),F(6),NCP,MNGRL
      COMMON/GEORG/VLE(100,6)
      COMMON/DAVEN/CB4(8,8)
   50 LMN=40
      NCOUNT = 0
      R = 0.082054
      T=(XX(1)+459.6)*5./9.
      P=XX(2)/14.696
      DO 20 M=1,NCP
      VC(M)=R*TC(M)/PC(M)
   20 CONTINUE
      EK(1)=ZY
      EK(2)=XX(3)
      EK(3)=XX(4)
   60 NCOUNT=NCOUNT+1
      CALL KVALUE (NCP,T,P,F,EK,XF,YF,I)
      BXM=0.0
      BYM=0.0
      AXM=0.0
      AYM=0.0
      CB1(1,3)=B(1)
      CB1(3,1)=B(1)
      CB2(1,3)=B(2)
      CB2(3,1)=B(2)
      DO 31 K=1,NCP
      DO 30 L=1,NCP
      TCM(K,L)=((TC(K)*TC(L))**0.5)*(1.-CB1(K,L))
      VCM(K,L)=(((VC(K)**0.33333333+VC(L)**0.33333333)*
     1(1.+0.0       ))/2.)**3                                    **1**
     1(1.+CB2(K,L)))/2.)**3                                      **2**
      TRM(K,L)=T/TCM(K,L)
      WM(K,L)=(W(K)*W(L))**0.5
      ALPHAM(K,L)=(1.+(0.480+1.574*WM(K,L)-0.176*WM(K,L)**2)*
     1(1.-TRM(K,L)**0.5))**2
      AM(K,L)=0.42747*ALPHAM(K,L)*VCM(K,L)*R*TCM(K,L)**1.5*
     1TRM(K,L)**0.5
      BA(L)=0.08664*VC(L)                                        **1**
      BA(K)=0.08664*VC(K)                                        **1**
      BM(K,L)=(BA(K)+BA(L))/2.*(1.+CB2(K,L))                     **1**
      BM(K,L)=0.08664*VCM(K,L)                                   **2**
      BXM=BXM+XF(K)*XF(L)*BM(K,L)
      BYM=BYM+YF(K)*YF(L)*BM(K,L)
      AYM=AYM+YF(K)*YF(L)*AM(K,L)
      AXM=AXM+XF(K)*XF(L)*AM(K,L)
   30 CONTINUE
   31 CONTINUE
C
C     CALCULATE LIQUID COMPRESSIBILITY FACTOR
C
      AC=(AXM*P)/(R**2*T**2.5)
      BC=BXM*P/(R*T)
      PL=-1.
      QL=AC-BC-BC**2
      RL=-(AC*BC)
      CALL ZSOL(PL,QL,RL,ZCLM,ZL)
C     CALL CUBIC(PL,QL,RL,ZCLM,ZL)
      VL=ZL*R*T/P
C
C     CALCULATE VAPOR  COMPRESSIBILITY FACTOR
C
      AC=(AYM*P)/(R**2*T**2.5)
      BC=BYM*P/(R*T)
      PL=-1.
      QL=AC-BC-BC**2
      RL=-(AC*BC)
      CALL ZSOL(PL,QL,RL,ZV,ZCAM)
C     CALL CUBIC(PL,QL,RL,ZV,ZCAM)
      VV=ZV*R*T/P
      DO 40 M=1,NCP
      CALL FUGA (VV,P,R,T,AYM,BYM,YF,AM,BM,VPHI,M,NCP)
      CALL FUGA (VL,P,R,T,AXM,BXM,XF,AM,BM,QPHI,M,NCP)
      PHIV(M)=VPHI
      PHIL(M)=QPHI
      EKC(M)=PHIL(M)/PHIV(M)
   40 ER(M)=(EKC(M)-EK(M))/EKC(M)
      DO 42M=1,NCP
      IF(DABS(ER(M)).GT.0.001)GO TO 220
   42 CONTINUE
      GO TO 210
  220 CONTINUE
      IF(LMN.EQ.NCOUNT) GO TO 211
      DO 44 M=1,NCP
   44 EK(M)=EK(M)+(EKC(M)-EK(M))*1.
      GO TO 60
  211 MNGRL=MNGRL+1
  210 ZZ=EK(1)
      MKL=NCP+1
      DO 45 JL=3,MKL
      VLE(I,JL)=EKC(JL-1)
   45 CONTINUE
      RETURN
      END
```

APPENDIX I

RAW DATA

This appendix presents the data which were recorded during the experimental work. Table XVI presents the data of the windowed cell experiment. The values presented in the table are the "number of counts" output by the digital integrator. These values are proportional to the sample size. The octane concentration in the vapor phase is very low and was not visible on the TC detector output. In two instances, faulty experimental technique caused the methane results from the hydrogen flame detector to be lost. The table lists results of only two of the calibration runs. The raw data were lost in the other cases. The calibration runs shown are for the last two calibration runs, mixtures 6 and 7. The windowed cell K-value data were taken with mixture 6 in the cell.

Tables XVII through XX present the data of the chromatographic experiment. All data taken using a given column are listed immediately after the data concerning the column weight, that is, after SWW, SWD, etc. Thus, eight of nine runs for a given column may be at 20°F and one may be at 0°F. This happened in a few cases where a bad run made it necessary to redo a data point. The numbers preceding the rows indicate the sample which corresponds to the data, where helium is 1, argon 2, CO_2 3, and H_2S 4. The "B" and "C" indicate whether the sample was passed through the column bypass, or through the column, respectively.

TABLE XVI

RAW DATA FOR CARBON DIOXIDE AND HYDROGEN SULFIDE K-VALUES IN THE METHANE+ N-OCTANE SYSTEM FROM THE CLASSICAL WINDOWED CELL EXPERIMENT

	TC				HF	
	Methane	CO_2	H_2S	Octane	Methane	Octane
1000 psia 0°C	195419	22873	32601	1057558	287325	5750030
	136253	8340	3976	–––	202934	1955.3
	130496	7927	3766	–––	201719	1959.5
	193952	24008	36070	1123242	283791	6237460
800 psia 0°C	84630	11111	17981	834169	154515	4024420
	149633	9375	4894	–––	280489	7374.3
	152276	9412	4883	–––	286169	4821.3
	85449	11245	18034	647394	152429	3802870
600 psia 0°C	83987	12057	22063	945230	181630	7621910
	506245	32059	17198	–––	1209431	4000.8
	507182	32107	17942	–––	1200096	4095.7
	53144	7365	13576	571637	120762	4516710
400 psia 0°C	34283	5029	10280	596393	76272	4382610
	325850	20906	11521	–––	761665	2905.8
	35064	5287	10850	602734	77280	4755810
	331209	21276	13038	–––	–––	–––
200 psia 0°C	16556	2561	5996	649141	36931	4785250
	153377	10233	6321	–––	358164	1804.6
	26343	3652	10434	1080761	56749	8722310
	148914	9957	6202	–––	350858	1764.1
1000 psia -20°C	176435	24104	37088	837750	395691	6829640
	103657	6261	2875	–––	244085	1759.4
	102179	6138	2905	–––	241890	1804.3
	174706	23836	36693	844112	–––	6409260
800 psia -20°C	85744	12717	21611	554591	184957	4268370
	126176	7720	3896	–––	294280	6617.9
	86488	12705	21679	534319	184503	4052430
	123299	7563	3793	–––	282615	3001.7

TABLE XVI (Continued)

	TC				HF	
	Methane	CO_2	H_2S	Octane	Methane	Octane
600 psia -20°C	102388	16415	31466	949477	224555	7491650
	513739	32016	16656	--	1192405	1609.1
	529227	33068	17613	--	1261166	2027.3
	98596	14872	27965	843306	210497	6685370
400 psia -20°C	66005	10633	18382	1001682	155654	877295
	335590	19769	8453	--	840650	982.9
	66276	10262	17966	970279	145516	7927350
	351567	20757	8993	--	851230	1085.3
200 psia -20°C	32642	5471	11448	1047787	73645	8882670
	174351	10904	5029	--	426642	1128.3
	164462	10221	4936	--	403284	572.1
	32040	5526	11916	1091588	71903	9019020
Mixture 6	428152	30262	23932	444250	710786	2332940
	709623	50028	39696	637581	1188395	3644630
	434504	30555	24503	419498	711913	2116690
	680622	48731	39786	701723	1115174	375551
Mixture 7	235414	61002	57501	399780	566853	3169290
	388016	98967	94675	630556	929611	5282490
	236444	61172	58301	399318	580005	3181920
	389773	99648	94523	629699	914235	5285040

TABLE XVII

RAW DATA FOR CARBON DIOXIDE AND HYDROGEN SULFIDE K-VALUES IN THE METHANE+n-HEPTANE SYSTEM FROM THE CHROMATOGRAPHIC EXPERIMENT

```
               t_B        t_R      P_a     T_a     V_R

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SWW =15.18200     PCF =72.88390      CW = 9.25863
SWD =13.57180     PCE =70.02669

     T = 20.0000       P = 101.50       VG =  6.475
 1 B  0.54.30    0.58.85    744.3   27.0    5.809
 1 C  0.54.20    2.04.96    744.3   27.2   12.342
 2 B  0.54.30    0.58.98    744.3   27.1    5.818
 2 C  0.54.20    2.09.22    744.3   27.2   12.763
 3 B  0.54.30    0.58.84    744.3   27.1    5.804
 3 C  0.54.20    2.34.56    744.3   27.3   15.257
 4 B  0.54.20    0.58.36    744.3   27.1    5.767
 4 C  0.54.20    4.01.58    744.3   27.3   23.847

     T = 20.0000       F = 198.50       VG =  6.494
 1 B  0.42.10    1.27.93    744.3   27.4    5.606
 1 C  0.42.10    3.10.98    744.4   27.5   12.171
 2 B  0.42.10    1.28.47    744.4   27.4    5.641
 2 C  0.42.05    3.19.03    744.4   27.5   12.699
 3 B  0.42.10    1.28.29    744.4   27.4    5.630
 3 C  0.42.05    3.59.16    744.4   27.5   15.259
 4 B  0.42.10    1.28.26    744.4   27.5    5.625
 4 C  0.42.05    6.08.99    744.4   27.5   23.542

     T = 20.0000       P = 399.50       VG =  6.493
 1 B  0.35.30    2.28.44    744.4   27.5    5.397
 1 C  0.35.30    5.28.93    744.3   27.5   11.959
 2 B  0.35.30    2.29.80    744.4   27.5    5.447
 2 C  0.35.30    5.43.33    744.3   27.5   12.482
 3 B  0.35.30    2.30.18    744.4   27.5    5.461
 3 C  0.35.30    6.50.68    744.2   27.5   14.929
 4 B  0.35.30    2.29.36    744.4   27.5    5.431
 4 C  0.35.30   10.16.26    744.2   27.5   22.402

     T = 20.0000       P = 600.50       VG =  6.466
 1 B  0.29.55    3.10.19    744.0   27.5    5.283
 1 C  0.29.60    7.06.36    743.6   27.5   11.816
 2 B  0.29.55    3.12.32    743.9   27.5    5.341
 2 C  0.29.60    7.25.50    743.5   27.5   12.345
 3 B  0.29.55    3.12.38    743.8   27.5    5.342
 3 C  0.29.60    8.49.28    743.4   27.5   14.665
 4 B  0.29.55    3.12.28    743.7   27.5    5.339
 4 C  0.29.60   12.48.84    743.4   27.5   21.302

     T = 20.0000       F = 797.50       VG =  6.425
 1 B  0.23.90    3.28.91    743.4   27.6    5.185
 1 C  0.23.90    7.51.03    743.0   27.7   11.677
 2 B  0.23.90    3.31.93    743.3   27.6    5.259
 2 C  0.23.90    8.13.14    742.9   27.7   12.224
 3 B  0.23.90    3.32.66    743.3   27.6    5.277
 3 C  0.23.90    9.42.24    742.9   27.7   14.432
 4 B  0.23.90    3.32.16    743.2   27.6    5.264
 4 C  0.23.90   13.40.83    742.8   27.8   20.332
```

```
               t_B        t_R      P_a     T_a     V_R

     T = 20.0000       P =1002.50       VG =  6.398
 1 B  0.20.10    3.45.46    742.2   27.7    5.077
 1 C  0.20.20    8.34.78    742.0   27.5   11.544
 2 B  0.20.15    3.49.60    742.2   27.7    5.157
 2 C  0.20.20    8.59.62    742.0   27.4   12.108
 3 B  0.20.15    3.49.98    742.2   27.6    5.169
 3 C  0.20.20   10.30.93    741.9   27.5   14.147
 4 B  0.20.15    3.50.05    742.2   27.6    5.170
 4 C  0.20.20   14.21.90    741.9   27.7   19.304

     T = 20.0000       F =1250.50       VG =  6.426
 1 B  0.18.20    4.20.75    741.9   27.8    4.953
 1 C  0.18.30   10.05.44    742.2   27.8   11.443
 2 B  0.18.20    4.26.05    741.9   27.9    5.051
 2 C  0.18.35   10.35.68    742.2   27.7   11.989
 3 B  0.18.20    4.27.71    742.0   27.9    5.083
 3 C  0.18.40   12.14.43    742.2   27.7   13.814
 4 B  0.18.20    4.27.52    742.0   27.9    5.080
 4 C  0.18.45   16.04.72    742.2   27.7   18.096

     T = 20.0000       P =1502.50       VG =  6.370
 1 B  0.15.80    4.36.34    742.5   27.7    4.836
 1 C  0.15.80   10.43.76    742.7   27.6   11.275
 2 B  0.15.80    4.41.48    742.5   27.7    4.925
 2 C  0.15.80   11.16.48    742.8   27.6   11.849
 3 B  0.15.80    4.43.19    742.6   27.7    4.956
 3 C  0.15.80   12.52.67    742.9   27.5   13.544
 4 B  0.15.80    4.43.31    742.6   27.7    4.958
 4 C  0.15.80   16.16.50    743.0   27.5   17.119

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SWW =15.59300     PCF =74.05560      CW = 9.25845
SWD =13.69757     PCE =71.28218

     T =   .0000       F = 100.50       VG = 11.582
 1 B  0.55.05    1.00.94    743.4   28.0    5.686
 1 C  0.55.20    3.06.96    743.1   28.5   17.339
 2 B  0.55.10    1.01.22    743.3   28.1    5.703
 2 C  0.55.20    3.12.64    743.0   28.6   17.853
 3 B  0.55.10    1.01.68    743.3   28.2    5.742
 3 C  0.55.15    3.46.95    743.0   28.7   21.039
 4 B  0.55.10    1.01.20    743.2   28.3    5.694
 4 C  0.55.15    5.52.73    742.9   28.7   32.695

     T =   .0000       P = 200.50       VG = 11.378
 1 B  0.44.85    1.35.39    742.9   28.6    5.338
 1 C  0.44.90    5.00.36    742.3   28.5   16.784
 2 B  0.44.85    1.36.04    742.8   28.6    5.373
 2 C  0.44.90    5.09.65    742.2   28.5   17.301
 3 B  0.44.85    1.35.92    742.7   28.6    5.366
 3 C  0.44.90    6.05.87    742.1   28.5   20.439
 4 B  0.44.85    1.35.94    742.6   28.5    5.369
 4 C  0.44.90    9.21.15    742.0   28.5   31.344
```

```
               t_B        t_R      P_a     T_a     V_R

     T =   .0000       F = 399.50       VG = 11.312
 1 B  0.35.85    2.31.64    742.0   28.5    5.091
 1 C  0.36.00    8.13.06    741.3   28.5   16.468
 2 B  0.35.85    2.33.25    741.9   28.5    5.144
 2 C  0.36.00    8.28.69    741.2   28.6   16.977
 3 B  0.35.85    2.33.74    741.8   28.5    5.160
 3 C  0.36.00    9.57.36    741.1   28.7   19.922
 4 B  0.35.85    2.33.27    741.7   28.5    5.143
 4 C  0.36.00   14.45.00    741.0   28.7   29.511

     T =   .0000       F = 598.50       VG = 11.303
 1 B  0.30.55    3.17.50    741.0   28.8    4.939
 1 C  0.30.60   10.53.93    740.4   28.8   16.312
 2 B  0.30.55    3.20.03    740.9   28.8    5.001
 2 C  0.30.60   11.16.09    740.4   28.8   16.865
 3 B  0.30.55    3.20.48    740.8   28.8    5.012
 3 C  0.30.65   13.08.70    740.4   28.8   19.642
 4 B  0.30.55    3.19.78    740.7   28.8    4.994
 4 C  0.30.70   18.45.00    740.4   28.8   27.971

     T =   .0000       P = 797.50       VG = 11.281
 1 B  0.22.90    3.20.70    740.0   28.5    4.786
 1 C  0.23.00   11.18.62    740.0   28.2   16.142
 2 B  0.23.00    3.23.68    740.0   28.4    4.839
 2 C  0.23.00   11.42.66    740.0   28.2   16.714
 3 B  0.23.00    3.24.34    740.0   28.4    4.855
 3 C  0.23.05   13.32.38    740.0   28.1   19.293
 4 B  0.23.00    3.24.36    740.0   28.3    4.858
 4 C  0.23.15   18.34.40    740.0   28.1   26.351

     T =   .0000       F = 996.50       VG = 11.250
 1 B  0.19.40    3.35.39    740.8   28.3    4.626
 1 C  0.19.40   12.20.93    741.2   28.0   15.950
 2 B  0.19.40    3.39.48    740.8   28.2    4.717
 2 C  0.19.40   12.49.07    741.2   28.0   16.556
 3 B  0.19.40    3.40.72    741.0   28.1    4.747
 3 C  0.19.40   14.38.29    741.2   28.0   18.907
 4 B  0.19.40    3.39.48    741.0   28.0    4.723
 4 C  0.19.45   19.22.70    741.2   28.0   24.965

     T =   .0000       F =1250.50       VG = 11.279
 1 B  0.17.85    4.15.14    741.2   27.9    4.480
 1 C  0.17.90   15.03.39    741.2   27.8   15.826
 2 B  0.17.85    4.21.12    741.2   27.8    4.587
 2 C  0.17.95   15.39.14    741.2   27.8   16.406
 3 B  0.17.85    4.21.60    741.2   27.8    4.596
 3 C  0.17.95   17.40.42    741.2   27.8   18.525
 4 B  0.18.00    4.22.04    741.2   27.8    4.565
 4 C  0.17.95   22.19.80    741.2   27.8   23.406

     T =   .0000       P =1506.50       VG = 11.200
 1 B  0.15.90    4.38.62    740.9   27.5    4.331
 1 C  0.16.00   16.55.64    740.6   28.2   15.617
 2 B  0.16.00    4.43.52    740.9   27.6    4.377
 2 C  0.15.95   17.36.28    740.4   28.4   16.270
 3 B  0.16.00    4.44.88    740.9   27.8    4.393
 3 C  0.15.90   19.34.05    740.2   28.4   18.135
 4 B  0.16.00    4.46.00    740.7   28.0    4.404
 4 C  0.16.00   23.44.80    740.8   28.0   21.941
```

TABLE XVII (Continued)

```
               tB          tR        Pa     Ta      VR

      T =-20.0000       F =1496.50       VG = 11.252
  1 B  0.16.05    4.40.37   738.6   28.3    3.769
  1 C  0.16.25   18.57.36   738.2   28.2   15.103
  2 B  0.16.20    4.47.22   738.6   28.3    3.826
  2 C  0.16.25   19.44.58   737.9   28.1   15.733
  3 B  0.16.20    4.48.28   738.6   28.3    3.840
  3 C  0.16.25   22.05.80   737.7   28.0   17.614
  4 B  0.16.30    4.50.42   738.6   28.3    3.845
  4 C  0.16.25   27.05.00   737.5   27.9   21.595


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SWW =15.55000      PCF =71.39851      CW = 9.25860
SWD =13.69402      PCE =68.21887


      T =-20.0000       F =  100.50      VG =  6.490
  1 B  0.50.72    0.53.94   741.0   26.4    5.239
  1 C  0.50.50    2.01.14   741.0   26.6   11.804
  2 B  0.50.60    0.54.06   741.0   26.5    5.260
  2 C  0.50.50    2.06.71   741.0   26.6   12.346
  3 B  0.50.55    0.54.08   741.0   26.5    5.267
  3 C  0.50.50    2.49.54   741.0   26.7   16.510
  4 B  0.50.50    0.53.80   741.0   26.6    5.242
  4 C  0.50.50    5.35.50   741.0   26.9   32.634

      T =-20.0000       P =  200.50      VG =  6.500
  1 B  0.42.70    1.28.77   740.9   26.9    4.991
  1 C  0.42.65    3.25.56   740.7   27.0   11.561
  2 B  0.42.65    1.29.94   740.9   26.9    5.063
  2 C  0.42.65    3.35.64   740.6   27.0   12.127
  3 B  0.42.60    1.29.88   740.8   26.9    5.065
  3 C  0.42.65    4.49.85   740.5   27.1   16.288
  4 B  0.42.60    1.29.28   740.8   27.0    5.028
  4 C  0.42.65    9.23.00   740.4   27.1   31.633

      T =-20.0000       F =  399.50      VG =  6.458
  1 B  0.31.95    2.12.03   740.4   27.2    4.710
  1 C  0.32.10    5.17.26   740.2   27.4   11.249
  2 B  0.32.00    2.13.70   740.4   27.2    4.762
  2 C  0.32.10    5.35.01   740.1   27.5   11.869
  3 B  0.32.00    2.13.94   740.4   27.2    4.771
  3 C  0.32.10    7.27.66   740.0   27.5   15.858
  4 B  0.32.00    2.14.00   740.3   27.3    4.769
  4 C  0.32.10   13.47.32   740.0   27.6   29.291

      T =-20.0000       F =  599.50      VG =  6.391
  1 B  0.25.50    2.43.86   739.0   27.9    4.579
  1 C  0.25.60    6.37.22   739.0   28.0   11.051
  2 B  0.25.45    2.46.54   739.0   27.9    4.663
  2 C  0.25.55    6.59.64   738.8   27.9   11.701
  3 B  0.25.50    2.46.02   739.0   27.9    4.640
  3 C  0.25.50    9.12.02   738.6   27.9   15.419
  4 B  0.25.60    2.46.52   739.0   27.9    4.636
  4 C  0.25.65   16.05.15   738.4   27.8   26.808
```

```
               tB          tR        Pa     Ta      VR

      T =-20.0000       F =  795.50      VG =  6.387
  1 B  0.20.60    3.00.00   738.4   27.8    4.388
  1 C  0.20.60    7.25.68   738.4   27.9   10.857
  2 B  0.20.60    3.03.08   738.4   27.8    4.463
  2 C  0.20.60    7.52.42   738.4   27.9   11.509
  3 B  0.20.55    3.03.58   738.4   27.9    4.483
  3 C  0.20.65   10.11.02   738.4   27.9   14.849
  4 B  0.20.60    3.04.12   738.4   27.9    4.485
  4 C  0.20.70   16.45.45   738.4   27.9   24.376

      T =-20.0000       F =  997.50      VG =  6.379
  1 B  0.17.50    3.14.50   739.2   27.5    4.202
  1 C  0.17.55    8.15.04   739.2   27.5   10.664
  2 B  0.17.50    3.18.34   739.2   27.5    4.285
  2 C  0.17.55    8.46.00   739.2   27.5   11.331
  3 B  0.17.50    3.19.28   739.2   27.5    4.305
  3 C  0.17.55   11.08.94   739.3   27.5   14.413
  4 B  0.17.55    3.20.08   739.2   27.5    4.310
  4 C  0.17.55   17.19.40   739.3   27.5   22.395

      T =-20.0000       P =1255.50       VG =  6.368
  1 B  0.16.95    3.58.74   739.7   27.0    3.916
  1 C  0.16.95   10.32.78   739.7   27.0   10.378
  2 B  0.16.95    4.03.88   739.7   27.0    4.000
  2 C  0.16.95   11.18.40   739.7   27.0   11.126
  3 B  0.16.95    4.08.60   739.7   27.0    4.077
  3 C  0.16.95   13.57.70   739.7   27.4   13.707
  4 B  0.16.95    4.07.14   739.7   27.0    4.053
  4 C  0.16.95   20.07.05   739.7   27.8   19.705


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SWW =14.64625      PCF =73.94495      CW = 9.25875
SWD =13.09970      PCE =71.28571


      T =-40.0000       F =  101.50      VG = 11.431
  1 B  0.55.40    1.00.33   743.3   27.3    5.041
  1 C  0.55.25    3.17.76   743.3   27.7   16.530
  2 B  0.55.40    1.00.24   743.3   27.5    5.027
  2 C  0.55.25    3.22.60   743.3   27.8   16.924
  3 B  0.55.40    1.00.29   743.3   27.4    5.034
  3 C  0.55.25    4.13.51   743.3   27.9   21.165
  4 B  0.55.25    1.00.04   743.3   27.6    5.021
  4 C  0.55.20    7.45.82   743.3   28.0   38.903

      T =-40.0000       P =  201.50      VG = 11.491
  1 B  0.43.95    1.33.51   743.4   28.1    4.795
  1 C  0.43.85    5.18.42   743.4   28.3   16.350
  2 B  0.43.95    1.34.00   743.4   28.2    4.818
  2 C  0.43.85    5.27.63   743.4   28.3   16.820
  3 B  0.43.95    1.34.44   743.4   28.2    4.840
  3 C  0.43.85    6.49.56   743.4   28.3   21.026
  4 B  0.43.95    1.34.00   743.4   28.3    4.815
  4 C  0.44.15   12.17.00   743.4   28.3   37.580
```

```
               tB          tR        Pa     Ta      VR

      T =-40.0000       F =  399.50      VG = 11.495
  1 B  0.33.85    2.23.22   743.5   28.4    4.504
  1 C  0.33.85    8.31.00   743.3   28.4   16.066
  2 B  0.33.85    2.25.72   743.5   28.4    4.583
  2 C  0.33.85    8.48.24   743.3   28.4   16.608
  3 B  0.33.85    2.26.56   743.4   28.4    4.608
  3 C  0.33.90   10.53.02   743.2   28.4   20.497
  4 B  0.33.85    2.25.54   743.4   28.4    4.576
  4 C  0.34.00   18.18.10   743.0   28.4   34.357

      T =-40.0000       P =  597.50      VG = 11.397
  1 B  0.27.25    2.56.03   742.9   28.3    4.277
  1 C  0.27.40   10.50.74   742.7   28.0   15.749
  2 B  0.27.25    2.58.60   742.9   28.2    4.342
  2 C  0.27.35   11.14.00   742.6   28.0   16.340
  3 B  0.27.25    2.59.54   742.8   28.2    4.365
  3 C  0.27.35   13.40.65   742.6   27.9   19.907
  4 B  0.27.35    2.59.30   742.8   28.1    4.345
  4 C  0.27.35   21.38.42   742.6   27.8   31.514

      T =-40.0000       F =  797.50      VG = 11.447
  1 B  0.21.95    3.12.32   742.3   27.7    4.019
  1 C  0.21.95   12.23.32   742.3   27.7   15.533
  2 B  0.21.95    3.16.52   742.3   27.7    4.107
  2 C  0.22.00   12.51.62   742.3   27.7   16.088
  3 B  0.21.95    3.17.58   742.3   27.7    4.129
  3 C  0.22.00   15.24.50   742.3   27.7   19.275
  4 B  0.21.95    3.17.23   742.3   27.7    4.121
  4 C  0.21.95   22.47.50   742.3   27.7   28.576

      T =-40.0000       P =1000.50       VG = 11.412
  1 B  0.18.25    3.25.68   742.8   27.7    3.770
  1 C  0.18.45   14.00.88   742.8   27.6   15.253
  2 B  0.18.25    3.29.79   742.8   27.7    3.845
  2 C  0.18.45   14.32.64   742.8   27.6   15.829
  3 B  0.18.25    3.30.40   742.8   27.7    3.856
  3 C  0.18.45   17.01.88   742.8   27.5   18.547
  4 B  0.18.25    3.30.52   742.8   27.7    3.858
  4 C  0.18.45   23.32.55   742.8   27.5   25.638

      T =-40.0000       P =1247.50       VG = 11.493
  1 B  0.16.00    3.47.92   743.2   27.3    3.419
  1 C  0.16.10   16.41.48   743.7   26.8   14.981
  2 B  0.16.00    3.53.08   743.3   27.3    3.497
  2 C  0.16.15   17.21.28   743.7   26.6   15.546
  3 B  0.16.00    3.53.89   743.4   27.3    3.509
  3 C  0.16.20   19.43.10   743.7   26.4   17.629
  4 B  0.16.05    3.53.24   743.7   26.9    3.498
  4 C  0.16.00   25.09.12   743.5   26.9   22.697


      T =-40.0000       P =1502.50       VG = 11.506
  1 B  0.14.60    4.13.70   743.8   26.3    3.200
  1 C  0.14.50   19.25.40   743.8   26.3   14.799
  2 B  0.14.60    4.17.48   743.8   26.3    3.247
  2 C  0.14.45   20.16.20   743.8   26.3   15.497
  3 B  0.14.55    4.18.42   743.8   26.3    3.270
  3 C  0.14.45   22.17.70   743.8   26.3   17.045
  4 B  0.14.50    4.18.06   743.8   26.3    3.277
  4 C  0.14.40   27.15.70   743.8   26.3   20.915
```

TABLE XVIII

RAW DATA FOR CARBON DIOXIDE AND HYDROGEN SULFIDE K-VALUES IN THE METHANE+METHYLCYCLOHEXANE SYSTEM FROM THE CHROMATOGRAPHIC EXPERIMENT

t_B t_R P_a T_a V_R

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***********************************************

SWW =14.59760      PCF =74.12320      CW = 9.25860
SWD =13.24980      PCE =71.28494

   T = 20.0000       F =  99.50       VG =  6.232
 1 B  0.55.50    0.58.74   741.5   26.0    5.797
 1 C  C.55.60    2.02.9C   741.7   26.5   12.075
 2 B  0.55.50    0.58.98   741.5   26.2    5.814
 2 C  0.55.60    2.06.46   741.7   26.6   12.418
 3 B  C.55.50    0.59.13   741.6   26.3    5.826
 3 C  C.55.55    2.28.56   741.8   26.7   14.595
 4 B  0.55.50    0.58.81   741.6   26.4    5.791
 4 C  C.55.50    4.01.96   741.8   26.9   23.765

   T = 20.0000       F = 2CC.50       VG =  6.286
 1 B  0.46.00    1.36.96   741.8   27.2    5.588
 1 C  0.46.00    3.27.33   741.8   27.5   11.928
 2 B  C.46.00    1.37.42   741.8   27.3    5.611
 2 C  C.46.05    3.34.56   741.8   27.5   12.331
 3 B  C.46.00    1.37.43   741.8   27.4    5.609
 3 C  C.46.05    4.13.31   741.8   27.6   14.549
 4 B  C.46.00    1.37.36   741.8   27.4    5.605
 4 C  C.46.10    6.47.8C   741.8   27.6   23.397

   T = 20.0000       F = 4C1.50       VG =  6.250
 1 B  0.34.75    2.26.84   741.8   27.7    5.371
 1 C  0.34.70    5.18.95   741.8   27.9   11.669
 2 B  C.34.75    2.28.96   741.8   27.7    5.448
 2 C  0.34.70    5.3C.36   741.8   27.9   12.087
 3 B  C.34.75    2.28.87   741.8   27.7    5.445
 3 C  C.34.70    6.28.28   741.8   28.C   14.198
 4 B  C.34.75    2.28.C2   741.8   27.8    5.411
 4 C  C.34.70   10.04.84   741.8   28.0   22.116

   T = 20.0000       P = 597.50       VG =  6.236
 1 B  C.30.95    3.20.CC   741.8   28.1    5.296
 1 C  C.31.15    7.20.79   741.8   28.3   11.583
 2 B  C.30.95    3.22.C6   741.8   28.1    5.350
 2 C  C.31.20    7.37.35   741.6   28.3   11.996
 3 B  C.31.00    3.22.93   741.8   28.2    5.362
 3 C  C.31.25    8.54.94   741.4   28.3   14.004
 4 B  C.31.05    3.22.86   741.8   28.2    5.351
 4 C  C.31.30   13.24.CC   741.2   28.3   21.009

   T = 20.0000       F = 798.50       VG =  6.236
 1 B  C.24.15    3.32.21   741.2   28.3    5.169
 1 C  C.24.10    7.5C.11   741.2   28.5   11.461
 2 B  C.24.15    3.35.24   741.2   28.3    5.243
 2 C  C.24.05    8.09.34   740.0   28.6   11.927
 3 B  C.24.15    3.35.56   741.2   28.3    5.250
 3 C  C.24.05    9.25.87   740.8   28.6   13.808
 4 B  C.24.15    3.35.26   741.2   28.3    5.243
 4 C  0.24.05   13.37.30   74C.6   28.7   19.926
```

t_B t_R P_a T_a V_R

```
   T = 20.0000       F = 995.50       VG =  6.105
 1 B  C.20.45    3.50.71   739.6   28.5    5.079
 1 C  C.20.70    8.38.54   739.4   29.0   11.241
 2 B  C.20.55    3.55.4C   739.6   28.7    5.151
 2 C  0.20.70    8.59.93   739.3   28.9   11.710
 3 B  C.20.65    3.55.76   739.5   28.8    5.130
 3 C  C.20.70   10.20.52   739.3   28.8   13.466
 4 B  0.20.65    3.55.8C   739.5   28.9    5.128
 4 C  C.2C.70   14.27.8C   739.3   28.6   18.854

   T = 20.0000       F =1246.50       VG =  6.184
 1 B  C.18.30    4.23.C2   739.3   28.5    4.947
 1 C  C.18.45    9.59.72   739.3   28.5   11.187
 2 B  0.18.40    4.28.68   739.3   28.5    5.026
 2 C  0.18.45   10.25.16   739.3   28.5   11.662
 3 B  C.18.40    4.29.9C   739.3   28.5    5.048
 3 C  C.18.45   11.48.52   739.3   28.5   13.217
 4 B  C.18.35    4.29.82   739.3   28.5    5.061
 4 C  0.18.50   15.52.85   739.3   28.5   17.726

   T = 20.0000       F =15C2.50       VG =  6.166
 1 B  0.15.75    4.36.45   739.3   28.5    4.808
 1 C  0.15.80   10.35.08   740.2   28.4   11.032
 2 B  0.15.80    4.42.26   739.6   28.5    4.896
 2 C  C.15.75   11.00.68   740.4   28.3   11.523
 3 B  0.15.80    4.43.88   739.8   28.5    4.926
 3 C  0.15.78   12.21.8C   740.6   28.2   12.924
 4 B  0.15.80    4.43.48   740.0   28.5    4.920
 4 C  C.15.78   15.56.9C   740.8   28.1   16.687

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SWW =14.47100      PCF =68.06660      CW = 9.25860
SWD =12.83220      PCE =65.12869

   T =   .0000       P = 1CC.50       VG =  6.579
 1 B  C.51.60    0.56.44   740.0   27.4    5.611
 1 C  C.51.50    2.03.14   740.2   27.7   12.248
 2 B  0.51.60    0.56.61   740.0   27.4    5.628
 2 C  0.51.40    2.07.12   740.2   27.7   12.669
 3 B  C.51.60    0.56.52   740.1   27.5    5.617
 3 C  C.51.30    2.35.54   740.2   27.8   15.522
 4 B  C.51.55    C.56.22   740.1   27.6    5.589
 4 C  0.51.30    4.42.43   740.2   27.9   28.169

   T =   .0000       F = 198.50       VG =  6.569
 1 B  C.44.70    1.34.16   740.0   28.2    5.331
 1 C  C.44.70    3.31.42   739.8   28.3   11.959
 2 B  C.44.70    1.34.74   740.0   28.3    5.360
 2 C  C.44.70    3.39.31   739.7   28.3   12.403
 3 B  0.44.70    1.35.21   739.9   28.4    5.383
 3 C  C.44.70    4.28.23   739.6   28.3   15.168
 4 B  C.44.70    1.34.8C   739.9   28.4    5.360
 4 C  C.44.70    8.00.16   739.5   28.3   27.148
```

t_B t_R P_a T_a V_R

```
   T =   .0000       P = 4CC.50       VG =  6.478
 1 B  C.34.50    2.26.86   739.4   28.4    5.095
 1 C  0.34.50    5.35.4C   739.3   28.5   11.627
 2 B  C.34.50    2.27.92   739.4   28.4    5.132
 2 C  C.34.50    5.47.64   739.3   28.6   12.044
 3 B  0.34.50    2.28.15   739.3   28.4    5.139
 3 C  0.34.50    7.03.99   739.3   28.6   14.689
 4 B  0.34.50    2.28.C6   739.3   28.5    5.133
 4 C  C.34.50   12.05.43   739.3   28.6   25.133

   T =   .0000       P = 598.50       VG =  6.460
 1 B  C.29.70    3.13.4C   739.0   28.8    4.961
 1 C  0.29.75    7.28.32   738.8   28.8   11.477
 2 B  0.29.75    3.14.76   739.0   28.8    4.987
 2 C  0.29.75    7.44.79   738.6   28.8   11.895
 3 B  0.29.75    3.15.14   738.9   28.8    4.996
 3 C  0.29.75    9.21.75   738.4   28.9   14.364
 4 B  C.29.75    3.15.12   738.9   28.8    4.996
 4 C  C.29.75   15.16.82   738.2   29.0   23.422

   T =   .00C0       F = 799.50       VG =  6.430
 1 B  C.25.50    3.45.CC   738.2   29.0    4.780
 1 C  0.25.50    8.50.8C   737.5   29.0   11.266
 2 B  C.25.50    3.48.CC   738.0   29.0    4.843
 2 C  0.25.50    9.12.26   737.5   29.0   11.721
 3 B  0.25.50    3.48.6C   737.8   29.0    4.854
 3 C  0.25.45   10.58.97   737.2   29.0   14.008
 4 B  0.25.50    3.48.44   737.7   29.0    4.850
 4 C  C.25.45   17.06.8C   737.0   29.0   21.821

   T =   .0000       P = 997.50       VG =  6.484
 1 B  C.20.70    3.49.C7   737.9   28.8    4.574
 1 C  C.2C.70    9.16.C4   738.0   28.8   11.104
 2 B  C.2C.70    3.55.18   737.9   28.8    4.696
 2 C  C.2C.70    9.38.48   738.0   28.8   11.552
 3 B  C.20.70    3.56.31   737.9   28.8    4.718
 3 C  0.20.70   11.2C.95   738.1   28.8   13.600
 4 B  C.20.70    3.56.54   737.9   28.8    4.723
 4 C  0.20.70   16.52.7C   738.1   28.8   20.226

   T =   .0000       F =1246.50       VG =  6.416
 1 B  C.17.40    4.08.88   738.3   28.7    4.458
 1 C  C.17.60   10.16.62   738.6   28.7   10.923
 2 B  0.17.50    4.15.26   738.4   28.7    4.546
 2 C  C.17.60   10.41.42   738.6   28.7   11.363
 3 B  0.17.55    4.17.6C   738.5   28.7    4.576
 3 C  C.17.65   12.23.47   738.6   28.6   13.141
 4 B  C.17.60    4.17.17   738.5   28.7    4.555
 4 C  C.17.65   17.27.8C   738.6   28.5   18.531

   T =   .0000       F =1498.50       VG =  6.409
 1 B  C.16.25    4.44.1C   738.8   28.4    4.308
 1 C  C.16.20   11.47.94   738.8   28.4   10.769
 2 B  C.16.25    4.5C.78   738.8   28.4    4.410
 2 C  C.16.20   12.17.83   738.8   28.3   11.230
 3 B  C.16.25    4.51.81   738.8   28.4    4.425
 3 C  C.16.25   14.00.CC   738.8   28.2   12.753
 4 B  C.16.25    4.5C.8C   738.8   28.4    4.410
 4 C  C.16.25   18.39.15   738.8   28.2   16.992
```

TABLE XVIII (Continued)

t_B t_R P_a T_a V_R

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SWW =14.47100     PCF =68.07680     CW = 9.25860
SWD =12.83220     PCE =65.12869

    T =-2C.0000       F = 1CC.50      VG =  6.522
 1 B  C.54.35    0.58.CC   741.4   26.3    5.263
 1 C  C.53.90    2.09.58   741.4   26.6   11.836
 2 B  C.54.35    0.58.28   741.4   26.4    5.285
 2 C  C.53.85    2.13.66   741.4   26.7   12.213
 3 B  C.54.00    0.58.23   741.4   26.5    5.312
 3 C  0.53.75    2.50.14   741.4   26.8   15.567
 4 B  C.54.00    0.58.C6   741.4   26.5    5.297
 4 C  C.53.70    5.47.C7   741.4   26.9   31.766

    T =-20.0000       P = 2CC.50      VG =  6.488
 1 B  C.45.45    1.35.68   741.4   27.0    5.055
 1 C  0.45.45    3.39.56   741.4   27.0   11.599
 2 B  C.45.45    1.36.31   741.4   27.0    5.088
 2 C  0.45.40    3.47.52   741.4   27.1   12.026
 3 B  C.45.45    1.36.70   741.4   27.0    5.109
 3 C  C.45.40    4.5C.68   741.4   27.2   15.356
 4 B  C.45.45    1.35.78   741.4   27.0    5.060
 4 C  C.45.40    9.42.68   741.4   27.3   30.764

    T =-20.0000       F = 357.50      VG =  6.490
 1 B  C.34.10    2.23.68   741.4   27.4    4.828
 1 C  C.34.15    5.39.C2   741.3   27.4   11.373
 2 B  C.34.10    2.25.3C   741.4   27.4    4.882
 2 C  C.34.15    5.52.16   741.2   27.4   11.812
 3 B  C.34.10    2.25.46   741.4   27.4    4.888
 3 C  0.34.15    7.26.16   741.1   27.4   14.963
 4 B  C.34.10    2.25.26   741.4   27.4    4.881
 4 C  C.34.15   14.03.1C   741.0   27.4   28.271

    T =-20.0000       F = 6C2.50      VG =  6.450
 1 B  C.26.90    2.53.82   741.0   27.4    4.608
 1 C  C.26.80    6.58.33   740.5   27.5   11.118
 2 B  0.26.90    2.55.16   741.0   27.4    4.644
 2 C  C.26.80    7.15.36   740.5   27.5   11.570
 3 B  0.26.90    2.56.12   741.0   27.4    4.669
 3 C  0.26.80    9.04.2C   740.5   27.5   14.463
 4 B  C.26.85    2.55.86   741.0   27.4    4.671
 4 C  C.26.80   16.04.CC   740.5   27.5   25.620

    T =-20.0000       F = 799.50      VG =  6.472
 1 B  0.22.40    3.15.91   740.3   27.7    4.406
 1 C  C.22.40    8.06.5C   740.0   27.8   10.930
 2 B  0.22.40    3.19.6C   740.3   27.7    4.489
 2 C  C.22.40    8.26.51   740.0   27.8   11.380
 3 B  C.22.40    3.20.94   740.2   27.7    4.519
 3 C  0.22.40   10.21.72   740.0   27.8   13.968
 4 B  0.22.40    3.20.82   740.1   27.7    4.515
 4 C  C.22.40   17.19.42   740.0   27.8   23.353
```

t_B t_R P_a T_a V_R

```
    T =-2C.0000       F =1CC1.50      VG =  6.388
 1 B  C.19.25    3.36.7C   739.3   28.C    4.227
 1 C  C.19.50    9.14.18   739.1   28.0   10.669
 2 B  C.19.35    3.42.15   739.3   28.0    4.311
 2 C  0.19.50    9.38.16   739.1   28.0   11.131
 3 B  C.19.45    3.43.8C   739.2   28.0    4.320
 3 C  C.19.50   11.35.84   739.0   28.0   13.395
 4 B  0.19.45    3.43.32   739.2   28.0    4.311
 4 C  C.19.50   18.08.3C   739.0   28.0   20.949

    T =-20.0000       P =1253.50      VG =  6.352
 1 B  C.16.60    3.58.52   739.0   27.6    3.983
 1 C  0.16.80   10.3C.7C   739.0   27.9   10.389
 2 B  C.16.75    4.05.9C   739.0   27.7    4.067
 2 C  0.16.80   10.58.74   739.0   27.9   10.850
 3 B  C.16.75    4.07.12   739.0   27.7    4.087
 3 C  C.16.80   12.53.C1   739.0   27.8   12.740
 4 B  0.16.80    4.07.31   739.0   27.7    4.078
 4 C  C.16.80   18.41.4C   739.0   27.8   18.482

    T =-2C.0000       P =15C2.50      VG =  6.339
 1 B  0.16.20    4.47.1C   740.0   27.7    3.830
 1 C  0.16.45   12.58.36   740.0   27.7   10.225
 2 B  0.16.30    4.53.77   740.0   27.7    3.895
 2 C  C.16.45   13.33.16   740.0   27.7   10.682
 3 B  0.16.40    4.57.2C   740.0   27.7    3.916
 3 C  0.16.45   15.34.55   740.0   27.7   12.277
 4 B  C.16.40    4.55.4C   740.0   27.7    3.892
 4 C  0.16.45   21.03.2C   740.0   27.7   16.594

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SWW =14.39900     PCF =73.C8286     CW = 9.25862
SWD =12.74685     PCE =7C.C0505

    T =-4C.0000       P = 1C1.50      VG =  6.357
 1 B  0.57.50    1.02.3C   740.4   26.3    5.023
 1 C  C.57.35    2.21.6C   740.5   26.5   11.436
 2 B  C.57.45    1.02.74   740.4   26.3    5.063
 2 C  0.57.30    2.26.9C   740.5   26.6   11.868
 3 B  0.57.45    1.02.76   740.4   26.4    5.062
 3 C  C.57.30    3.2C.76   740.6   26.6   16.221
 4 B  0.57.45    1.02.48   740.4   26.4    5.039
 4 C  C.57.35    8.05.48   740.6   26.7   39.170

    T =-4C.0000       F = 199.50      VG =  6.357
 1 B  C.47.45    1.39.27   740.6   26.8    4.780
 1 C  C.47.40    3.52.49   740.6   27.0   11.193
 2 B  C.47.50    1.40.2C   740.6   26.9    4.817
 2 C  C.47.40    4.01.44   740.6   27.C   11.624
 3 B  0.47.45    1.39.7C   740.6   27.0    4.795
 3 C  C.47.40    5.3C.18   740.6   27.0   15.896
 4 B  C.47.45    1.39.74   740.6   27.0    4.797
 4 C  C.47.40   12.55.8C   740.6   27.0   37.349
```

t_B t_R P_a T_a V_R

```
    T =-4C.0000       F = 398.50      VG =  6.331
 1 B  C.32.45    2.16.75   740.5   27.0    4.515
 1 C  C.32.45    5.30.29   740.5   27.0   10.905
 2 B  C.32.40    2.18.33   740.5   27.0    4.574
 2 C  C.32.45    5.44.52   740.4   27.0   11.373
 3 B  C.32.40    2.18.33   740.5   27.0    4.574
 3 C  C.32.45    7.44.C6   740.3   27.0   15.317
 4 B  0.32.40    2.17.95   740.5   27.0    4.562
 4 C  C.32.45   16.48.1C   740.2   27.0   33.269

    T =-4C.0000       F = 598.50      VG =  6.354
 1 B  C.25.90    2.47.52   740.1   27.1    4.289
 1 C  0.25.95    6.59.16   740.1   27.2   10.704
 2 B  C.25.90    2.49.8C   740.1   27.1    4.347
 2 C  C.25.95    7.18.34   740.1   27.2   11.194
 3 B  0.25.90    2.50.48   740.1   27.1    4.364
 3 C  C.25.95    9.38.24   740.1   27.2   14.766
 4 B  0.25.90    2.49.85   740.1   27.1    4.348
 4 C  C.25.95   19.19.76   740.1   27.3   29.600

    T =-4C.0000       F = 796.50      VG =  6.266
 1 B  C.19.60    2.51.14   739.8   27.3    4.005
 1 C  C.19.65    7.22.88   739.6   27.4   10.330
 2 B  C.19.60    2.54.74   739.8   27.3    4.089
 2 C  C.19.65    7.44.C4   739.5   27.4   10.822
 3 B  0.19.60    2.55.27   739.7   27.3    4.101
 3 C  C.19.65    9.57.24   739.5   27.4   13.928
 4 B  C.19.60    2.55.17   739.7   27.3    4.099
 4 C  C.19.65   18.30.1C   739.5   27.4   25.888

    T =-4C.0000       P =1C01.50      VG =  6.225
 1 B  C.16.95    3. 9.9C   739.2   27.4    3.731
 1 C  C.16.95    8.30.0C   739.2   27.4   10.021
 2 B  0.16.95    3.13.56   739.2   27.4    3.803
 2 C  C.16.95    8.56.56   739.2   27.4   10.543
 3 B  0.16.95    3.15.64   739.2   27.4    3.844
 3 C  0.16.95   11.09.67   739.2   27.3   13.165
 4 B  C.16.95    3.14.1C   739.2   27.4    3.814
 4 C  0.16.95   18.49.CC   739.2   27.3   22.196

    T =-40.0000       P =125C.50      VG =  6.166
 1 B  C.15.10    3.36.CC   739.4   27.2    3.408
 1 C  0.15.15   10.12.C7   739.5   27.1    9.633
 2 B  C.15.10    3.40.84   739.4   27.2    3.485
 2 C  0.15.15   10.43.CC   739.5   27.1   10.120
 3 B  C.15.10    3.42.17   739.4   27.2    3.506
 3 C  C.15.15   12.51.20   739.5   27.0   12.145
 4 B  C.15.10    3.4C.76   739.5   27.2    3.484
 4 C  C.15.15   19.20.72   739.5   27.0   18.279

    T =-4C.0000       P =1502.50      VG =  6.217
 1 B  C.15.40    4.29.24   740.2   27.0    3.177
 1 C  0.15.40   13.20.74   740.5   27.0    9.454
 2 B  0.15.40    4.35.24   740.3   27.0    3.249
 2 C  C.15.40   14.02.2C   740.6   27.0    9.945
 3 B  C.15.40    4.36.35   740.4   27.0    3.262
 3 C  C.15.40   16.1C.12   740.7   27.0   11.457
 4 B  C.15.40    4.36.82   740.4   27.0    3.268
 4 C  C.15.40   22.00.C7   740.8   27.0   15.592
```

TABLE XIX

RAW DATA FOR CARBON DIOXIDE AND HYDROGEN SULFIDE K-VALUES IN THE METHANE+TOLUENE SYSTEM FROM THE CHROMATOGRAPHIC EXPERIMENT

t_B t_R P_a T_a V_R

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SWW =14.75050     PCF =67.95506     CW = 9.25865
SWD =13.24605     PCE =65.11584


    T = 2C.0000        P = 1C1.50        VG =  6.691
 1 B  C.48.75   0.52.57  740.8  27.7    5.728
 1 C  C.48.70   1.54.21  740.8  27.9   12.442
 2 B  C.48.75   C.52.76  740.8  27.7    5.749
 2 C  C.48.65   1.55.79  740.8  27.9   12.628
 3 B  0.48.75   0.52.69  740.8  27.8    5.738
 3 C  C.48.65   2.16.94  740.8  28.0   14.925
 4 B  C.48.75   0.52.12  740.8  27.8    5.676
 4 C  C.48.60   5.10.CC  740.8  28.0   33.822

    T = 20.0000        F = 2CC.50        VG =  6.778
 1 B  C.41.70   1.28.C2  740.8  28.2    5.556
 1 C  0.41.55   3.15.24  740.6  28.3   12.357
 2 B  C.41.65   1.28.51  740.8  28.2    5.593
 2 C  0.41.55   3.18.4C  740.5  28.3   12.555
 3 B  C.41.55   1.28.28  740.7  28.3    5.588
 3 C  0.41.55   4.01.63  740.4  28.3   15.289
 4 B  C.41.55   1.28.49  740.7  28.3    5.601
 4 C  C.41.55   8.43.32  740.4  28.3   33.112

    T = 2C.0000        P = 4CC.50        VG =  6.756
 1 B  0.33.40   2.21.19  740.4  28.4    5.354
 1 C  C.33.40   5.20.46  740.0  28.5   12.138
 2 B  0.33.45   2.22.3C  740.3  28.4    5.387
 2 C  0.33.40   5.26.55  739.8  28.5   12.365
 3 B  0.33.40   2.22.62  740.2  28.5    5.403
 3 C  C.33.40   6.34.16  739.6  28.5   14.921
 4 B  0.33.40   2.22.39  740.1  28.5    5.394
 4 C  0.33.40  13.29.46  739.5  28.5   30.637

    T = 2C.0000        P = 595.50        VG =  6.779
 1 B  C.28.20   3.02.CC  739.5  28.5    5.277
 1 C  0.28.30   6.58.2C  738.9  28.5   12.073
 2 B  C.28.20   3.03.83  739.4  28.5    5.330
 2 C  C.28.40   7.05.72  738.7  28.5   12.244
 3 B  0.28.20   3.05.36  739.3  28.5    5.373
 3 C  C.28.40   8.29.16  738.7  28.5   14.643
 4 B  C.28.20   3.03.85  739.2  28.5    5.329
 4 C  C.28.40  16.31.44  738.7  28.5   28.513


    T = 20.0000        P = 8C2.50        VG =  6.422
 1 B  0.22.80   3.17.3C  738.7  28.5    4.846
 1 C  C.23.65   7.57.62  738.2  28.6   11.295
 2 B  C.23.00   3.21.41  738.6  28.5    4.903
 2 C  0.23.65   8.08.32  738.0  28.7   11.538
 3 B  C.23.20   3.25.CC  738.5  28.6    4.944
 3 C  0.23.75   9.37.25  737.7  28.7   13.576
 4 B  0.23.50   3.26.48  738.4  28.6    4.915
 4 C  0.23.80  17.44.15  737.5  28.7   24.967
```

t_B t_R P_a T_a V_R

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SWW =15.67600     PCF =73.89191     CW = 9.25875
SWD =13.75525     PCE =71.26849


    T = 2C.0001        P =1CCC.50        VG =  6.606
 1 B  0.17.70   3.10.67  745.0  22.7    5.042
 1 C  C.17.75   7.22.35  745.0  22.7   11.666
 2 B  C.17.75   3.14.76  745.0  22.7    5.136
 2 C  0.17.75   7.3C.34  745.0  22.7   11.876
 3 B  C.17.75   3.15.27  745.0  22.7    5.150
 3 C  0.17.75   8.44.83  744.9  22.7   13.839
 4 B  0.17.75   3.15.16  745.0  22.7    5.147
 4 C  C.17.75  15.12.85  744.7  22.7   24.063

    T = 2C.0001        P =1250.50        VG =  6.446
 1 B  C.16.40   3.47.94  745.0  22.6    4.968
 1 C  C.16.90   9.01.72  744.8  22.7   11.447
 2 B  0.16.50   3.52.C5  745.0  22.6    5.026
 2 C  C.17.05   9.20.79  744.7  22.7   11.744
 4 B  0.16.60   3.53.69  744.9  22.6    5.031
 4 C  0.17.45  17.42.35  744.6  22.8   21.724


************************************************


SWW =14.75050     PCF =67.98225     CW = 9.25865
SWD =13.24605     PCE =65.11584


    T =    .0000       F =  99.50        VG =  6.589

 1 B  C.51.00   0.53.C8  741.4  25.7    5.456
 1 C  0.51.00   1.57.52  741.4  25.9   12.066
 2 B  C.51.00   0.53.5C  741.4  25.7    5.499
 2 C  0.50.98   1.59.33  741.4  25.9   12.257
 3 B  0.51.00   0.53.42  741.4  25.8    5.488
 3 C  0.5C.95   2.31.46  741.4  25.9   15.566
 4 B  C.51.00   0.52.91  741.4  25.9    5.432
 4 C  C.5C.90   6.34.24  741.4  25.9   40.557

    T =    .0000       F = 199.50        VG =  6.806
 1 B  C.43.20   1.3C.16  741.3  26.0    5.331
 1 C  C.43.05   3.25.39  741.3  26.4   12.160
 2 B  C.43.20   1.3C.68  741.3  26.1    5.359
 2 C  0.43.05   3.28.47  741.3  26.3   12.350
 3 B  C.43.20   1.3C.7C  741.3  26.2    5.357
 3 C  C.43.05   4.24.36  741.2  26.3   15.658
 4 B  0.43.05   1.30.54  741.3  26.3    5.363
 4 C  C.43.05  11.1C.CC  741.2  26.3   39.684
```

t_B t_R P_a T_a V_R

```
    T =    .0000       F = 398.50        VG =  6.749
 1 B  0.35.25   2.27.84  741.2  26.3    5.119
 1 C  0.35.25   5.43.6C  741.6  26.5   11.891
 2 B  0.35.30   2.29.18  741.3  26.3    5.159
 2 C  C.35.25   5.49.22  741.8  26.5   12.089
 3 B  C.35.25   2.29.36  741.4  26.3    5.173
 3 C  0.35.25   7.16.88  742.0  26.5   15.128
 4 B  C.35.25   2.28.86  741.5  26.4    5.154
 4 C  C.35.25  17.15.25  742.0  26.5   35.847

    T =    .0000       F = 599.50        VG =  6.789
 1 B  0.31.00   3.18.66  742.0  26.6    4.957
 1 C  C.31.00   7.51.91  741.7  26.6   11.771
 2 B  C.30.95   3.20.61  742.0  26.6    5.014
 2 C  0.31.00   8.01.06  741.6  26.6   11.998
 3 B  0.30.95   3.21.72  741.9  26.6    5.041
 3 C  C.31.00   9.51.6C  741.5  26.6   14.752
 4 B  C.31.00   3.21.CC  741.8  26.6    5.014
 4 C  0.31.00  21.39.4C  741.4  26.6   32.398

    T =    .0000       P = 8C1.50        VG =  6.802
 1 B  C.23.90   3.28.18  740.8  27.6    4.764
 1 C  C.23.75   8.24.04  740.5  27.8   11.588
 2 B  C.23.85   3.30.8C  740.8  27.6    4.834
 2 C  C.23.75   8.33.85  740.4  27.8   11.812
 3 B  C.23.85   3.31.1C  740.7  27.7    4.837
 3 C  0.23.75  10.2C.54  740.3  27.9   14.254
 4 B  C.23.85   3.30.64  740.7  27.7    4.826
 4 C  0.23.75  21.08.2C  740.2  27.9   29.126

    T =    .0000       F = 999.50        VG =  6.828

 1 B  C.2C.20   3.44.58  739.9  28.0    4.621
 1 C  C.20.20   9.17.68  739.8  28.1   11.466
 2 B  0.20.20   3.48.27  739.9  28.0    4.697
 2 C  C.2C.20   9.27.2C  739.7  28.1   11.660
 3 B  0.20.20   3.49.C4  739.9  28.0    4.712
 3 C  0.2C.20  11.16.CC  739.6  28.1   13.894
 4 B  C.2C.20   3.49.94  739.9  28.0    4.731
 4 C  C.2C.20  21.23.75  739.6  28.2   26.371

    T =    .0000       P =1249.50        VG =  6.823
 1 B  C.17.55   4.10.82  739.7  28.2    4.465
 1 C  0.17.65  10.38.26  739.8  28.1   11.307
 2 B  0.17.60   4.16.4C  739.7  28.2    4.552
 2 C  C.17.65  10.49.86  739.9  28.0   11.520
 3 B  C.17.60   4.18.16  739.8  28.2    4.584
 3 C  C.17.65  12.35.16  740.0  28.0   13.389
 4 B  C.17.65   4.17.33  739.8  28.2    4.556
 4 C  C.17.65  21.54.1C  740.1  28.0   23.302

    T =    .0000       F =15CC.50        VG =  6.726
 1 B  C.16.25   4.44.48  740.4  27.9    4.331
 1 C  C.16.50  12.17.41  740.8  27.7   11.075
 2 B  0.16.30   4.51.32  740.5  27.8    4.424
 2 C  0.16.70  12.41.04  741.0  27.7   11.296
 3 B  0.16.35   4.52.CC  740.6  27.8    4.422
 3 C  C.15.00  12.55.85  741.2  27.7   12.824
 4 B  C.16.40   4.52.95  740.7  27.8    4.423
 4 C  C.14.93  20.39.6C  741.4  27.6   20.604
```

TABLE XIX (Continued)

* * *

SWW =14.47280 PCF =72.97650 CW = 9.25864
SWD =12.96688 PCE =70.02631

T =-20.0000 P = 100.50 VG = 6.589

		t_B	t_R	P_a	T_a	V_R
1	B	0.55.75	0.59.38	741.5	25.9	5.265
1	C	0.55.75	2.13.97	742.0	26.0	11.881
2	B	0.55.75	0.59.33	741.6	26.0	5.259
2	C	0.55.75	2.16.07	742.2	26.1	12.064
3	B	0.55.75	0.59.64	741.7	26.0	5.287
3	C	0.55.75	3.06.78	742.4	26.2	16.555
4	B	0.55.75	0.59.42	741.8	26.0	5.268
4	C	0.55.85	10.22.24	742.6	26.3	55.038

T =-20.0000 P = 200.50 VG = 6.643

		t_B	t_R	P_a	T_a	V_R
1	B	0.42.65	1.29.50	742.6	26.4	5.065
1	C	0.42.80	3.27.81	743.4	26.4	11.731
2	B	0.42.65	1.30.10	742.8	26.4	5.100
2	C	0.42.85	3.31.60	743.4	26.4	11.931
3	B	0.42.70	1.30.18	743.0	26.4	5.100
3	C	0.42.90	4.50.04	743.4	26.4	16.335
4	B	0.42.75	1.30.04	743.2	26.4	5.087
4	C	0.42.95	15.32.40	743.4	26.4	52.452

T =-20.0000 P = 397.50 VG = 6.658

		t_B	t_R	P_a	T_a	V_R
1	B	0.32.15	2.15.71	743.4	26.4	4.878
1	C	0.32.25	5.23.78	741.0	26.4	11.563
2	B	0.32.15	2.17.46	742.5	26.4	4.935
2	C	0.32.30	5.31.34	740.5	26.4	11.806
3	B	0.32.15	2.17.64	742.0	26.4	4.938
3	C	0.32.40	7.24.04	740.5	26.4	15.773
4	B	0.32.20	2.17.31	741.5	26.4	4.915
4	C	0.32.50	21.45.90	740.5	26.4	46.245

T =-20.0000 P = 597.50 VG = 6.707

		t_B	t_R	P_a	T_a	V_R
1	B	0.24.70	2.40.68	740.5	26.5	4.699
1	C	0.24.80	6.32.70	740.3	26.6	11.428
2	B	0.24.70	2.42.88	740.4	26.5	4.763
2	C	0.24.90	6.41.84	740.2	26.6	11.646
3	B	0.24.70	2.43.84	740.4	26.6	4.788
3	C	0.25.00	8.45.21	740.0	26.7	15.147
4	B	0.24.75	2.43.38	740.4	26.6	4.765
4	C	0.25.15	23.32.52	740.0	26.8	40.472

T =-20.0000 P = 800.50 VG = 6.565

		t_B	t_R	P_a	T_a	V_R
1	B	0.22.00	3.13.37	739.5	26.6	4.445
1	C	0.22.20	8.04.39	739.3	26.6	11.033
2	B	0.22.00	3.16.98	739.4	26.6	4.528
2	C	0.22.20	8.14.81	739.3	26.6	11.270
3	B	0.22.05	3.17.84	739.4	26.6	4.537
3	C	0.21.95	10.29.09	739.3	26.6	14.491
4	B	0.22.10	3.17.91	739.3	26.6	4.528
4	C	0.21.95	25.38.45	739.3	26.6	35.439

T =-20.0000 P =1000.50 VG = 6.647

		t_B	t_R	P_a	T_a	V_R
1	B	0.19.20	3.37.07	739.4	26.6	4.285
1	C	0.19.25	9.15.72	739.4	26.6	10.941
2	B	0.19.30	3.40.62	739.4	26.6	4.332
2	C	0.19.30	9.23.00	739.5	26.6	11.057
3	B	0.19.35	3.41.60	739.4	26.6	4.340
3	C	0.19.20	11.41.58	739.6	26.6	13.853
4	B	0.19.40	3.41.35	739.4	26.6	4.324
4	C	0.19.15	26.01.45	739.8	26.6	30.920

T =-20.0000 P =1250.50 VG = 6.690

		t_B	t_R	P_a	T_a	V_R
1	B	0.16.50	3.57.86	740.0	26.6	4.034
1	C	0.16.60	10.36.86	740.1	26.6	10.739
2	B	0.16.55	4.03.29	740.0	26.6	4.114
2	C	0.16.65	10.49.29	740.1	26.6	10.915
3	B	0.16.65	4.06.24	740.0	26.6	4.139
3	C	0.16.65	12.57.64	740.2	26.6	13.075
4	B	0.16.80	4.05.14	740.0	26.6	4.084
4	C	0.16.75	25.39.30	740.2	26.6	25.726

T =-20.0000 P =1500.50 VG = 6.636

		t_B	t_R	P_a	T_a	V_R
1	B	0.15.55	4.32.22	740.0	26.6	3.812
1	C	0.15.60	12.29.85	740.1	26.6	10.469
2	B	0.15.60	4.38.52	740.0	26.6	3.888
2	C	0.15.60	12.45.43	740.2	26.6	10.688
3	B	0.15.60	4.40.68	740.0	26.6	3.918
3	C	0.15.65	14.49.15	740.2	26.6	12.376
4	B	0.15.70	4.40.78	740.0	26.6	3.894
4	C	0.15.65	25.59.20	740.2	26.6	21.702

* * *

SWW =14.70580 PCF =69.24345 CW = 9.25870
SWD =13.12523 PCE =66.75020

T =-40.0000 P = 101.50 VG = 6.318

		t_B	t_R	P_a	T_a	V_R
1	B	0.44.25	0.47.62	733.3	24.0	5.004
1	C	0.44.40	1.48.38	733.3	24.1	11.343
2	B	0.44.25	0.47.34	733.3	24.0	4.974
2	C	0.44.45	1.49.66	733.3	24.1	11.464
3	B	0.44.35	0.47.04	733.3	24.0	4.931
3	C	0.44.50	2.36.43	733.3	24.2	16.326
4	B	0.44.35	0.47.58	733.3	24.0	4.988
4	C	0.44.60	10.14.27	733.3	24.2	63.966

T =-40.0000 P = 201.50 VG = 6.482

		t_B	t_R	P_a	T_a	V_R
1	B	0.34.65	1.11.76	742.7	22.2	4.818
1	C	0.34.55	2.48.43	741.9	22.3	11.323
2	B	0.34.65	1.12.25	742.5	22.2	4.850
2	C	0.34.50	2.51.22	741.7	22.4	11.518
3	B	0.34.65	1.12.50	742.3	22.2	4.865
3	C	0.34.50	4.01.52	741.6	22.4	16.245
4	B	0.34.65	1.11.96	742.1	22.2	4.828
4	C	0.34.50	14.56.15	741.5	22.4	60.269

T =-40.0000 P = 400.50 VG = 6.500

		t_B	t_R	P_a	T_a	V_R
1	B	0.28.65	1.56.58	741.4	22.5	4.452
1	C	0.28.70	4.47.79	741.2	22.6	10.963
2	B	0.28.65	1.57.84	741.4	22.6	4.498
2	C	0.28.80	4.52.08	741.0	22.6	11.085
3	B	0.28.65	1.58.24	741.4	22.6	4.513
3	C	0.28.80	6.42.00	740.9	22.6	15.254
4	B	0.28.65	1.57.14	741.3	22.6	4.471
4	C	0.28.80	22.40.45	740.8	22.6	51.617

T =-40.0000 P = 601.50 VG = 6.543

		t_B	t_R	P_a	T_a	V_R
1	B	0.21.55	2.15.38	740.7	22.6	4.253
1	C	0.21.70	5.46.94	740.5	22.7	10.814
2	B	0.21.80	2.18.66	740.7	22.6	4.306
2	C	0.21.75	5.53.65	740.4	22.7	10.997
3	B	0.21.85	2.19.12	740.6	22.6	4.310
3	C	0.21.75	7.49.87	740.4	22.7	14.610
4	B	0.21.85	2.19.30	740.6	22.6	4.315
4	C	0.21.80	23.35.75	740.4	22.8	43.897

T =-40.0000 P = 798.50 VG = 6.517

		t_B	t_R	P_a	T_a	V_R
1	B	0.18.10	2.33.07	740.4	22.8	3.971
1	C	0.18.35	6.50.52	740.4	22.8	10.504
2	B	0.18.20	2.36.06	740.4	22.8	4.026
2	C	0.18.35	6.57.20	740.4	22.8	10.675
3	B	0.18.20	2.36.54	740.4	22.8	4.038
3	C	0.18.35	8.54.80	740.3	22.9	13.675
4	B	0.18.25	2.36.60	740.4	22.8	4.029
4	C	0.18.40	24.03.70	740.3	22.9	36.814

T =-40.0000 P =1000.50 VG = 6.503

		t_B	t_R	P_a	T_a	V_R
1	B	0.17.55	3.09.76	740.3	22.8	3.704
1	C	0.17.80	8.51.13	740.3	22.8	10.221
2	B	0.17.60	3.12.95	740.3	22.8	3.755
2	C	0.17.80	8.58.94	740.2	22.8	10.369
3	B	0.17.65	3.14.83	740.3	22.8	3.781
3	C	0.17.80	11.07.13	740.1	22.8	12.834
4	B	0.17.70	3.14.28	740.3	22.8	3.760
4	C	0.17.80	26.02.00	740.0	22.8	30.045

T =-40.0000 P =1250.50 VG = 6.509

		t_B	t_R	P_a	T_a	V_R
1	B	0.15.95	3.40.14	739.9	22.7	3.374
1	C	0.16.25	10.58.14	739.6	22.7	9.897
2	B	0.15.90	3.44.66	739.9	22.7	3.454
2	C	0.16.20	11.07.94	739.5	22.7	10.074
3	B	0.15.95	3.45.43	739.8	22.7	3.455
3	C	0.16.20	13.06.43	739.4	22.7	11.859
4	B	0.16.05	3.46.36	739.7	22.7	3.447
4	C	0.16.30	25.49.30	739.3	22.7	23.216

T =-40.0000 P =1504.50 VG = 6.499

		t_B	t_R	P_a	T_a	V_R
1	B	0.18.10	5.10.00	736.5	23.2	3.171
1	C	0.12.50	10.56.18	735.1	23.5	9.685
2	B	0.17.95	5.13.12	736.4	23.2	3.229
2	C	0.12.50	11.07.02	735.1	23.5	9.845
3	B	0.18.05	5.14.84	736.2	23.3	3.227
3	C	0.12.40	12.33.78	735.1	23.6	11.209
4	B	0.18.40	5.20.84	736.1	23.4	3.223
4	C	0.12.35	21.23.00	735.1	23.7	19.146

T = 20.0000 P =1256.50 VG = 6.581

		t_B	t_R	P_a	T_a	V_R
1	B	0.14.90	3.33.29	743.6	25.0	5.016
1	C	0.15.30	8.27.82	743.6	24.9	11.637
2	B	0.14.90	3.38.00	743.6	25.0	5.127
2	C	0.15.30	8.45.00	743.6	24.9	12.031
3	B	0.14.90	3.38.50	743.6	25.0	5.139
3	C	0.15.30	9.47.75	743.6	24.9	13.469

T = 20.0000 P =1500.50 VG = 6.388

		t_B	t_R	P_a	T_a	V_R
1	B	0.14.70	4.10.51	733.0	24.6	4.738
1	C	0.15.30	10.14.82	733.0	24.6	11.171
2	B	0.14.70	4.10.42	733.0	24.6	4.736
2	C	0.15.40	10.36.50	733.0	24.6	11.490
3	B	0.14.70	4.16.41	733.0	24.6	4.849
3	C	0.15.50	11.53.52	733.0	24.6	12.797
4	B	0.14.70	4.16.32	733.0	24.6	4.847
4	C	0.15.65	18.13.40	733.0	24.6	19.423

TABLE XX

RAW DATA FOR CARBON DIOXIDE AND HYDROGEN SULFIDE K-VALUES IN THE METHANE+N-OCTANE SYSTEM FROM THE CHROMATOGRAPHIC EXPERIMENT

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            tB           tR        Pa      Ta       VR

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SWW =13.91990     PCF =64.51010     CW = 9.25870
SWD =12.51320     PCE =61.98590

     T = 32.0000      F = 101.50      VG =  6.099
 1 B  0.45.65   0.49.67   743.8   23.7    6.092
 1 C  0.45.80   1.40.21   743.8   23.8   12.245
 2 B  0.45.65   0.49.28   743.8   23.8    6.041
 2 C  0.45.80   1.42.82   743.8   23.8   12.564
 3 B  0.45.70   0.49.36   743.8   23.8    6.045
 3 C  0.45.80   1.58.76   743.8   23.8   14.511
 4 B  0.45.80   0.49.62   743.8   23.8    6.063
 4 C  0.45.80   2.53.64   743.8   23.8   21.217

     T = 32.0000      F = 198.50      VG =  6.304
 1 B  0.38.20   1.18.96   743.9   24.1    5.808
 1 C  0.38.10   2.44.97   744.3   24.4   12.153
 2 B  0.38.20   1.20.04   744.0   24.2    5.885
 2 C  0.38.05   2.49.66   744.4   24.4   12.516
 3 B  0.38.15   1.20.20   744.0   24.3    5.901
 3 C  0.37.95   3.17.03   744.4   24.5   14.566
 4 B  0.38.15   1.19.76   744.1   24.4    5.866
 4 C  0.38.00   4.45.40   744.5   24.6   21.062

     T = 32.0000      F = 399.50      VG =  6.204
 1 B  0.32.35   2.16.50   744.4   24.8    5.674
 1 C  0.32.40   4.47.64   744.4   25.0   11.924
 2 B  0.32.35   2.17.76   744.4   24.9    5.723
 2 C  0.32.45   4.57.16   744.4   25.0   12.300
 3 B  0.32.30   2.18.30   744.4   24.9    5.754
 3 C  0.32.45   5.43.56   744.3   25.1   14.211
 4 B  0.32.35   2.17.33   744.4   25.0    5.702
 4 C  0.32.60   8.08.50   744.2   25.0   20.121

     T = 32.0000      P = 600.50      VG =  6.140
 1 B  0.22.30   2.18.18   743.3   25.5    5.324
 1 C  0.22.20   4.57.70   743.2   25.5   11.520
 2 B  0.22.35   2.20.34   743.3   25.5    5.395
 2 C  0.22.10   5.08.32   743.2   25.5   11.985
 3 B  0.22.25   2.20.31   743.3   25.5    5.418
 3 C  0.22.00   5.52.74   743.2   25.5   13.774
 4 B  0.22.25   2.20.06   743.3   25.5    5.408
 4 C  0.21.95   8.08.44   743.2   25.5   19.116
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```
            tB           tR        Pa      Ta       VR

     T = 32.0000      F = 801.50      VG =  6.181
 1 B  0.19.20   2.45.88   742.3   25.2    5.370
 1 C  0.19.50   6.04.29   742.3   25.4   11.600
 2 B  0.19.40   2.49.80   742.3   25.2    5.441
 2 C  0.19.50   6.17.08   742.4   25.4   12.009
 3 B  0.19.45   2.50.38   742.3   25.3    5.442
 3 C  0.19.50   7.11.47   742.5   25.4   13.743
 4 B  0.19.50   2.51.01   742.3   25.3    5.448
 4 C  0.19.50   9.41.70   742.5   25.4   18.528

     T = 32.0000      P =1003.50      VG =  6.188
 1 B  0.16.30   3.00.64   742.7   25.5    5.309
 1 C  0.16.65   6.41.18   742.7   25.5   11.543
 2 B  0.16.60   3.08.21   742.7   25.5    5.432
 2 C  0.16.65   6.56.55   742.7   25.5   11.986
 3 B  0.16.60   3.07.72   742.7   25.5    5.418
 3 C  0.16.70   7.52.40   742.7   25.5   13.552
 4 B  0.16.65   3.08.60   742.7   25.5    5.427
 4 C  0.16.70  10.19.28   742.7   25.5   17.766

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SWW =13.85270     PCF =69.26030     CW = 9.25865
SWD =12.47792     PCE =66.74879

     T = 32.0000      P =  99.50      VG =  6.324
 1 B  0.48.90   0.51.15   743.0   24.5    5.942
 1 C  0.48.15   1.44.51   743.0   24.7   12.317
 2 B  0.48.75   0.51.48   743.0   24.5    5.999
 2 C  0.47.95   1.47.60   743.0   24.8   12.727
 3 B  0.48.65   0.51.44   743.0   24.6    6.003
 3 C  0.47.85   2.03.54   743.0   24.9   14.634
 4 B  0.48.10   0.51.90   743.0   24.6    6.126
 4 C  0.47.65   2.59.79   743.0   25.0   21.375

     T = 32.0000      F = 199.50      VG =  6.298
 1 B  0.41.00   1.24.17   743.0   25.3    5.694
 1 C  0.40.95   2.57.40   743.0   25.0   12.036
 2 B  0.41.00   1.24.90   743.0   25.2    5.747
 2 C  0.40.95   3.02.62   743.0   24.9   12.397
 3 B  0.41.00   1.25.31   743.0   25.1    5.778
 3 C  0.40.90   3.31.53   743.0   24.9   14.377
 4 B  0.41.00   1.24.61   743.0   25.0    5.734
 4 C  0.40.85   5.06.74   743.0   24.9   20.874
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```
            tB           tR        Pa      Ta       VR

     T = 32.0000      P = 398.50      VG =  6.269
 1 B  0.31.60   2.09.82   742.9   24.9    5.523
 1 C  0.31.60   4.38.38   742.8   24.9   11.842
 2 B  0.31.60   2.11.38   742.9   24.9    5.590
 2 C  0.31.60   4.48.16   742.7   24.9   12.257
 3 B  0.31.60   2.12.21   742.9   24.9    5.625
 3 C  0.31.65   5.32.33   742.6   24.9   14.111
 4 B  0.31.60   2.11.34   742.9   24.9    5.588
 4 C  0.31.65   7.51.30   742.6   24.9   20.012

     T = 32.0000      P = 598.50      VG =  6.281
 1 B  0.26.70   2.44.71   742.6   24.9    5.330
 1 C  0.26.75   6.01.22   742.0   24.9   11.658
 2 B  0.26.70   2.46.80   742.5   24.9    5.397
 2 C  0.26.75   6.13.46   741.9   24.9   12.052
 3 B  0.26.70   2.47.42   742.4   24.9    5.417
 3 C  0.26.80   7.10.12   741.7   24.9   13.850
 4 B  0.26.75   2.47.52   742.1   24.9    5.407
 4 C  0.26.90   9.54.76   741.6   24.9   19.078

     T = 32.0000      F = 800.50      VG =  6.219
 1 B  0.21.30   3.00.21   741.5   24.9    5.269
 1 C  0.21.30   6.34.83   741.2   24.9   11.538
 2 B  0.21.30   3.02.44   741.4   24.9    5.333
 2 C  0.21.30   6.49.42   741.0   24.9   11.961
 3 B  0.21.30   3.03.74   741.3   24.9    5.370
 3 C  0.21.30   7.48.24   740.8   24.9   13.676
 4 B  0.21.30   3.03.17   741.2   24.9    5.353
 4 C  0.21.30  10.29.76   740.8   24.9   18.394

     T = 32.0000      P =1003.50      VG =  6.205
 1 B  0.17.40   3.06.26   740.7   25.0    5.128
 1 C  0.17.50   6.56.09   740.4   25.0   11.386
 2 B  0.17.45   3.09.84   740.7   25.0    5.212
 2 C  0.17.50   7.12.52   740.4   25.0   11.836
 3 B  0.17.45   3.10.60   740.6   25.0    5.232
 3 C  0.17.55   8.10.46   740.4   25.0   13.383
 4 B  0.17.45   3.10.16   740.5   25.0    5.219
 4 C  0.17.60  10.43.83   740.4   25.0   17.518
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TABLF XX (Continued)

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          tB        tR      Pa     Ta     VR
*********************************************

SWW =14.77800      PCF =72.96738      CW = 9.25848
SWD =13.14878      PCE =70.03937

      T = 32.0000       P =   98.50       VG = 11.713
  1 B  0.59.30    1.04.00   740.0  27.8    6.053
  1 C  0.58.80    3.07.04   740.1  28.0   17.823
  2 B  0.59.20    1.03.88   740.0  27.8    6.052
  2 C  0.58.70    3.10.84   740.1  28.0   18.216
  3 B  0.59.10    1.03.62   740.0  27.9    6.034
  3 C  0.58.60    3.35.34   740.2  28.0   20.593
  4 B  0.59.00    1.03.30   740.0  27.9    6.014
  4 C  0.58.50    4.58.28   740.2  28.0   28.573

      T = 32.0000       P =  201.50       VG = 11.582
  1 B  0.47.50    1.41.84   740.2  28.0    5.775
  1 C  0.47.50    5.07.42   740.0  28.1   17.418
  2 B  0.47.45    1.42.16   740.1  28.1    5.795
  2 C  0.47.50    5.15.34   740.0  28.1   17.867
  3 B  0.47.40    1.43.52   740.0  28.1    5.878
  3 C  0.47.50    5.55.86   740.0  28.1   20.163
  4 B  0.47.40    1.42.44   740.0  28.1    5.817
  4 C  0.47.50    8.09.56   740.0  28.1   27.739

      T = 32.0000       P =  399.50       VG = 11.532
  1 B  0.39.00    2.45.86   740.0  28.1    5.578
  1 C  0.39.10    8.33.27   738.8  28.2   17.168
  2 B  0.39.00    2.47.78   740.0  28.1    5.642
  2 C  0.39.15    8.48.02   738.7  28.3   17.636
  3 B  0.39.00    2.49.52   740.0  28.1    5.701
  3 C  0.39.20    9.54.14   738.6  28.3   19.816
  4 B  0.39.00    2.48.80   738.9  28.2    5.665
  4 C  0.39.20   13.20.00   738.5  28.4   26.663

      T = 32.0000       P =  598.50       VG = 11.546
  1 B  0.32.80    3.32.52   738.3  28.3    5.458
  1 C  0.32.80   11.03.73   738.6  28.2   17.063
  2 B  0.32.75    3.34.92   738.3  28.3    5.528
  2 C  0.32.85   11.23.43   738.8  28.2   17.548
  3 B  0.32.75    3.35.60   738.4  28.3    5.546
  3 C  0.32.85   12.43.78   738.9  28.2   19.614
  4 B  0.32.75    3.35.48   738.4  28.3    5.543
  4 C  0.32.85   16.43.24   739.0  28.1   25.782
```

```
          tB        tR      Pa     Ta     VR

      T = 32.0000       P =  799.50       VG = 11.480
  1 B  0.25.15    3.41.12   739.2  27.9    5.372
  1 C  0.25.15   11.35.96   739.6  27.9   16.917
  2 B  0.25.15    3.45.34   739.3  27.9    5.475
  2 C  0.25.15   11.59.02   739.7  27.9   17.480
  3 B  0.25.15    3.45.64   739.4  27.9    5.483
  3 C  0.25.15   13.18.26   739.7  27.8   19.418
  4 B  0.25.15    3.45.55   739.5  27.9    5.482
  4 C  0.25.15   17.03.42   739.7  27.7   24.910

      T = 32.0000       P =  998.50       VG = 11.626
  1 B  0.20.80    3.54.14   740.4  27.4    5.344
  1 C  0.20.80   12.22.90   740.8  26.9   17.016
  2 B  0.20.80    3.58.24   740.5  27.3    5.442
  2 C  0.21.00   12.47.90   740.8  26.8   17.431
  3 B  0.20.80    3.59.68   740.6  27.1    5.482
  3 C  0.21.00   14.06.92   740.8  26.8   19.225
  4 B  0.20.80    3.59.65   740.7  27.0    5.485
  4 C  0.21.05   17.41.80   740.8  26.8   24.045

*********************************************

SWW =14.77800      PCF =72.96738      CW = 9.25848
SWD =13.14878      PCE =70.03937

      T = -4.0000       P =   99.50       VG = 11.732
  1 B  0.57.25    1.02.87   739.1  29.0    5.577
  1 C  0.57.20    3.15.49   739.0  28.9   17.366
  2 B  0.57.30    1.02.73   739.1  28.9    5.563
  2 C  0.57.20    3.19.78   738.9  28.9   17.744
  3 B  0.57.20    1.02.78   739.1  28.9    5.578
  3 C  0.57.30    3.55.12   738.8  28.9   20.844
  4 B  0.57.20    1.02.77   739.1  28.8    5.580
  4 C  0.57.30    6.09.60   738.7  28.9   32.761

      T = -4.0000       P =  200.50       VG = 11.572
  1 B  0.45.05    1.36.72   738.7  28.9    5.294
  1 C  0.45.20    5.10.13   738.1  28.7   16.923
  2 B  0.45.00    1.37.32   738.6  28.9    5.332
  2 C  0.45.20    5.18.04   738.1  28.6   17.365
  3 B  0.45.05    1.37.61   738.4  28.9    5.340
  3 C  0.45.20    6.13.50   738.0  28.5   20.402
  4 B  0.45.05    1.37.20   738.3  28.9    5.317
  4 C  0.45.20    9.37.03   738.0  28.5   31.520
```

```
          tB        tR      Pa     Ta     VR

      T = -4.0000       P =  400.50       VG = 11.521
  1 B  0.38.40    2.43.20   738.0  28.4    5.018
  1 C  0.38.40    8.59.56   737.5  28.2   16.598
  2 B  0.38.40    2.45.36   737.8  28.3    5.086
  2 C  0.38.40    9.14.88   737.5  28.1   17.080
  3 B  0.38.40    2.45.89   737.6  28.3    5.101
  3 C  0.38.50   10.46.26   737.5  28.0   19.852
  4 B  0.38.40    2.45.19   737.5  28.3    5.079
  4 C  0.38.60   16.01.55   737.5  28.0   29.461

      T = -4.0000       P =  598.50       VG = 11.519
  1 B  0.32.90    3.33.04   737.5  27.8    4.885
  1 C  0.32.85   11.56.36   737.4  27.6   16.469
  2 B  0.32.85    3.35.88   737.5  27.7    4.961
  2 C  0.32.85   12.19.11   737.4  27.5   17.002
  3 B  0.32.85    3.36.79   737.4  27.6    4.984
  3 C  0.32.90   14.13.36   737.5  27.4   19.615
  4 B  0.32.85    3.35.57   737.4  27.6    4.956
  4 C  0.32.95   20.18.71   737.6  27.3   27.990

      T = -4.0000       P =  800.50       VG = 11.455
  1 B  0.25.00    3.41.24   737.7  27.1    4.763
  1 C  0.25.10   12.37.18   738.2  26.7   16.285
  2 B  0.25.05    3.44.86   737.8  27.0    4.835
  2 C  0.25.10   13.02.06   738.3  26.7   16.822
  3 B  0.25.10    3.45.56   737.9  26.9    4.844
  3 C  0.25.10   14.54.26   738.4  26.7   19.238
  4 B  0.25.10    3.45.75   738.0  26.8    4.851
  4 C  0.25.20   20.30.60   738.5  26.7   26.373

      T = -4.0000       P = 1001.50       VG = 11.465
  1 B  0.19.30    3.37.52   738.7  26.6    4.620
  1 C  0.19.30   12.39.79   738.8  26.5   16.150
  2 B  0.19.30    3.42.80   738.8  26.6    4.733
  2 C  0.19.30   13.06.30   738.8  26.5   16.713
  3 B  0.19.30    3.43.76   738.8  26.6    4.753
  3 C  0.19.30   14.50.60   738.8  26.4   18.941
  4 B  0.19.30    3.44.09   738.8  26.6    4.760
  4 C  0.19.30   19.35.20   738.8  26.4   24.993
```

The columns in the tables are: t_B, bubble time in V_B; t_R, retention time; P_A = ambient pressure (mmHg); T_a = ambient temperatures (°C). The column labeled V_R refers to the calculated retention volume. T, P, and V_g refer to the system temperature (°F), system pressure (psia) and the calculated free gas volume. V_R and V_g are not actually a part of the raw data.

Three sets of data are present for the methane-octain system at 0°C, corresponding to the three runs which tested experimental consistency of the data.

APPENDIX J

NOMENCLATURE

a - parameter from original Redlich-Kwong equation

A - Redlich-Kwong term = $\frac{ap}{R^2T^{2.5}}$ (Eq. 3-27)

a'(T) = parameter in Soave modification of R-K

a - $\sum_{jk}\sum n_j n_k a_{jk}$

b - parameter from original Redlich-Kwong equation

B - Redlich-Kwong term = $\frac{bp}{RT}$ (Eq. 3-28)

B_1, B_2, B_3, B_4 - empirical correlation factors [Eq. (3-50) to(3-53)]

b - $\sum_{jk}\sum n_j n_k b_{jk}$

CW - crucible weight (Eq. 5-1)

f, f_a - carrier gas flow at system conditions and ambient conditions

f_{iL}, f_{ig} - liquid and vapor fugacity for component i

GLC - gas liquid chromatography

ΔH - heat of adsorption

k_i - partition coefficient (Eq. 3-1)

k'_{ij} - empirical correlation parameter for components i and j. Modifies the energy term (T_{cij}) for one parameter method.

k_{ij} - empirical correlation parameter for components i and j. Modifies the energy term (T_{cij}) for two parameter method.

K_i - K-value of component i

L - length of the chromatograph column (Eq. 3-5)

L - weight of liquid on solid support in packing mixture

LMW - solvent of molecular weight

ℓ_{ij} - empirical correlation parameter for components i and j. Modifies the distance term (V'_{cij}) for two parameter method.

m_i - slope of $\alpha^{0.5}$ vs. $T_R^{0.5}$ (Eq. 3-36)

PCE - weight of GLC column empty, that is, stainless stell tubing and fittings

n - number of moles of a component

P, P_a - system and ambient pressure

P_c - critical pressure

PCF - weight of GLC column full of solvent saturated solid support

P_{H_2O} - water vapor pressure (Eq. 3-18a)

R - gas constant

RF_i - response factor of component i

$$= \frac{\text{number of counts of component i}}{\text{number of moles of component i}}$$

R_{1i} - relative response of methane to component i (Eq. 3-20)

S - weight of solid support in packing mixture

SWW - solid weight wet, that is, weight of solid support + solvent + crucible

SWD - solid weight dry, that is, weight of solid support + crucible

T, T_a - system and ambient temperature

T_c - critical temperature

T_R - reduced temperature - T/T_c

t_{Ri} - retention time of component i, that is, the time required for a sample of component i to elute from the sample valve to the strip chart recorder.

t_B - residence time of a bubble in V_B

u - velocity

V_B - calibrated volume of the bubblemeter

V_{Ri} - retention volume of solute i

V_L - volume of liquid in the GLC column

V_g - void volume, or free gas volume, in the GLC column

V_c' - ideal critical volume $= \frac{RT_c}{P_c}$

$\bar{V}$ - molar volume $= \frac{V}{n}$

WFL - weight fraction liquid on the GLC column (Eq. 5-1)

W_L^o - moles of pure stationary liquid on the GLC column

W_L - moles of stationary liquid and gas solution on the GLC column

W_i - acentric factor of component i

x_i - liquid mole fraction of component i (sometimes used to denote any mole fraction)

χ_1 - solubility (or mole fraction) of methane in the liquid phase

y_i - vapor mole fraction of component i

Z - compressibility factor

Z_g - carrier gas compressibility factor

$\alpha_i(T)$ - correlation factor of Soave modification of R-K equation

α_i - polarizability of component i

β - extrapolation parameter for determining V_g

ε_i - maximum expected uncertainty in property i

ρ - density

ϕ_i - fugacity coefficient of component i

Subscripts

Ar - argon

a - ambient conditions

c - critical

ci - component i

CO_2 - carbon dioxide

C1 - methane

C8 - octane

C7 - heptane

g - vapor phase

He - helium

H_2S - hydrogen sulfide

i - component i

L - liquid phase

MCH - methylcyclohexane

TOL - toluene

Superscripts

B - indicates run was made when GLC column was being bypassed

C - indicates run was made while GLC column was in stream

Other

α - "proportional to"

$\cong$ - "approximately equal to"

VITA

Charles Joseph Mundis

Candidate for the Degree of

Doctor of Philosophy

Thesis: VAPORIZATION EQUILIBRIUM RATIOS FOR CO_2 AND H_2S IN PARAFFINIC, NAPHTHENIC, AND AROMATIC SOLVENTS

Major Field: Chemical Engineering

Biographical:

Personal Data: Born in Jefferson City, Missouri, August, 1945, the son of Mr. and Mrs. L. E. Mundis.

Education: Graduated from Muskogee Central High School, Muskogee, Oklahoma, in May, 1963; received Bachelor of Science degree from Oklahoma State University in July, 1968, with a major in Chemical Engineering; received Master of Science degree from Oklahoma State University in May, 1970, with a major in Chemical Engineering; completed requirements for Doctor of Philosophy degree in May, 1976.

Professional Experience: Employed as a process engineer trainee by Phillips Petroleum Company during the summer of 1967. Employed as a research engineer trainee by Monsanto Company during the summer of 1969. Employed as a research engineer trainee by Amoco Production Company during the summer of 1970. Currently employed as a research engineer by Cities Service Oil Company, Tulsa, Oklahoma.