

THE PHASE BEHAVIOR IN SIX COMPONENT
SYSTEMS CONTAINING METHANE,
ETHANE, PROPANE, N-PENTANE,
N-HEXANE, N-DECANE,
DECAHYDRONAPHTHALENE, AND
1-METHYLNAPHTHALENE

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PREFACE

Experimental vapor-liquid equilibrium K-values were obtained for three systems at 150 and 250°F with pressures of 100 psia up to the single phase pressure. The first system used contained methane, ethane, propane, n-pentane, n-hexane, and n-decane. The second and third systems were identical to the first except decahydronaphthalene and 1-methylnaphthalene were used in place of n-decane. The generalized form of the Benedict-Webb-Rubin equation of state was examined and optimized for use in direct K-value calculation.

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TABLE OF CONTENTS

Chapter	Page
I. INTRODUCTION	1
II. AVAILABLE DATA AND TECHNIQUES	4
A. Multicomponent System Data	4
B. Techniques	7
C. Present Technique	12
D. System Selection	12
III. THEORY	19
A. Convergence Pressure	19
B. Fugacity Correlations	22
C. Equations of State	25
IV. EXPERIMENTAL APPARATUS	31
A. Equilibrium Apparatus	31
B. Analytical Equipment	42
V. EXPERIMENTAL PROCEDURE	43
A. Charging of Components	43
B. Equilibration	45
C. Sampling	47
D. Analysis	48
VI. EXPERIMENTAL RESULTS	51
A. Base System K-Values	52
B. Non-Paraffin Substituted System K-Values	56
C. Error Analysis	67
VII. CORRELATION WORK	70
A. Use of BWR Equation for K-Value Prediction	70
B. Use of Binary Data	81
C. Correlation Procedure	82
VIII. CORRELATION RESULTS	90

Chapter	Page
IX. CONCLUSIONS AND RECOMMENDATIONS	102
A. Experimental	103
B. Theoretical	105
BIBLIOGRAPHY	110
NOMENCLATURE	115
APPENDIX A - CALIBRATION OF TEMPERATURE AND PRESSURE MEASURING EQUIPMENT	118
APPENDIX B - CHROMATOGRAPH CALIBRATION	125
APPENDIX C - SAMPLE CALCULATIONS OF EXPERIMENTAL DATA	131
APPENDIX D - RAW EXPERIMENTAL DATA	135
APPENDIX E - EXPERIMENTAL RESULTS	151
APPENDIX F - THE BWR EQUATION OF STATE	164
APPENDIX G - PROGRAM LISTING	168
APPENDIX H - BINARY SYSTEM DATA USED IN CORRELATION DEVELOPMENT	186
APPENDIX I - CARBONDIOXIDE SYSTEM DATA	194
APPENDIX J - PHYSICAL CONSTANTS	198

LIST OF TABLES

Table	Page
I. Natural Gas Condensate Wellstream Analysis	14
II. Hydrocarbon Mixtures Used in Study	15
III. Hydrocarbon Mixtures Supplied by Phillips Petroleum Company	17
IV. Comparison of NGPA Chart Values and Unsmoothed Experimental K-Values for Base System	55
V. Comparison of Poettmann Correlation and Unsmoothed Experimental Non-Paraffinic K-Values	61
VI. Optimization Results for Generalized BWR Equation Constants " B_0 " and " C_0 " Based on Paraffinic Binary System Literature Data	91
VII. Interaction Coefficients, θ , Developed for the Optimized BWR Equation Mixture Constants Based on Binary System Literature Data	92
VIII. Comparison of Generalized BWR and Redlich-Ackerman Values and Experimental Literature Binary System K-Values	93
IX. Comparison of Optimized BWR Equation Values Using Different " B_0 " Mixing Rules With Interaction Coefficients and Experimental Literature Binary System K-Values	95
X. Comparison of Literature Correlation Values and Experimental Multicomponent System K-Values and System Pressures for Bubble Point Calculations	97
XI. Experimental Data for Calibration of Gas Compressor Level	123

Table	Page
XII. Experimental Data for Calibration of Gas Compressor Level	123
XIII. Chromatograph Calibration Data	126
XIV. Chromatograph Calibration Constants	130
XV. Raw Experimental Data: n-Decane as Heavy Component	136
XVI. Raw Experimental Data: Decahydronaphthalene as Heavy Component . . .	137
XVII. Raw Experimental Data: 1-Methylnaphthalene as Heavy Component . . .	139
XVIII. Raw Experimental Chromatographic Composition Data With n-Decane as Heavy Component at 150°F	141
XIX. Raw Experimental Chromatographic Composition Data With n-Decane as Heavy Component at 250°F	142
XX. Raw Experimental Chromatographic Composition Data With Decahydronaphthalene as Heavy Component at 150°F	143
XXI. Raw Experimental Chromatographic Composition Data With Decahydronaphthalene as Heavy Component at 250°F	145
XXII. Raw Experimental Chromatographic Composition Data With 1-Methylnaphthalene as Heavy Component at 150°F	147
XXIII. Raw Experimental Chromatographic Composition Data With 1-Methylnaphthalene as Heavy Component at 250°F	149
XXIV. Experimental xy Data and K-Values for Base System at 150°F	151
XXV. Experimental xy Data and K-Values for Base System at 250°F	153
XXVI. Experimental xy Data for Base System With Decahydronaphthalene Substituted for n-Decane at 150°F	154

Table	Page
XXVII. Experimental xy Data for Base System With Decahydronaphthalene Substituted for n-Decane at 250°F	156
XXVIII. Experimental xy Data for Base System With 1-Methylnaphthalene Substituted for n-Decane at 150°F	158
XXIX. Experimental xy Data for Base System With 1-Methylnaphthalene Substituted for n-Decane at 250°	160
XXX. Ratios of Substituted System K-Values to the Base System	162
XXXI. Paraffin Data	186
XXXII. Naphthene Data	188
XXXIII. Aromatic Data	191
XXXIV. Experimental xy Data: Low CO ₂ at 150°F	194
XXXV. Experimental xy Data: Low CO ₂ at 250°F	195
XXXVI. Experimental xy Data: High CO ₂ at 150°F	196
XXXVII. Experimental xy Data: High CO ₂ at 250°F	197
XXXVIII. Calculation Constants for Pure Components	198

LIST OF FIGURES

Figure	Page
1. Schematic Diagram of Vapor-Liquid Equilibrium Apparatus	32
2. Sectional View of Gas Compressor	35
3. Equilibrium Cell (Hart)	37
4. Sampling Valve	39
5. Heater and Blower Arrangement Front View of Thermostat	41
6. Experimental K-Values at 150°F Base System	53
7. Experimental K-Values at 250°F Base System	54
8. Experimental K-Values at 150°F Base System With Decahydro- naphthalene Substituted for n-Decane	57
9. Experimental K-Values at 250°F Base System With Decahydro- naphthalene Substituted for n-Decane	58
10. Experimental K-Values at 150° Base System With 1- Methylnaphthalene Substituted for n-Decane	59
11. Experimental K-Values at 250°F Base System With 1- Methylnaphthalene Substituted for n-Decane	60
12. Ratios of Substituted System Methane K-Values to the Base System	62
13. Ratios of Substituted System Ethane K-Values to the Base System	63

Figure	Page
14. Ratios of Substituted System Propane K-Values to the Base System	64
15. Ratios of Substituted System Pentane K-Values to the Base System	65
16. Ratios of Substituted System Hexane K-Values to the Base System	66
17. Gas Compressor Level Calibration Apparatus	121
18. Apparatus for Preparation of Gaseous Calibration Samples	129

CHAPTER I

INTRODUCTION

This investigation was undertaken with two objectives. The first was to obtain experimental K-values for multi-component systems resembling natural gas condensates in over-all composition. The new experimental data provides information about the effect of the characteristics of the heaviest component on the K-values of the lighter components. The other objective was the study of the generalized BWR equation of state for direct calculation of phase equilibrium K-values.

The phase equilibrium K-value is defined as the ratio of the mole fraction of the component in the vapor phase, y_1 , to that in the liquid, x_1 .

$$K_1 = \frac{y_1}{x_1}. \quad (I-1)$$

The ability to calculate this K-value accurately is of great importance in the petroleum and chemical industries, such as natural gas processing.

The experimental program has two applications. One is to demonstrate the effects of hydrocarbon types in the C_7+ fraction on the K-values of the lighter mixture

components. These effects are important in natural gas condensate mixtures. This data will be useful for guiding the extrapolation of existing equilibrium ratio correlations when applied to natural gas condensate systems. The other application is to check the extension of the correlations developed from binary system data to multi-component systems.

The second part of this investigation dealt with the development of improved techniques for predicting these K-values accurately. The equation of state approach to calculating K-values has the advantage of being numerical and also not requiring any "hypothetical reference states" for any of the components in either the liquid or vapor phase. The generalized BWR equation of state was chosen for this work.

The K-value data were determined for three multi-component systems. The components chosen to represent the first natural gas condensate system best were methane, ethane, propane, n-pentane, n-hexane, and n-decane. The other two systems were identical with the exception that n-decane was substituted with decahydronaphthalene and 1-methyl naphthalene to study heavy component effects on lighter component K-values. The equilibrium K-values were determined at 150 and 250°F and pressures ranging from 100 psia to the single phase pressure. These conditions are similar to those encountered in underground petroleum reservoirs.

To attain equilibrium conditions, the two phase system must first be agitated and then allowed to remain undisturbed at constant temperature and pressure. This situation was attained using a stainless steel equilibrium cell and monitoring the system's temperature and pressure. Both phases were sampled to determine the equilibrium compositions. The following chapters describe the experimental work and examine the generalized equation of state approach to K-value calculation.

CHAPTER II

AVAILABLE DATA AND TECHNIQUES

In the past, most of the efforts in the field of vapor-liquid equilibrium for hydrocarbon systems have been utilized on binary systems. Even though the amount of phase equilibrium data on hydrocarbon systems is extensive, studies of more than three component systems are not numerous. The greatest obstacle to the study of multicomponent systems has been the difficulty of obtaining accurate phase composition analysis. Gas chromatography has contributed the most toward overcoming this difficulty.

First, short reviews of multicomponent hydrocarbon vapor-liquid equilibrium studies and available experimental data are presented. Special emphasis is placed on hydrocarbon systems containing at least one naphthenic or aromatic component. Present system selection and experimental technique are also described.

A. Multicomponent System Data

The earliest interest in multicomponent vapor-liquid equilibrium prediction was developed in the petroleum industry. Design of natural hydrocarbon system processing equipment

required a better knowledge of vapor-liquid equilibrium than could be obtained using Raoult's and Dalton's laws. As a result, many natural hydrocarbon systems were investigated. However, before the use of gas chromatography, the accuracy of the phase analysis was quite limited. A good review of natural hydrocarbon system vapor-liquid equilibrium literature was given by Stuckey (65).

Extensive studies of vapor-liquid equilibrium in multicomponent hydrocarbon systems have been conducted by Sage, Lacy et al. (44, 47, 48, 57, 58, 59) starting around 1936. However, their work has been done on three component systems using methane, ethane, propane, n-butane, and n-decane. Other studies of three component systems were made et al. on the methane, propane, n-butane and ethane, n-butane, n-pentane systems (35, 53).

The most recent work in three component vapor-liquid equilibrium has been conducted by Kobayashi and coworkers (30) using gas-liquid partition chromatography. This has resulted in the study of systems such as methane, propane, n-decane and methane, propane, n-hexane by Koonce and Kobayashi (32), and methane, ethane, n-hexane and methane, propane, toluene by Van Horn and Kobayashi (69). This method promises to provide phase equilibrium data faster than conventional methods.

Work on hydrocarbon systems of more than three components is less extensive. Hanson and Brown (22) in 1945 studied the methane, ethane, propane, n-butane, n-pentane,

n-hexane system. They worked with two mixtures of different over-all composition at 100°F. System pressures ranged from 517 to 1736 psia and a variable volume static equilibrium cell was used. The analytical separation was performed using a fractionating column. Only ten data points were reported.

Charmichael, Hwang, Berry, and Sage (10) investigated a six component hydrocarbon system in 1962. They studied the separation of hydrocarbons of similar molecular weight and volatility. The system used contained isobutane, isobutene, n-butane, 1-butene, trans-2-butene, and cis-2-butene. Ten different mixtures were investigated at temperatures from 126°F to 220°F. The phase composition analysis was performed using a combination of chromatographic and mass spectrographic methods.

Yarborough and Vogel (76) most recently have studied a six component hydrocarbon system used to simulate a natural gas condensate. This work was done using a rocking equilibrium cell with gas chromatography as an analytical tool. Published results are limited to one mixture of 200°F and pressures ranging from 100 to 3000 psia.

Results of experimental studies of the effects of naphthenic and aromatic components on multicomponent hydrocarbon vapor-liquid equilibrium are also very limited. Solomon (62) obtained phase equilibrium data on mixtures of methane, ethylene, isobutane with n-hexadecane, dicyclohexyl, on 1-methylnaphthalene as the heaviest

component. However, very few data points are presented.

Kirkbride and Bertetti (30) reported K-values for methane, ethane, propane, n-butane, and n-pentane in three types of absorber oil: paraffinic, naphthenic, and aromatic. The accuracy of the results was somewhat limited due to poor temperature regulation and difficulty in analysis since the work was done with a natural system. This investigation does, however, give an indication that the K-values of a given component at a given temperature and pressure are affected by the type of absorber oil used.

As indicated earlier, some work is being done by Kobayashi and coworkers (69) on ternary systems containing one aromatic component. This work is restricted to relatively low temperatures depending on the volatility of the heaviest component in the system. In this case, toluene was studied at -40°F .

The advent of new analytical and experimental techniques should see a large increase in the amount of data generated for the study of effects due to naphthenic and aromatic components on multicomponent vapor-liquid equilibrium.

B. Techniques

Many experimental methods are available for the study of high pressure multicomponent vapor-liquid equilibrium. In all cases, the goal is to measure the pressure,

temperature, and composition of the coexisting equilibrium phases. The determination of density may also be a desired feature but is not necessary to characterize the equilibrium state. Good reviews on experimental techniques in use are given by Robinson and Gilliland (55), Hipkin (24), and Thompson (67).

The more successful techniques used for high pressure vapor-liquid equilibrium determination are the static bomb, the bubble- and dew-point method, vapor-recirculation, and gas-liquid partition chromatography.

Non-Flow Method

The non-flow method is one of the more common methods for determining phase equilibrium. An equilibrium bomb is evacuated and then filled with the sample under investigation. Once equilibrium is obtained, samples are removed from each of the two phases for analysis.

Two common experimental difficulties encountered in the non-flow method are the attainment of equilibrium and sampling. Theoretically, the two phases in the bomb will reach thermodynamic equilibrium after a sufficiently long time. Since this is experimentally impractical, several methods are used to increase contact between the two phases.

A common and relatively simple method of reaching equilibrium is to rock the bomb, thus agitating its contents. Another method is to use mechanical stirring

devices. The drawback in this method is the need for having a good high pressure seal where the stirring mechanism enters the equilibrium bomb. Magnetic stirring is a method that requires no mechanical seals. However, one drawback here is that the equilibrium cell must be made of non-magnetic material, thus restricting the choice of materials. Also, significant power is required to move the metal stirrer inside the cell. This often causes the cell to become heated due to the energy absorbed from the fluctuating magnetic field. This can cause considerable difficulty in temperature control.

The two types of bombs used are the constant and variable volume types. With the constant volume bomb, the sample is in a system of constant volume. The only way the pressure in the system can be changed is by changing the temperature or by introducing more of the sample material. In the variable volume cell, one is free to adjust the pressure by simply changing the system volume in the bomb. This volume change is produced by either introducing mercury into the equilibrium cell cavity or by movement of a piston. Sage, Lacey et al. (44) illustrate the use of a variable volume cell.

Sampling is a more severe problem in the constant volume cell than in the variable volume one. When the sample is removed from the constant volume cell, a change in pressure takes place inside the cell due to removal of material from the system. The pressure change causes an

upset in the equilibrium of the system. This makes it important to remove only very small samples. In the variable volume cell case, larger samples can be removed since the pressure can be maintained by decreasing the volume of the system. Larger samples are especially important if phase densities are to be evaluated.

Bubble-and Dew-Point Methods

These techniques are essentially the same as the variable volume non-flow method but without sampling, which limits these methods to binary systems. A mixture of known composition is introduced into an evacuated variable volume equilibrium cell. Holding the system temperature constant, the mixture is pressurized by decreasing the volume of the system. The pressures are recorded when the first drop of condensation forms from the vapor, i.e., the dew point is reached. The bubble point technique starts with a liquid system where the pressure decreases until the first bubble of vapor appears.

The conditions of phase equilibrium are determined from cross plots of pressure against temperature for the dew and bubble points for a large number of mixtures. The dew and bubble points can be determined both visually and as discontinuities in the pressure-temperature plot.

Vapor Recirculation Method

Vapor recirculation can be viewed as a technique for

agitation in the nonflow method. Vapor is continuously removed from the top of the equilibrium cell and recirculated to the bottom where it contacts the liquid phase.

Care must be taken that condensation does not occur in the vapor line since this would cause a change in the composition of the vapor contacting the liquid. The use of a magnetic pump is a good technique of obtaining recirculation of the vapor without the need to seal on a moving shaft. Magnetic recirculation pumps have been employed successfully by Roberts and McKetta (20) and Stuckey (65).

Gas-Liquid Partition Chromatography

Gas-liquid partition chromatography is one of the newest methods for determining high pressure vapor-liquid equilibrium. It has been successfully applied to a large number of hydrocarbon systems. A good literature survey on the subject is presented by Kobayashi et al. (31).

In this method, the equilibrium K-value are derived from the retention volume of a solution to its equilibrium partition coefficient using a relationship derived in the work. The heaviest component is used as the stationary liquid phase in a chromatograph column and the lighter component of the mixture as the carrier gas. The measurements may be performed using a radioactive tracer of the desired light component to determine its K-value. One drawback of this method is that it assumes the heaviest

component to have a K-value equal to zero. This greatly limits the temperature range that can be studied for a given system. The maximum operating temperature would be determined by the vapor pressure of the heaviest component.

C. Present Technique

A constant volume equilibrium cell with vapor recirculation was used in this study. Natural gas reservoirs are essentially constant volume and temperature systems, the composition of which changes with pressure. This makes the equilibrium system compatible with the study of the simulated natural gas condensate system.

The apparatus, in part, was identical to that used by Stuckey (65). The vapor was recirculated by means of a magnetic pump. The pressure was measured using either a pressure balance or a 0 to 3000 psia Heise gage depending on the range of operation. No provisions for measuring phase densities were made on the equilibrium cell. The phase analysis was performed using an F and M Model 810 gas chromatograph. A detailed description of the apparatus used in this study appears in Chapter IV with the experimental procedure discussed in Chapter V.

D. System Selection

The objective of this study was to investigate the phase behavior of natural gas condensate systems at conditions encountered in natural reservoirs. It was decided

to use an artificial system of fewer components to simulate the natural gas condensate in order to improve the resulting K-value accuracy by more precise phase composition analysis. The characteristics of the C_7+ fraction could also be more closely controlled.

A study of 85 wellstream analyses supplied by the American Petroleum Institute was made to determine a representative synthetic system. The summary of the study is shown in Table I. Since this study was concerned with the effects of the C_7+ fraction, non hydrocarbon components such as nitrogen, carbon dioxide, and hydrogen sulfide were not used.

Based on the averages in Table I and on experimental convenience, the liquid and gas mixtures were chosen as shown in Table II. Six components were considered sufficient for the study of the mixture hydrocarbon K-values.

The requirement of compression at room temperature to any desired pressure without condensation is satisfied by the gas mixture.

The liquid mixture is non-volatile at room temperature for easy handling and storage. The response of the K-values of the lighter hydrocarbons to the presence of different C_7+ characteristics is of interest here.

Three different compounds are used to characterize the C_7+ fraction. These components were chosen on basis of similar molecular weight compatible with the average C_7+ fraction molecular weight. The three representative

TABLE I
NATURAL GAS CONDENSATE
WELLSTREAM ANALYSES

Component	Range	Mole Per Cent	Average
N ₂	0-28		-
C ₁	31-96		76
CO ₂	0-12		-
C ₂	1-14		6
H ₂ S	0-27		-
C ₃	0-10		4
C ₄ 's	0-5		2
C ₅ 's	0-4		1
C ₆ 's	0-2		1
(C ₇ +)	0-12		5
Mol. wt.	110-235		157
Sp. gr.	0.74-0.85		0.8

TABLE II
HYDROCARBON MIXTURES USED IN STUDY

Component	Mole % Gas	Mole % Liquid
C ₁	88	-
C ₂	7	-
C ₃	5	-
n-C ₅	-	20
n-C ₆	-	20
C ₇ +	-	60

components studied were paraffins, naphthenes, and aromatics.

The paraffinic component used was n-decane with a molecular weight of 142. The naphthenic component used was decahydronaphthalene with a molecular weight of 138. Decahydronaphthalene exists in both a cis and trans configuration. However, neither configuration is stable at elevated temperatures and the difference between their normal boiling points is only 8.4°C (195.65 and 187.25°C, respectively). A mixture of approximately equal concentration was used in this study and analyzed as one component. 1-methylnaphthalene was used for the aromatic component with a molecular weight of 142.

Materials

The gas mixture used in this work was an 88-7-5 mole per cent mixture of methane, ethane, and propane prepared from Phillips Petroleum Company's Research-Grade gases. This mixture was obtained using a 76-14-10 mixture prepared by Phillips and diluting it with Research-Grade methane. The analysis, as supplied by the Phillips Petroleum Company, of these two gases is given in Table III.

The liquid mixtures were made using Phillips Petroleum Company's Research-Grade n-pentane, n-hexane, and n-decane.

The 1-methylnaphthalene used was Eastman Organic

TABLE III
HYDROCARBON MIXTURES SUPPLIED BY
PHILLIPS PETROLEUM COMPANY

Component	Mole % in Gas Cylinder	
	No. 1	No. 2
C ₁	75.72	75.71
C ₂	15.12	15.13
C ₃	8.73	8.73
N ₂	0.43	0.43
O ₂	81ppm	81ppm

Chemicals Practical Grade Lot. 2415 and the decahydro-naphthalene was Practical Grade Matheson Coleman and Bell Lot. P2854.

CHAPTER III

THEORY

Thermodynamics can be used to describe the conditions necessary for phase equilibrium. These conditions provide theoretical basis for the development of vapor-liquid equilibrium correlations. K-values are correlated using empirical convergence correlations, correlations involving fugacity, or based entirely on an equation of state.

The K-value for a component in mixture can be expressed as follows:

$$K_i = \frac{y_i}{x_i} = \frac{\bar{f}_{i,L}}{\bar{f}_{i,V}} \bigg/ \frac{y_i}{x_i} \quad (\text{III-1})$$

where $i = 1$ to N .

$\bar{f}_{i,L}$ and $\bar{f}_{i,V}$ are the fugacities of the component in the two phases.

Normally, multicomponent vapor-liquid equilibrium data are correlated using the K-value expression illustrated in Equation (III-1).

A. Convergence Pressure

The convergence pressure of a vapor-liquid equilibrium system is the pressure at a given temperature at

which the K-values of all components are equal to unity. The convergence pressure for a binary system is the critical pressure for the mixture of two components that has a critical temperature equal to the system temperature. A good review of the convergence pressure concept for determining vapor-liquid equilibrium is given by Edmister (16). The most recent methods of correlating via convergence pressures and methods of correcting for aromatic and naphthenic components are presented in this chapter.

The most recent development in convergence pressure correlations is the NGPA K-charts (37). These charts are not new, but an improved version of an earlier set. The basis for the NGPA charts is a convergence pressure derived from a hypothetical binary liquid phase. The composition of this pseudo-binary mixture is the lightest component and a hypothetical heavy component composed of all the other components.

The K-values for a given component are presented as a function of temperature, pressure, and convergence pressure. A separate chart exists for each compound and convergence pressure. The NGPA charts apply only to paraffinic hydrocarbons and a few non-hydrocarbons. These charts are widely used and give good results when applied to many multicomponent systems.

The Winn correlation (72) attempts to compensate for

composition effects by using both the convergence pressure and a solvent-character parameter. The Winn correlation is a nomograph applicable from 40 to 800°F. and 10 to 5,000 psia for systems of paraffins, olefins, and certain specific components and narrow petroleum cuts. This correlation is easy to use and is quite useful if results for narrow petroleum cuts instead of pure hydrocarbons are desired.

The Organick and Brown correlation (39) is based on binary paraffin systems containing methane as one of the components. The molal average boiling point of the liquid phase determines the convergence pressure of the system. The extra parameter here is the Watson characterization factor which classifies the solvent by giving it an equivalent molecular weight of a normal paraffin. This correlation is difficult to use since it is a trial-and-error procedure and not susceptible for use with a computer. However, this method does try to account for phase equilibrium non-idealities due to non-paraffinic hydrocarbons.

Another correction method for non-paraffinic hydrocarbons is given by Solomon (62). This correlation is simply an extension of the Polyco K-charts (2) by introducing the Watson characterization factor. Solomon gives charts with correction factors for the Polyco K-charts as a function of the characterization factor. The Solomon

correlation is fast and easy to use. However, its results are not as good as those obtained from the Organick and Brown correlation (39).

B. Fugacity Correlations

Fugacity based correlations were the first step toward a theoretical procedure for vapor-liquid equilibrium calculation. Most of these correlations involve the use of the law of corresponding states. Often, equations of state are used to calculate the vapor phase fugacity coefficient. The more significant of these correlations will be briefly discussed here.

The Polycy K-charts, also known as the Kellogg K-charts (2), were developed for 12 light hydrocarbons using the Benedict-Webb-Rubin (BWR) equation of state (8) to calculate their fugacities. The composition effects on fugacity for each phase were represented by the molal average boiling point of the mixture.

De Priester (15) condensed these charts to 24 by modifying the atmospheric to 1000 psia charts to the form of two parameter charts, one for each phase and hydrocarbon. This improved the accuracy of the results while greatly decreasing the number of charts needed. Results can be obtained for pressures up to 3600 psia. Price, Leland, and Kobayashi (43) developed a lower temperature extension of these charts for the higher hydrocarbons.

Poettmann and Mayland (41) developed a correlation

for high boiling petroleum fractions using normal boiling point and Watson's characterization factor. This is presented in the form of charts for different boiling point fractions and is useful to a maximum pressure of only 1000 psia.

Edmister and Ruby (17) developed a generalized correlation giving vapor and liquid phase fugacity coefficients as functions of reduced temperature, reduced pressure, and boiling point ratio. This correlation is based on the Benedict (8) fugacity values and is in the form of six charts. The results obtained are as good as those of the DePriester Polyco chart improvements (15).

Prausnitz, Edmister, and Chao (42) developed a general correlation allowing the user to incorporate any special technique or data he may have available. The K-value is expressed as

$$K_i = \frac{y_i}{x_i} = \frac{\gamma_i v_i}{\phi_i} \quad (\text{III-2})$$

where

$$\phi_i = \gamma_i^V \frac{f_i^{Vo}}{P} = \frac{f_i^V}{P y_i} \quad (\text{III-3})$$

$$v_i = \frac{f_i^{Lo}}{P} \quad (\text{III-4})$$

To use this correlation, the parameters ϕ_i , v_i , and γ_i^L must be specified. ϕ_i is evaluated using the Redlich-Kwong

(RK) equation of state (52). γ_i^L is calculated assuming Scatchard-Hildebrand regular solution relationships (23). The flexibility of this method enters through the parameter v_i , the liquid phase fugacity coefficient of the pure component. The authors suggest that the user obtain his own specific values from experimental solubility data or some generalized source.

This method is difficult to use since the need for extensive correlation excludes the casual user from utilizing this method and also determines the final accuracy of the correlation. However, this method is numerical and can be used to develop specialized computer programs applying to select groups of compounds.

The Chao-Seader correlation (11) is simply a generalization of Equation (III-2) used in the Prausnitz-Edmister-Chao correlation (42). The R-K equation is still used to evaluate ϕ_i and the Scatchard-Hildebrand equation gives γ_i^L . The difference is that v_i is correlated as a function of reduced temperature, reduced pressure, and acentric factor based on over 3000 experimental x-y data points. This method is completely numerical and easily programmed on a computer. The accuracy is sufficient for the use in industrial calculations. It is too tedious for hand calculations, but the use of computers makes this one of the most widely used methods in the petroleum industry today.

A recent correlation for multicomponent phase

equilibrium is proposed by Adler et al. (1). This method uses the R-K equation of state for the vapor-phase fugacity coefficient calculation and the Wohl equation (73, 74) for the liquid-phase activity coefficient, and generalized fugacity charts for the standard-state fugacities of the pure liquid components. This method indicates good results for systems of light hydrocarbons even when approaching the convergence pressure. However, this method has one great drawback. To use the Wohl equation on multicomponent systems, the interaction coefficients for all possible constituent binary systems must be known. This may be impossible to obtain in practice for highly complex systems of interest.

C. Equations of State

Equations of state are an important tool in the development of most vapor-liquid equilibrium correlations (2, 11, 42). Few attempts have been made to use equations of state entirely for K-value calculations.

Benedict et al. (8) used the Benedict-Webb-Rubin equation of state as basis for the Polycy charts. Equation (III-1) gives a direct K-value calculation method for use with an equation of state.

Until recently, little effort was made to calculate K-values directly from equations of state (63). The major reason for this low level of activity is a lack of a sufficiently good equation of state to represent liquid and

vapor phase properties. Such an equation of state is essential to the success of this method. Various attempts made will be examined here. Only two equations of state have been seriously used for this purpose.

The less complex of the two equations is the Redlich-Kwong equation of state (52) given in the form for pressure

$$P = \frac{RT}{(V-b)} - \frac{a}{T^{\frac{1}{2}}V(V+b)} \quad (\text{III-5})$$

where coefficients "a" and "b" are functions of the critical properties.

Wilson (71) modified the temperature dependence of the "a" parameter. He used pure component vapor pressure data and phase equilibrium data from the binary system in question at one temperature. This gave a set of equation-of-state constants that were used on the methane-nitrogen and helium-hydrogen systems. The equation was found to represent these equilibrium data adequately.

Redlich et al. (51) developed an extension to the Redlich-Kwong equation of state giving it 43 constants which give the best possible fit to the Pitzer et al. (40) data. Although the author did not calculate phase equilibrium values, they did derive the necessary fugacity coefficient expressions and showed the utility of their equation for both liquid and vapor phase calculations. The increase in accuracy over the original R-K equation of state is not warranted by the excessive increase in the

complexity of the equation.

The Benedict-Webb-Rubin (BWR) equation of state (6, 7, 8) was developed for correlation of vapor-liquid equilibria and prediction of thermodynamic properties. The equation consists of eight constants that can be obtained from pure component PVT data. The pressure form of the equation is as follows:

$$P = RT d + \left(B_0 RT - A_0 - \frac{C_0}{T^2} \right) d^2 + \\ (b RT - a) d^3 + a \alpha d^6 + \\ \left(\frac{cd_3}{T^2} \right) (1 + \gamma d^2) \exp(-\gamma d^2) \quad (\text{III-6})$$

where A_0 , B_0 , C_0 , a , b , c , α , and γ are the equation-of-state constants and d is the density. This equation is a modification of the Beattie-Bridgeman equation of state (5) for use at higher densities. Rules were set for combining constants of the constituent components when applying this equation to a mixture. This method was originally applied successfully to 12 light hydrocarbons.

Benedict et al. (7) applied their equation of state to phase equilibrium of mixtures of light hydrocarbons. The methane-propane, methane-n-butane, and ethane-n-butane systems were examined at moderate pressures. Deviations of about one per cent were observed.

Schiller and Canjar (61) used the original BWR method to predict nitrogen-carbon monoxide vapor-liquid equilibrium. Satisfactory results were obtained within the

degree of uncertainty of the experimental measurements for temperatures between 85 and 120°K. and pressures of 0.5 to 25 atmospheres.

Stotler and Benedict (64) applied the same method to the nitrogen-methane system and found it necessary to adjust the mixing rule for calculating A_0 as follows:

$$A_0 = x_1^2 A_{01} + 2.874x_1 x_2 + x_2^2 A_{02} . \quad (\text{III-7})$$

This adjustment was necessary to obtain satisfactory results for the vapor-liquid equilibrium calculations.

Cullen and Kobe (14) obtained rather poor results using the BWR equation to calculate the carbon dioxide-propane system phase equilibrium ratio. They observed large deviations in carbon dioxide K-values at lower temperatures and found it necessary to use two sets of equation-of-state constants for different temperature ranges. The constants were developed from PVT and vapor pressure data. It is believed that the deviations were caused by the use of the mixing rules proposed by Benedict, Webb, and Rubin in their original work.

Motard and Organick (36) used the BWR equation to correlate hydrogen-hydrocarbon system phase equilibrium. They found it necessary to specify different values of the constants C_0 and γ for hydrogen at different temperatures to increase the accuracy of the results. A temperature range between -300 and 0°F. and pressure range from 250 to 2000 psia was covered. The K-values for the heavier

components, such as propane, showed large errors.

A new approach for using the BWR equation of state for phase equilibrium calculation was proposed by Starling (63). Starling used experimental K-values to develop generalized expressions for the eight BWR equation of state constants using the conventional mixing rules. The original BWR constants (84) were used for the lighter components, but constants for components as heavy as twenty-two carbon atoms were correlated as a function of carbon atom number. Temperature dependence was also introduced into the constant C_0 . Condensate reservoir fluid equilibrium data were used to determine the BWR equation-of-state parameters. The comparison was also made on natural hydrocarbon system equilibrium data. Good results were obtained for temperatures greater than 0°F. and at phase densities less than 0.55 lb moles/ft³ using this correlation.

Wolfe (75) used the original BWR correlation (8) to predict natural gas equilibrium phase compositions. Components heavier than heptane were combined and treated as a heavy fraction. Results obtained were as accurate as those resulting from standard K-value correlation methods. However, the error increased with an increase in concentration of components heavier than heptane.

Kaufmann (26) used the BWR equation as generalized by Su (66) for phase equilibrium calculations. The generalized constants were evaluated from experimental data of

structurally similar compounds. The generalized BWR equation constant C_0 was developed as a polynomial function of reduced temperature. Phase equilibrium constants were evaluated for systems containing cis-2-butane, 1-pentene, and 1, 3-butadiene. Good agreement was observed for pressures of 14.7 and 120.0 psia and temperatures between 28 and 155°F.

The results of Kaufmann (26) and Starling (63) indicate the usefulness of generalized forms of equation of state for phase calculations. Generalized equation of state forms make it possible to rapidly obtain the necessary equation of state parameters for a large number of compounds.

CHAPTER IV

EXPERIMENTAL APPARATUS

This chapter describes the flow diagram of the apparatus, and gives a detailed description of the equilibrium cell with its supporting apparatus and the analytical equipment.

A. Equilibrium Apparatus

The description of the Equilibrium Apparatus is divided into three sections. These are: (1) feed, (2) pressure regulation and measurement, and (3) the equilibrium cell and thermostat section. Figure 1 shows a schematic diagram of the entire experimental apparatus.

Feed Section

The gas mixture was fed from a supply cylinder through a gauge block and a needle valve to the gas compressor. Three hundred and sixteen stainless steel valves, fittings, and 1/8" O.D. x 1/16" I.D. tubing were used in this section.

The liquid hydrocarbon mixture was fed from a 100cc. burette through a section of 1/8" O.D. tubing to a needle

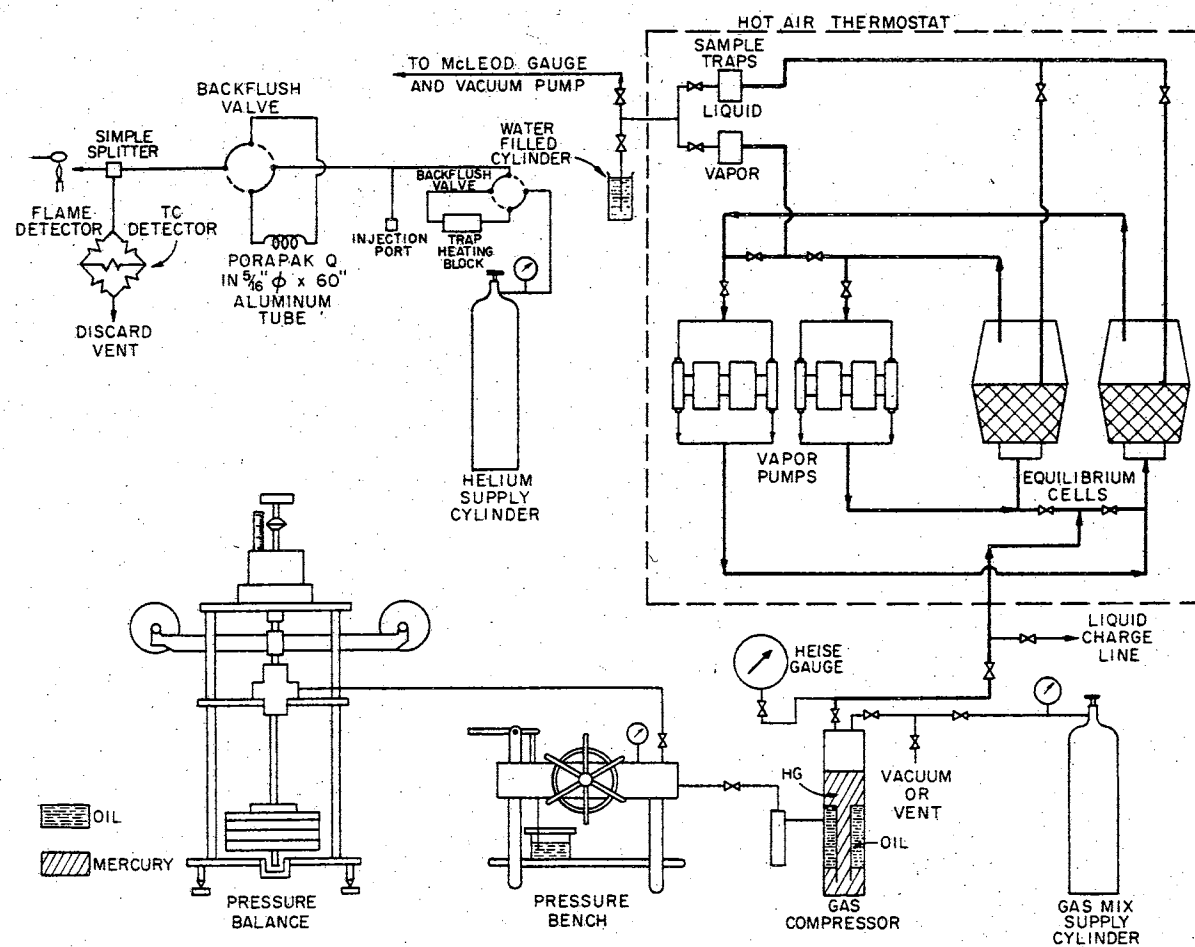


Figure 1. Schematic Diagram of Vapor-Liquid Equilibrium Apparatus

valve connected to the line entering the bottom of the equilibrium cell.

Pressure Regulation and Measuring Section

Pressure regulation was accomplished through the use of a pressure gauge in conjunction with a gas compressor. A Heise pressure gauge was used for pressures below 3000 psia and a Hart pressure balance for pressures above this value. A pressure bench was used to generate and maintain the system pressure. The pressure balance, pressure bench, gas compressor, and the equilibrium cell were manufactured by W. C. t'Hart und Zn, Instrumenten-en Apparatenfabriek N.V., Rotterdam, Holland. The Heise pressure gauge was manufactured by The Heise Bourdon Tube Co., Inc., Newtown, Conn.

The Heise gauge is a brass bourdon tube gauge with a 0 to 3000 psi range in 2 psi divisions. The gauge, serial number H32438, was read to the nearest 0.5 psi. The Heise gauge was checked against the Michels pressure balance and gave the identical results within the accuracy of the Heise gauge.

The Michels pressure balance is a dead weight gauge using a differential piston. The operation of this dead weight tester is based on the use of a piston placed in a cylinder and loaded with a known weight. The maximum allowable pressure for the balance is 3,000 atm. with a claimed accuracy of about 1 part in 10,000. A detailed

description of the Michels pressure balance and its operation may be found elsewhere (65).

The pressure bench has a hand pump to transfer oil from a reservoir into the system. A screw press is used to provide a fine control of the system volume. The oil is pumped to the pressure balance and the gas compressor. A special, filtered, petroleum oil having good viscosity-pressure properties was used in this system. The pressure bench is rated for the same maximum operating conditions as the pressure balance.

Figure 2 shows a sectional view of the gas compressor. The upper and lower chambers of the compressor are connected by a short tube. The gas to be compressed is confined in the upper compartment. Mercury flows from the lower compartment through the connecting center tube into the upper compartment. The mercury is moved by oil flowing from the pressure bench into the upper end of the lower chamber over the mercury.

The position of the mercury in the upper compartment must be known to calculate the system pressure when using the Michels pressure balance. The mercury meniscus position is measured by means of a bridge circuit having for one leg a platinum wire which extends the length of the upper compartment. The calibration of the mercury level as a function of the level indicator reading is described in Appendix A.

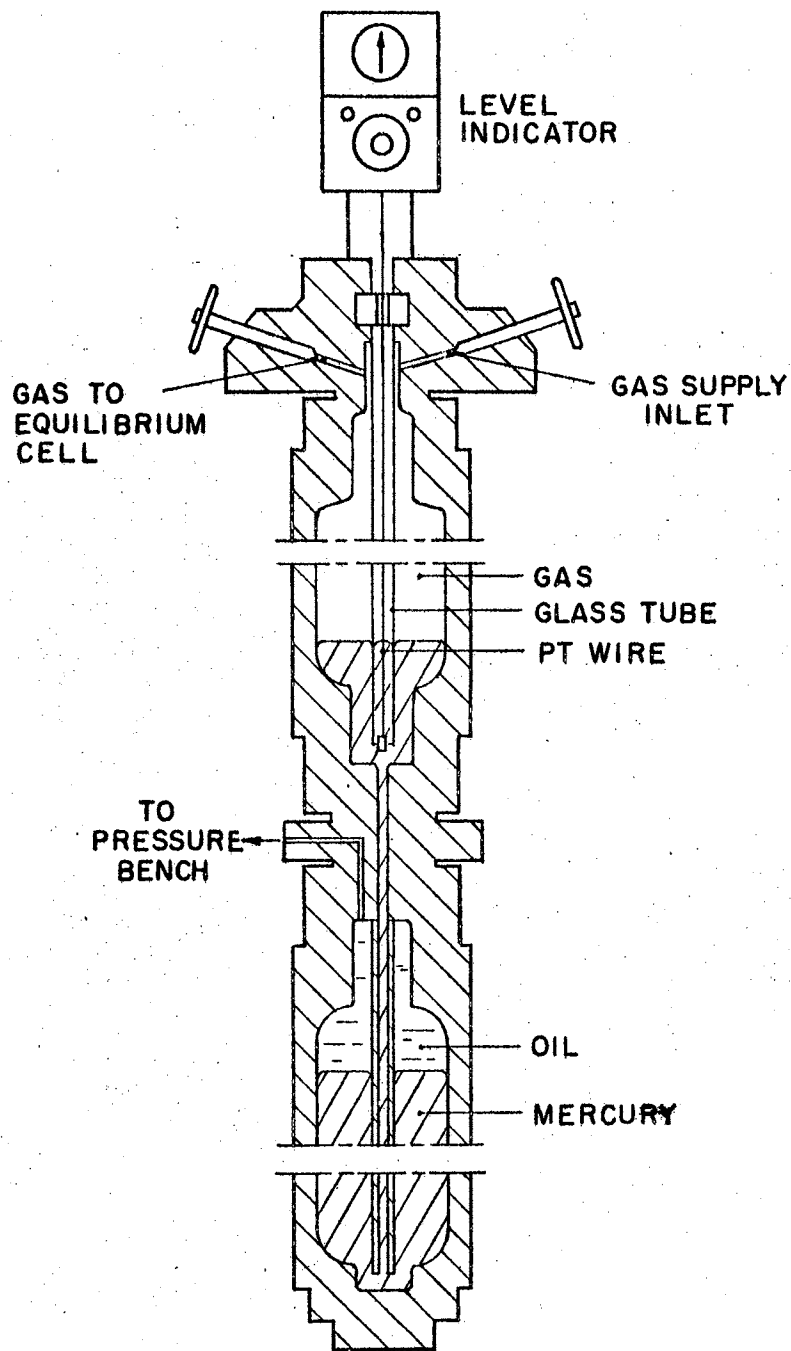


Figure 2. Sectional View of Gas Compressor

The gas compressor has a capacity of 500 cc. and a maximum operating pressure of 1500 atmospheres.

The Equilibrium Cell and Thermostat

The cell used is of the Michels design and is the cell used by Thompson (67) and Stuckey (65) in their investigations of high pressure vapor-liquid equilibrium. A cross-sectional view of the equilibrium cell is presented in Figure 3. The air thermostat also contains another equilibrium cell with its associated vapor recirculation equipment. This cell was used in another experimental project and caused no interference since the two cells were completely isolated through a series of high pressure valves as illustrated in Figure 1.

The gas enters at the bottom of the cell through a capillary tube. Next, the gas is broken into numerous small streams by 0.05 mm deep grooves in Cone E. A 2-11/16" deep section of packed coarse woven fiberglass cloth is inserted to provide more contact between the liquid and the vapor. The fiberglass cloth is held in place by two metal distribution plates perforated by numerous conical-shaped holes.

Line C is used to remove vapor phase samples while line D is used for liquid samples. All connecting lines to the cell are 0.6 mm. I.D. capillary tubes. The liquid dip tube D, extends 1-15/16" into the cell.

The cell has a total internal capacity of about 150 cc.

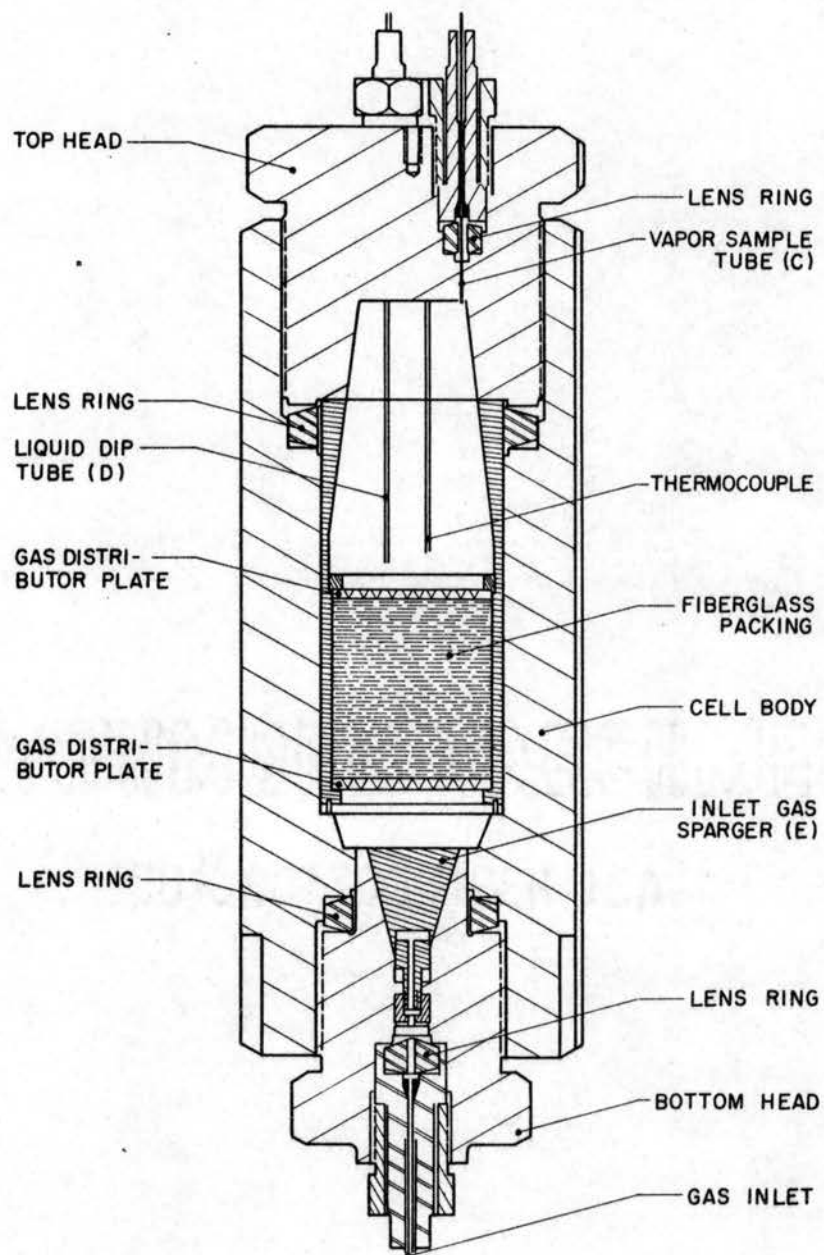


Figure 3. Equilibrium Cell (Hart)

and is rated for a maximum working pressure of 1000 atm. The cell and most of its parts are constructed from stainless steel.

A constant volume magnetic pump was used to remove vapor from the top of the cell and recirculate it through the liquid phase by forcing it into the bottom of the cell. The recirculation rate can be adjusted by varying the speed of the pump. Mechanical details as well as operating information for the magnetic recirculation pump and its control unit may be found elsewhere (65).

Samples of both the vapor and liquid phases were collected in sample traps placed a short distance from the equilibrium cell. These sample traps are illustrated in Figure 4.

The sample trap design was obtained from Pan American Petroleum Corporation (76) and has dimensions nearly the same as an Autoclave model 30 VM valve. Standard Autoclave valve stems, glands, gland nuts, and high temperature glass filled Teflon packings were used in their construction. Two piece valve stems were used and the Teflon washer seals around them were placed close to the stem tip to give a low dead volume. The body of the trap was constructed from 416 stainless steel. An insert of 316 stainless steel was used in the area of the sample cavity because 416 steel was too soft to give a good seal for the valve stem. The body, however, was not constructed entirely of 316 stainless steel due to fabrication

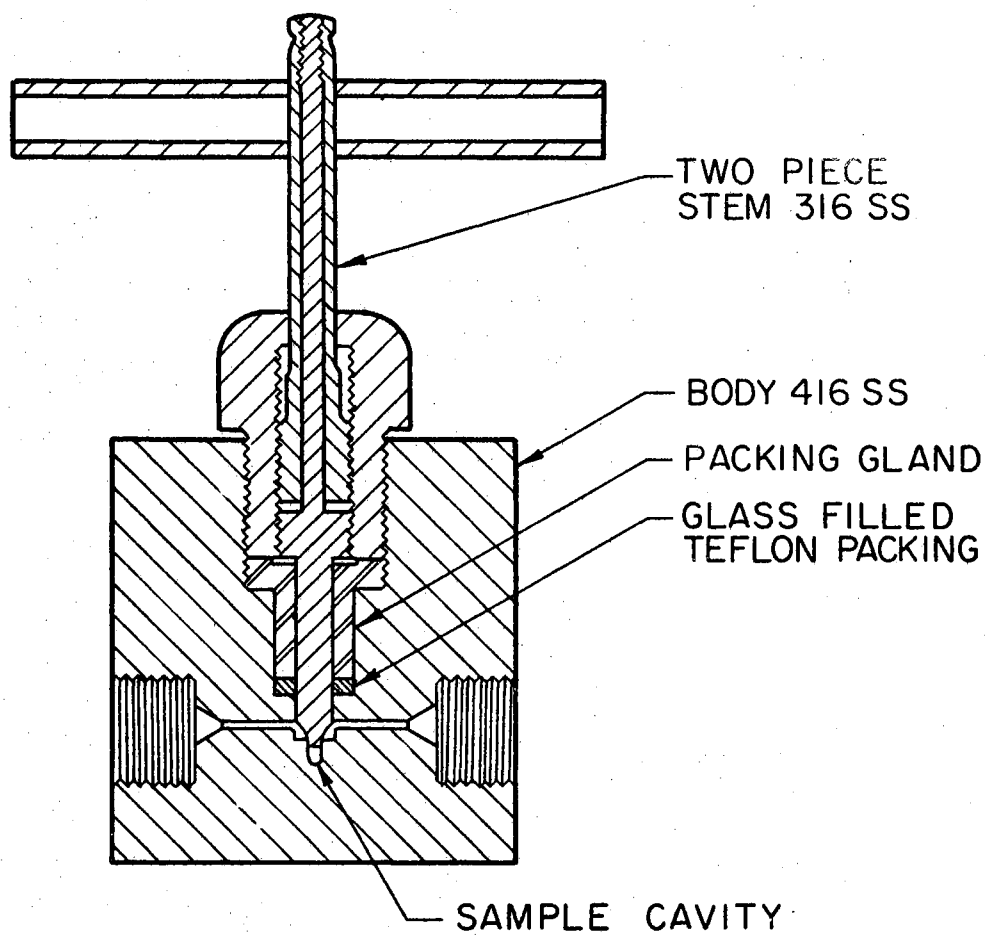


Figure 4. Sampling Valve

difficulties. Just above the sample cavity, the valve stem has a very loose fit in the valve body allowing fluid to flow around the valve stem and through the valve when the sampling cavity is sealed. The sample cavities were made in two sizes of about 2 and 40 microliters to give samples of optimum size for both vapor and liquid phases.

The sample traps were mounted using vise grips to facilitate removal for analysis. One-fourth inch autoclave fittings connect the sample traps to the equilibrium cell through 1/8" O.D. stainless steel tubing spliced to capillary tubing about 1" from the cell. The autoclave connections could be rapidly opened for sample trap removal.

A large air thermostat was used as a constant temperature bath. The details of the thermostat box construction are given by Stuckey (65).

Air was circulated using a 6" squirrel cage blower located in a back corner in the top of the box. The blower was driven by a 1/2" HP electric motor outside the bath. The intake of the blower was located at the bottom of the box and the discharge at the top to provide good air circulation throughout the box. Figure 5 illustrates the blower, heater, and cooling coil arrangement.

Eight 250 watt Chromalox PTF-10 finned air heaters supplied the heat input. Four heaters were used for constant heat input and were controlled by a Superior Type 116 Powerstat. The remaining four heaters were

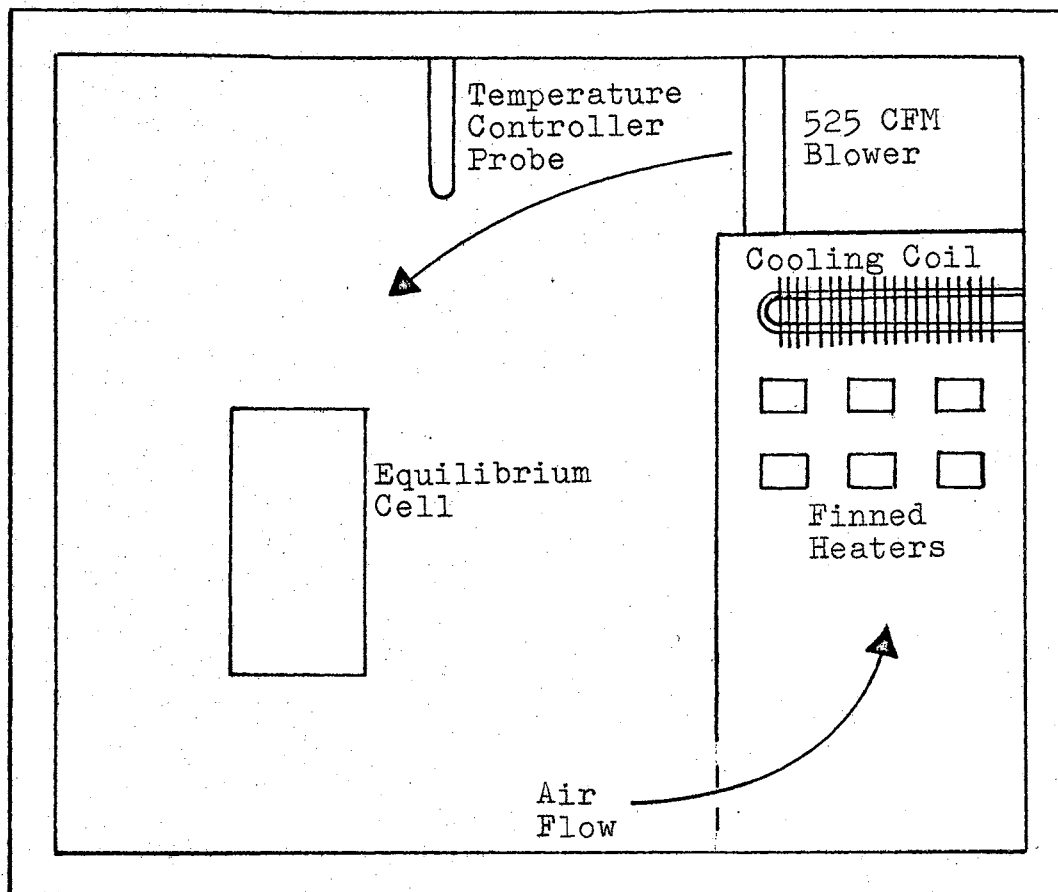


Figure 5. Heater and Blower Arrangement Front View of Thermostat

controlled by a Fisher Model 44 temperature controller. Heat was removed from the bath with a 8" x 8" x 1.5" deep finned cooling coil placed after the heaters at the blower intake. Conoco Antifreeze at 70°F. was pumped through this coil from a chilling unit at a controlled rate. The temperature sensing element was placed at the outlet of the blower.

B. Analytical Equipment

Analysis of the equilibrium samples was performed using a dual column F and M Model 810 research chromatograph. The analytical section can be seen in Figure 1.

The removed sample traps are placed in a heated aluminum block and connected to the chromatograph through heated 1/8" O.D. stainless steel tubing. Separation is performed in a 5/16" O.D. aluminum column three feet long and filled with 11 grams of Waters Associates Inc. Poropak Q 50-80 mesh base material. A standard backflush valve is provided for removing the heaviest component from the column. USP grade helium was used as the carrier gas.

The stream leaving the packed column was split in a 1:3 ratio to the hydrogen flame ionization detector and the thermal conductivity detector, respectively. The hydrogen flame detector response was used for the sample analysis calculation.

CHAPTER V

EXPERIMENTAL PROCEDURE

A four step procedure was followed to obtain the experimental data points. These were charging of components, equilibration, sampling, and analysis.

A. Charging of Components

Two types of charging procedures were employed. One procedure was used to charge both liquid and gaseous material to the cell. Another procedure was used in charging only gaseous material to the cell.

The first charging procedure was used at the beginning of a series of runs at a single temperature. At this point the equilibrium cell, gas compressor, sampling lines, and sample traps were evacuated to a pressure of 15 to 20 microns by connecting a vacuum pump to the system and operating it for 8 hours or longer. The vacuum pump was then shut off and the system pressured to about 100 psia with the charge gas. After 10 minutes the gas was bled off and the entire system again evacuated. The latter step of the procedure was performed twice.

The equilibrium cell was then isolated from the rest of the system by closing the appropriate valves. A

burette was connected by means of a plastic line to the cell drainage line. Approximately 100 cc of deaerated liquid charge was then fed into the evacuated cell by atmospheric pressure exerted on the liquid in the burette. Care was taken to assure that no air would enter the cell through the burette. The chromatograph analysis showed no air in the system samples.

The liquid charge was a 20-20-60 mole per cent mixture of n-pentane, n-hexane, and n-decane, respectively. This mixture was deaerated by connecting the charge gas cylinder to the burette filled with the liquid mixture and slowly bubbling the gas through the liquid for five minutes.

After charging the liquid, the equilibrium cell was immediately pressured up to prevent air leakage into the cell. The gas was added to the cell by letting some flow into the mercury piston compressor and then using the compressor to force it into the cell. The second charging procedure was used only to increase pressure in the cell.

The charge gas was prepared by diluting two gas cylinders containing a mixture of methane, ethane, and propane (illustrated in Table III) with pure methane. This dilution was accomplished by pumping research grade methane into the gas cylinders containing the three component gas mixture.

B. Equilibration

The equilibrium system temperature was attained by heating the thermostat to the desired temperature and allowing it to stabilize after the initial charging of the equilibrium cell.

The optimum coolant rate setting was found to be 35 and the powerstat setting of 155 watts for operation in the vicinity of 150°F. For operation near 250°F the corresponding settings were 12 and 840 watts.

For runs at pressures less than 3000 psia the pressure was monitored and measured on the Heise gauge. At pressures of 3000 psia and higher the Hart pressure balance and bench were utilized. For this system only one pressure cylinder was needed thus eliminating the need for change during a series of runs.

The weights needed to obtain the operating pressure were placed on the balance. The weights were lightly oiled every time they were handled to prevent corrosion. The valve isolating the pressure balance from the pressure bench was then opened. The hand pump was used to inject oil into the system and lift the piston and the rotating parts to the operating level. The weights were set in rotation. The above procedure was used to check the pressure balance before continuing with the run.

The pressure balance was next isolated from the system. The mercury piston compressor was filled with the hydrocarbon gas mixture. Then the valve separating the

pressure bench and the compressor was opened. Oil was pumped into the compressor until the pressure gauge indicated that the pressure was near the desired operating level. At this time, the valve separating the gas compressor and the equilibrium cell was slowly opened and the gas mixture allowed to flow into the cell.

The system pressure was maintained by the injection of oil into the gas compressor forcing more of the gas mixture into the equilibrium cell. Most of the pressure adjustments were made during the first ten minutes after the activation of the magnetic vapor circulating pump. During this time the charged liquid was being saturated with the charged gas mixture. Meanwhile, the temperature was checked frequently by means of a thermocouple inserted into the cell. Manual adjustment of the temperature controller set point was necessary to compensate for set point drift over a period of six or more hours.

The vapor was recirculated at the desired operating temperature and pressure for a minimum of two hours. After this period, the pump was shut down and isolated from the system. The constant heat input of the powerstat was increased by approximately 100 watts to compensate for the heat given off by the magnet coils. The outlet valves from the equilibrium cell were closed and the contents allowed to settle for 15 minutes.

C. Sampling

Meanwhile, the lines leading to the sampling traps were evacuated. The sample traps and the sample line exhaust shut-off valve were closed. Next, the sampling lines were filled with the fluid from the cell up to the shut-off valves. The vapor line was filled first. The contents were allowed to settle for 15 additional minutes. To compensate for pressure drop in the cell due to filling of the lines, additional gas was injected into the cell as the lines were filled. Immediately before the filling of the lines, enough gas was injected into the cell to raise the pressure about 1% above the system equilibrium pressure.

After the total settling period of 30 minutes at equilibrium system pressure, the vapor samples were taken as follows. The tip of the tube on the atmospheric side of the exhaust shut off valve was dipped into a graduated cylinder filled with water. The valve was then very carefully cracked to produce a bubble rate of 1 bubble per second. This was allowed to continue for 15 minutes at which time the valve was closed. The sample trap was then opened and closed, thus trapping a vapor sample.

A similar procedure was followed for the liquid sample. During low pressure runs, decane tended to collect in the cylinder. When 1 ml of decane had collected on the surface of the water, the sampling procedure was terminated. During sampling, additional gas was injected into

the cell to maintain the pressure.

D. Analysis

After the completion of the sampling process, the cell was isolated again and, with the sample traps closed, the sample lines were emptied. The thermostat door was opened and both sample traps removed from the lines and replaced with fresh traps. The liquid sample trap was left in the thermostat to be maintained at the appropriate temperature. When executed rapidly, in less than three minutes, the sample trap removal process allowed the air temperature to drop about 5 degrees or less.

The excess fluid left in the crevices and on the surface of the trap outside the sample cavity was removed by purging the trap body with compressed air while the sample remained trapped by the valve stem in the cavity. The trap was next placed in the heating block, the helium lines connected and helium allowed to flow through the trap body for 6 to 10 minutes to remove the final traces of hydrocarbons inside the trap body but outside the sample cavity. The back-flush valve on the chromatograph oven has two positions. The "light ends" position means that the column is flowing helium through it in the normal direction to the detector while the "heavy ends" position means that the helium flow through the column is reversed and the sample material leaves the same end of the column where it entered before passing to the detector. The

back-flush valve is turned from the initial "heavy ends" position to the "light ends" position after this valve body flush with helium and allowed to remain there for a period of 10-20 minutes. During this time the amount of material swept into the chromatograph column was monitored on a recorder. When no significant signal was detected, the chromatograph oven was cooled down from 200°C used during the purge stage to 40°C with the use of a cooling water coil.

At the start of the sample analysis, the sample trap in the heating block was opened to release the sample from the trap cavity. Simultaneously, the temperature programmer "injection start" button was depressed. The temperature programmer was always set on a four minute delay which was necessary for the complete separation of CO₂ and ethane.

Three minutes from the start of the analysis, the cooling water was shut off and the line blown out with compressed air for one minute. At the end of four minutes the air was shut off and the temperature programmer started heating the oven at the rate of 10°C/min. Twenty-six minutes after the start of the analysis the back-flush valve was turned to the "heavy end" position. That reversed the flow of the carrier gas in the column and eluted the n-decane through the inlet end. The total analysis took 45 minutes.

After the vapor sample was analyzed, the same

procedure was followed with the liquid sample trap. During the purge periods, the equilibrium cell was raised to the next higher pressure and the equilibration started to speed up the over-all process. In this manner, three runs could be made in a 12-hour day while preventing reruns on the same charge if the sample traps had leaked or the analysis was ruined in some other way.

CHAPTER VI

EXPERIMENTAL RESULTS

Composition data were determined for the coexisting equilibrium phases of three different six component hydrocarbon systems at 150 and 250°F. The pressures ranged from 100 to 8000 psia. The base system contained n-decane as the heaviest component which was replaced by decahydronaphthalene and 1-methylnaphthalene in the non paraffinic studies. The temperatures were selected on basis of conditions encountered in producing natural gas condensate reservoirs with consideration for the limitations of the experimental apparatus.

The pressure limitations were based on the characteristics of the system rather than on the physical limitations of the apparatus. At low pressures, below 100 psia, insufficient amounts of light components are dissolved in the liquid phase to permit accurate analyses. The quantity of heavy components in the vapor sample is also decreased. The upper pressure limit is set by the critical pressure of the system at the temperatures studied. At this point, the mixture in the equilibrium cell becomes one phase. The values of experimental pressures used were selected on basis of approximately equal logarithmic

increments of pressure. An error analysis was made to determine possible errors resulting from the chromatographic analysis of equilibrium phase compositions.

A sample calculation of P-T-x-y data from raw experimental data is illustrated in Appendix C. The raw experimental data are tabulated in Appendix D. The experimental P-T-x-y results are listed in Appendix E.

A. Base System K-Values

The experimental K-values for the base system are presented graphically in Figures 6 and 7 and tabulated in Appendix E. Figures 6 and 7 show some scatter in the experimental K-values. The maximum error band expected for each of these points based on a predictable error analysis is also presented. This scatter in the experimental results can be accounted for by these errors.

A comparison of selected base system K-values and the NGPA Chart (37) values is presented in Table IV. A convergence pressure of 4000 psia was used for the 150°F values and 3000 psia for the 250°F points. Good agreement is observed for all components. The largest deviations are observed in the n-decane K-values. The comparison of base system experimental K-values and bubble point calculation results using numerical correlation methods are presented in Table X.

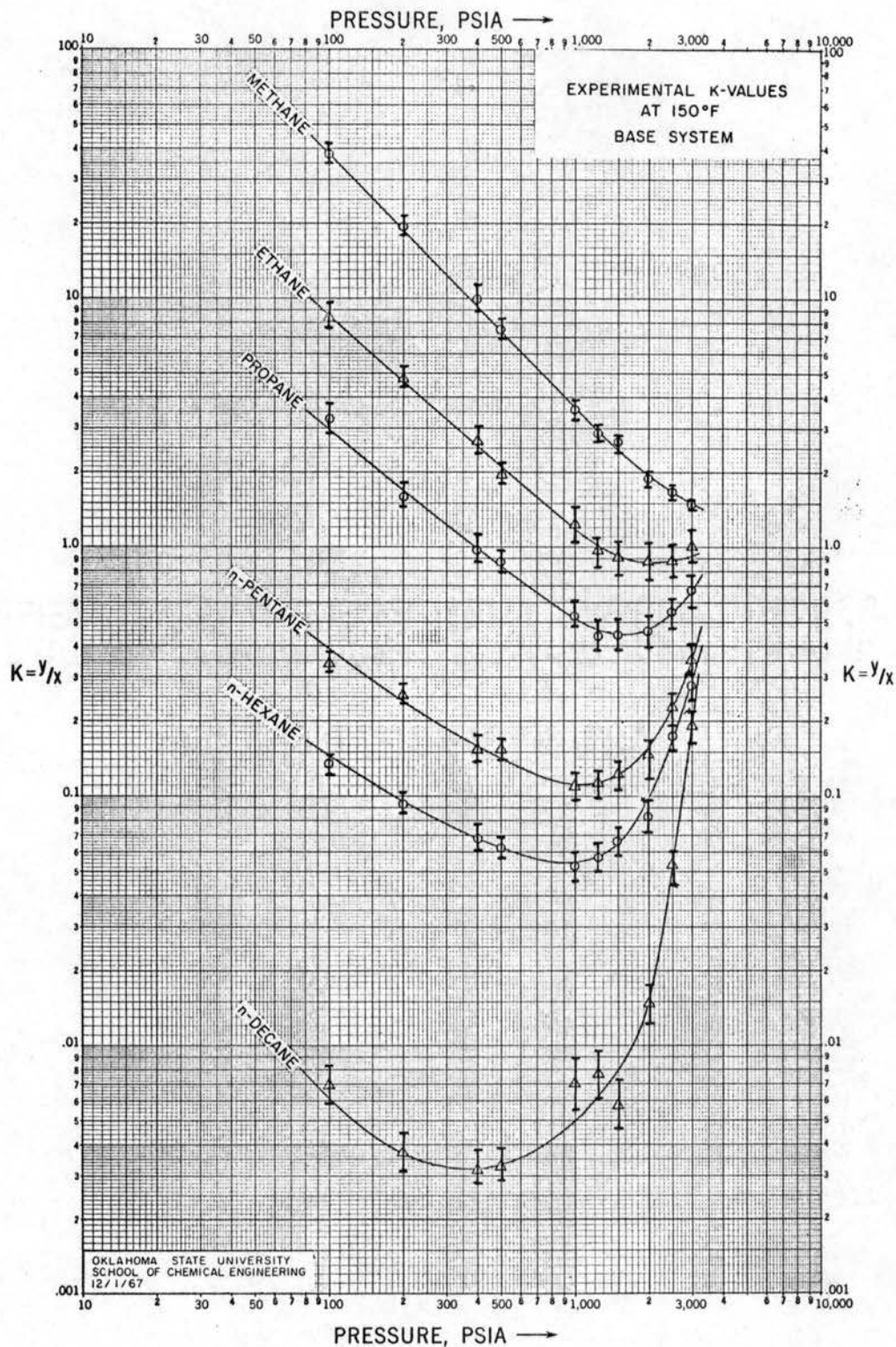


Figure 6. Experimental K-Values at 150°F
Base System

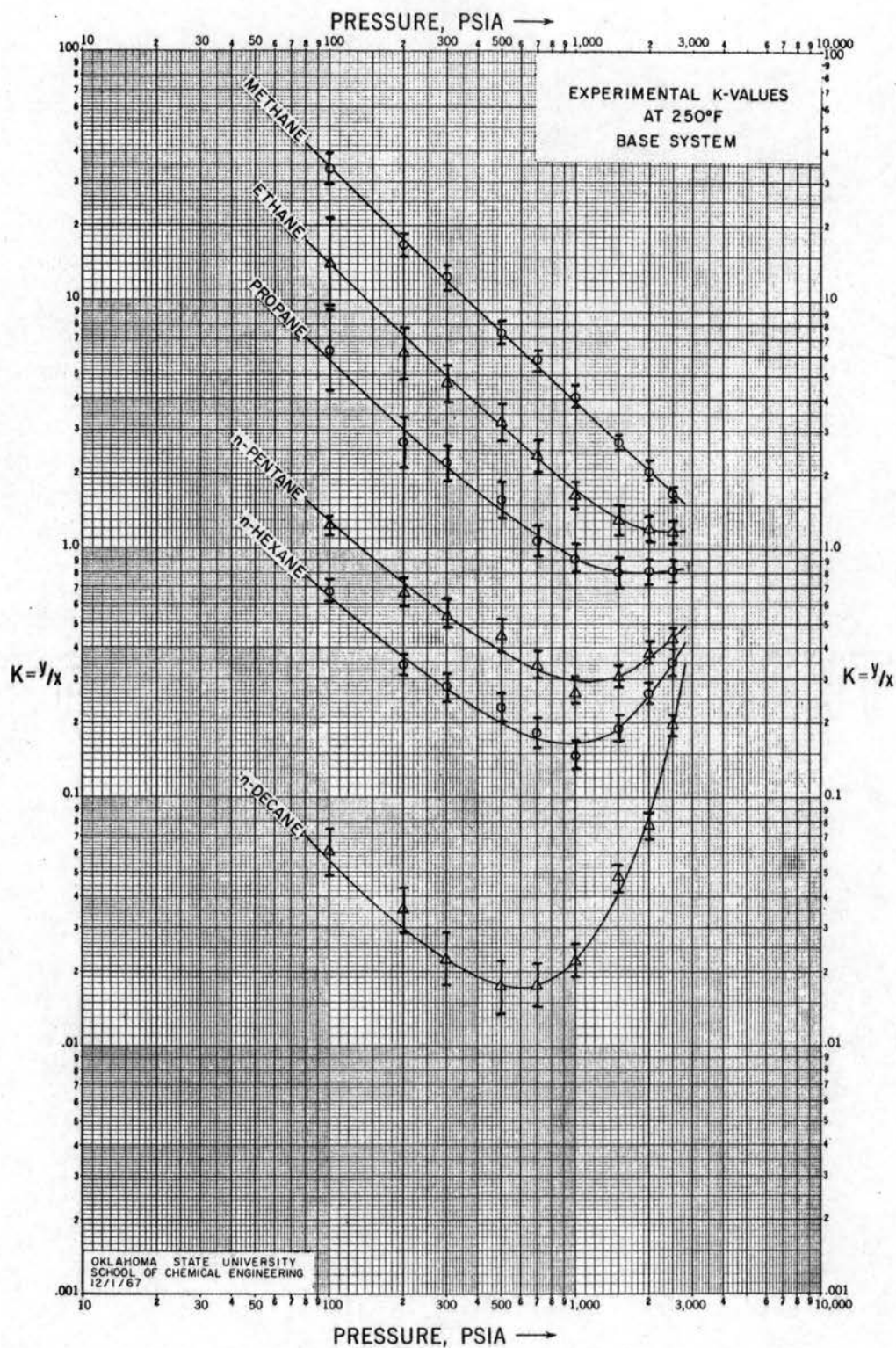


Figure 7. Experimental K-Values at 250°F
Base System

TABLE IV

COMPARISON OF NGPA CHART VALUES AND UNSMOOTHED EXPERIMENTAL K-VALUES
FOR BASE SYSTEM

System Pressure = Component	100 psia		500 psia		1000 psia		2000 psia	
	NGPA	EXP.	NGPA	EXP.	NGPA	EXP.	NGPA	EXP.
TEMPERATURE = 150°F, Convergence Pressure = 4000 psia								
Methane	31.0	38.6	7.0	7.65	3.8	3.59	2.15	1.88
Ethane	7.8	8.54	1.88	1.98	1.2	1.24	0.92	0.87
Propane	2.8	3.32	0.75	0.88	0.55	0.53	0.57	0.46
n-Pentane	0.4	0.35	0.13	0.16	0.12	0.11	0.19	0.15
n-Hexane	0.16	0.13	0.092	0.063	0.056	0.053	0.112	0.083
n-Decane	0.004	0.007	0.0016	0.0033	0.0029	0.0071	0.0096	0.015
TEMPERATURE = 250°F, Convergence Pressure = 3000 psia								
Methane	33.0	33.9	7.1	7.45	3.8	4.08	2.7	2.71
Ethane	12.0	14.1	2.9	3.24	1.7	1.65	1.3	1.31
Propane	5.8	6.31	1.4	1.59	0.97	0.92	0.84	0.81
n-Pentane	1.3	1.24	0.39	0.45	0.34	0.27	0.36	0.30
n-Hexane	0.63	0.68	0.21	0.23	0.18	0.15	0.23	0.19
n-Decane	0.037	0.060	0.014	0.018	0.018	0.022	0.036	0.048

B. Non-Paraffin Substituted System K-Values

The experimental K-values for the base system with decahydronaphthalene substituted for n-decane are presented graphically in Figures 8 and 9. The 1-methylnaphthalene substituted results are presented in Figures 10 and 11. The experimental K-values and xy data are tabulated in Appendix E. The same temperatures and pressure increments were used in obtaining the substituted system data as was used for the base system data. Some of the K-values were checked by rerunning. However, in a constant volume system such as this, the exact conditions cannot be reproduced.

A comparison of selected non-paraffinic heavy component K-values and Poettmann (41) correlation values is presented in Table V. Good agreement is observed for the decahydronaphthalene K-values. However, the 1-methylnaphthalene K-values show poor agreement with the Poettmann correlation which predicts higher K-values. Comparisons of substituted system experimental results and bubble point calculations using numerical correlation methods are presented in Table X.

The Appendix Table XXX and Figures 12 through 16 present the ratios, α , of decahydronaphthalene and 1-methylnaphthalene substituted system K-values to those in the base system at similar system temperatures and pressures for the lighter components. Systems containing the naphthenic component show a lower ratio than aromatic

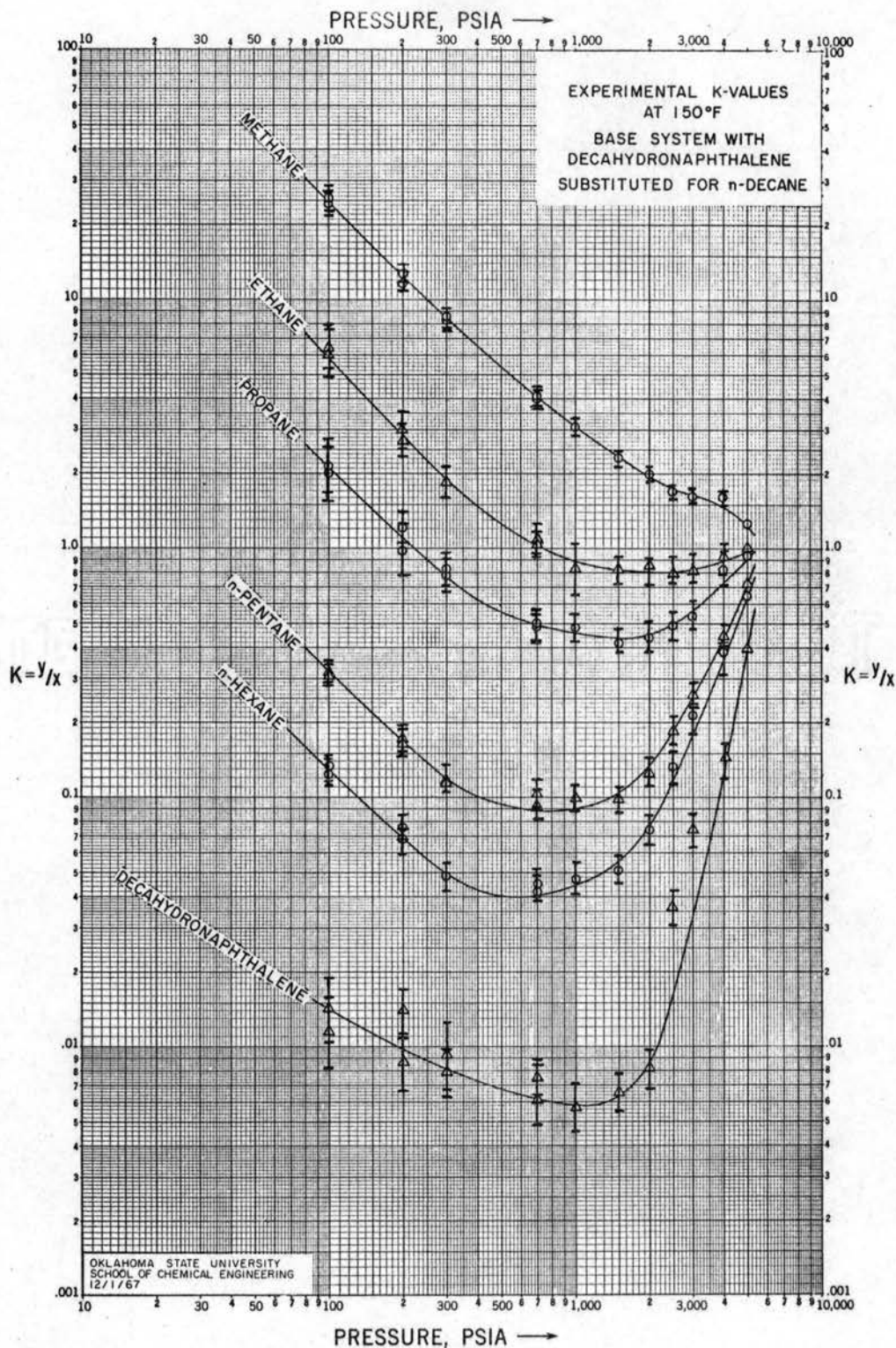


Figure 8. Experimental K-Values at 150°F
Base System With Decahydro-
naphthalene Substituted for
n-Decane

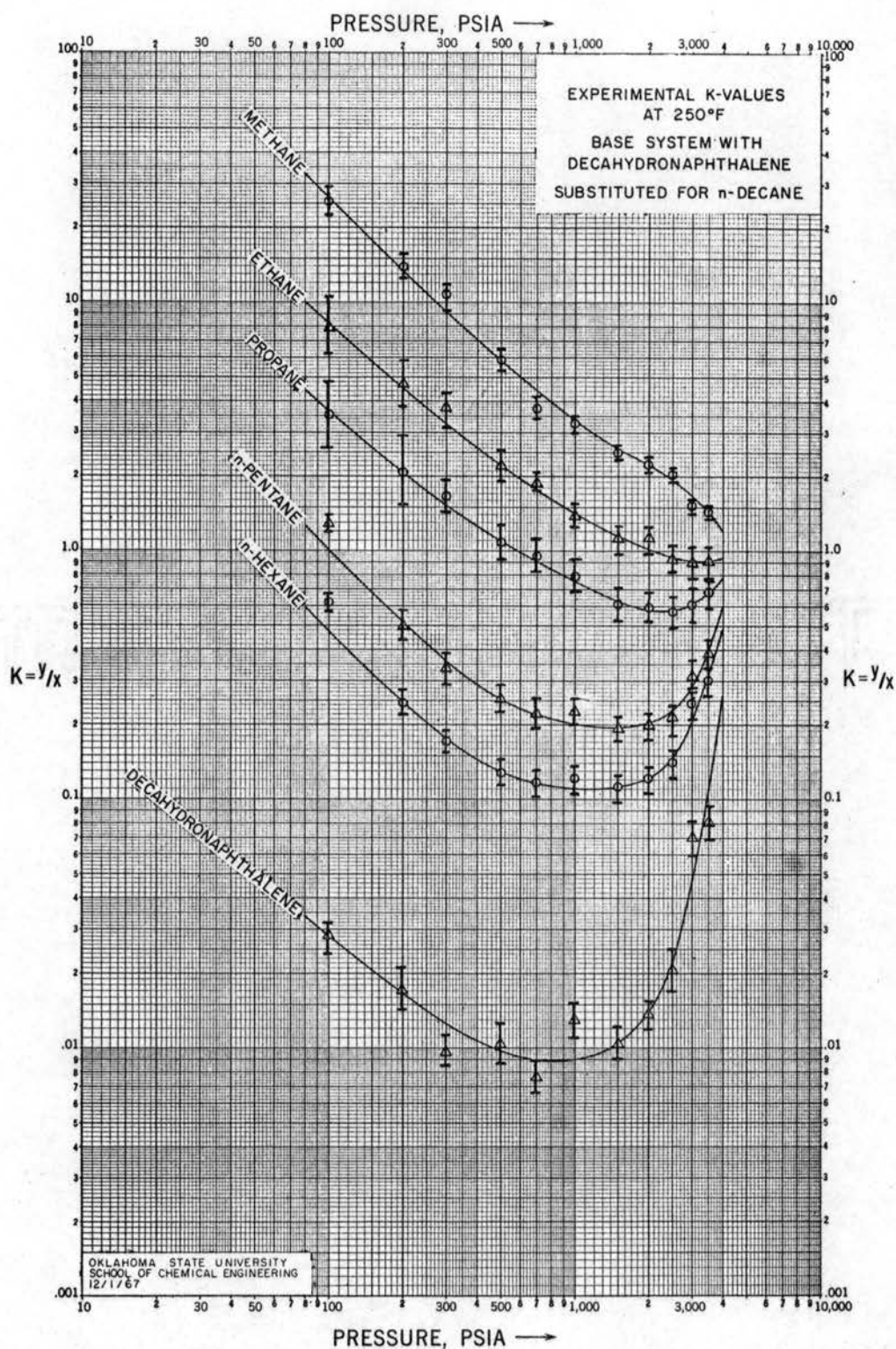


Figure 9. Experimental K-Values at 250°F
Base System With Decahydro-
naphthalene Substituted for
n-Decane

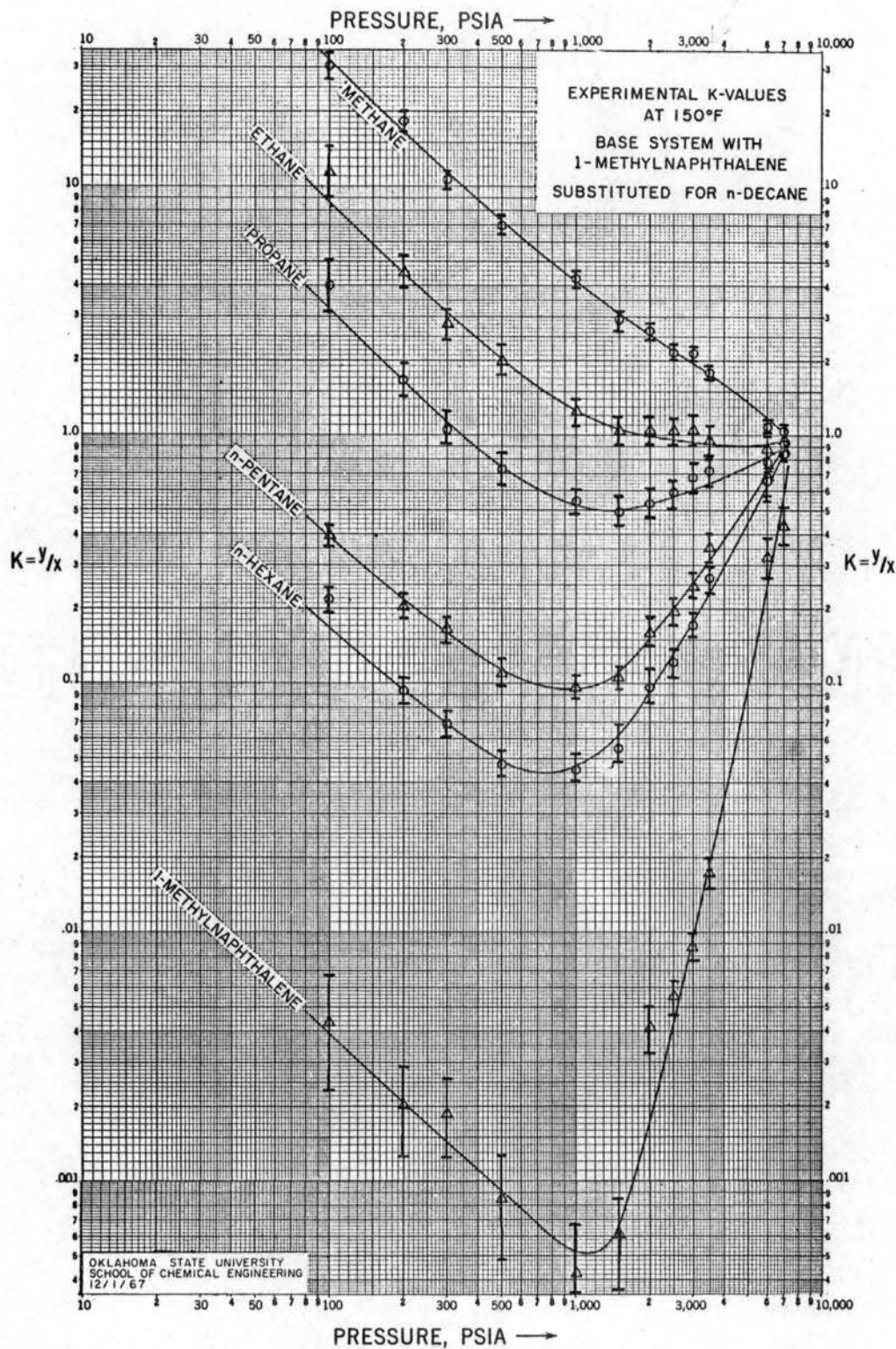


Figure 10. Experimental K-Values at 150°F
Base System With 1-
Methylnaphthalene Substituted
for n-Decane

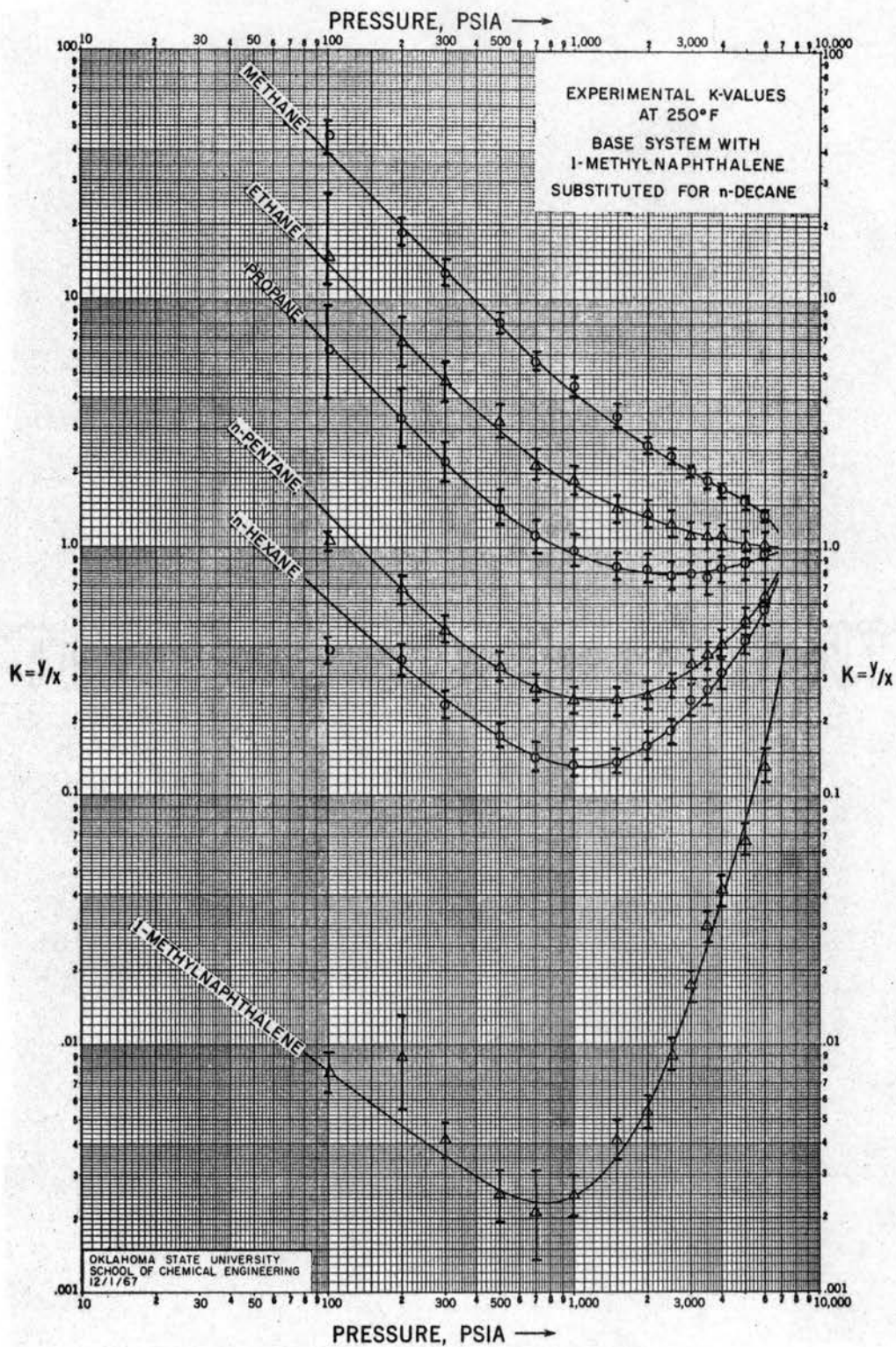


Figure 11. Experimental K-Values at 250°F
Base System With 1-
Methylnaphthalene Substituted
for n-Decane

TABLE V

COMPARISON OF POETTMANN CORRELATION AND UNSMOOTHED
EXPERIMENTAL NON-PARAFFINIC K-VALUES

Pressure	150°F		250°F	
	Poettmann	Exp.	Poettmann	Exp.
DECAHYDRONAPHTHALENE				
100.	0.0072	0.0116	0.016	0.0281
200.	0.0060	0.00866	0.012	0.0173
300.	0.0054	0.00793	0.011	0.00973
500.	----	-----	0.010	0.0104
700.	0.0050	0.00604	0.011	0.00762
1000.	0.0050	0.00568	0.015	0.0130
1-METHYLNAPHTHALENE				
100.	0.0070	0.00435	0.016	0.00768
200.	0.0053	0.00203	0.012	0.00895
300.	0.0046	0.00187	0.011	0.00415
500.	0.0043	0.000849	0.010	0.00250
700.	----	-----	0.011	0.00212
1000.	0.0050	0.000429	0.012	0.00249

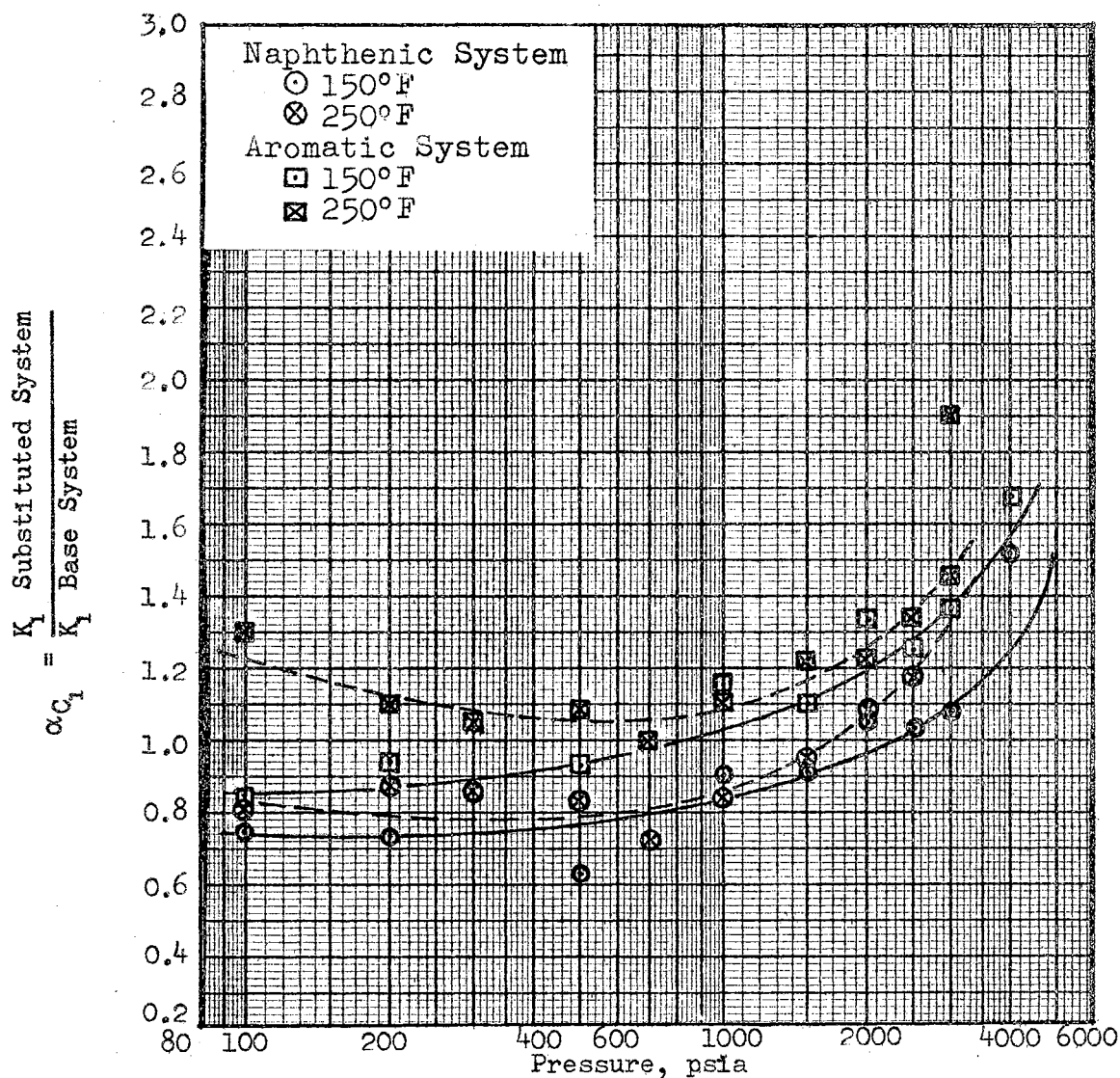


Figure 12. Ratios of Substituted System Methane K-Values to the Base System

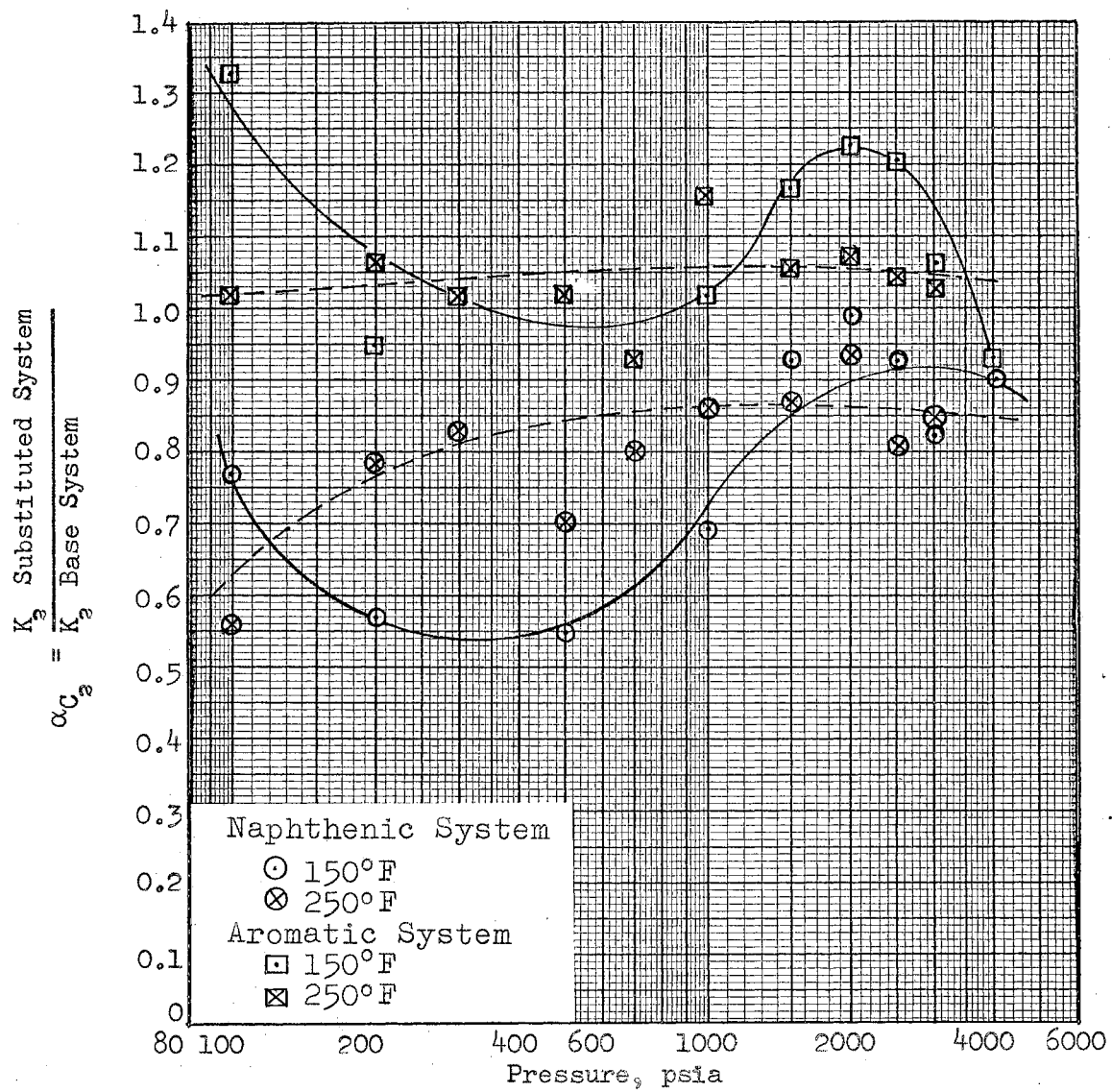


Figure 13. Ratios of Substituted System Ethane K-Values to the Base System

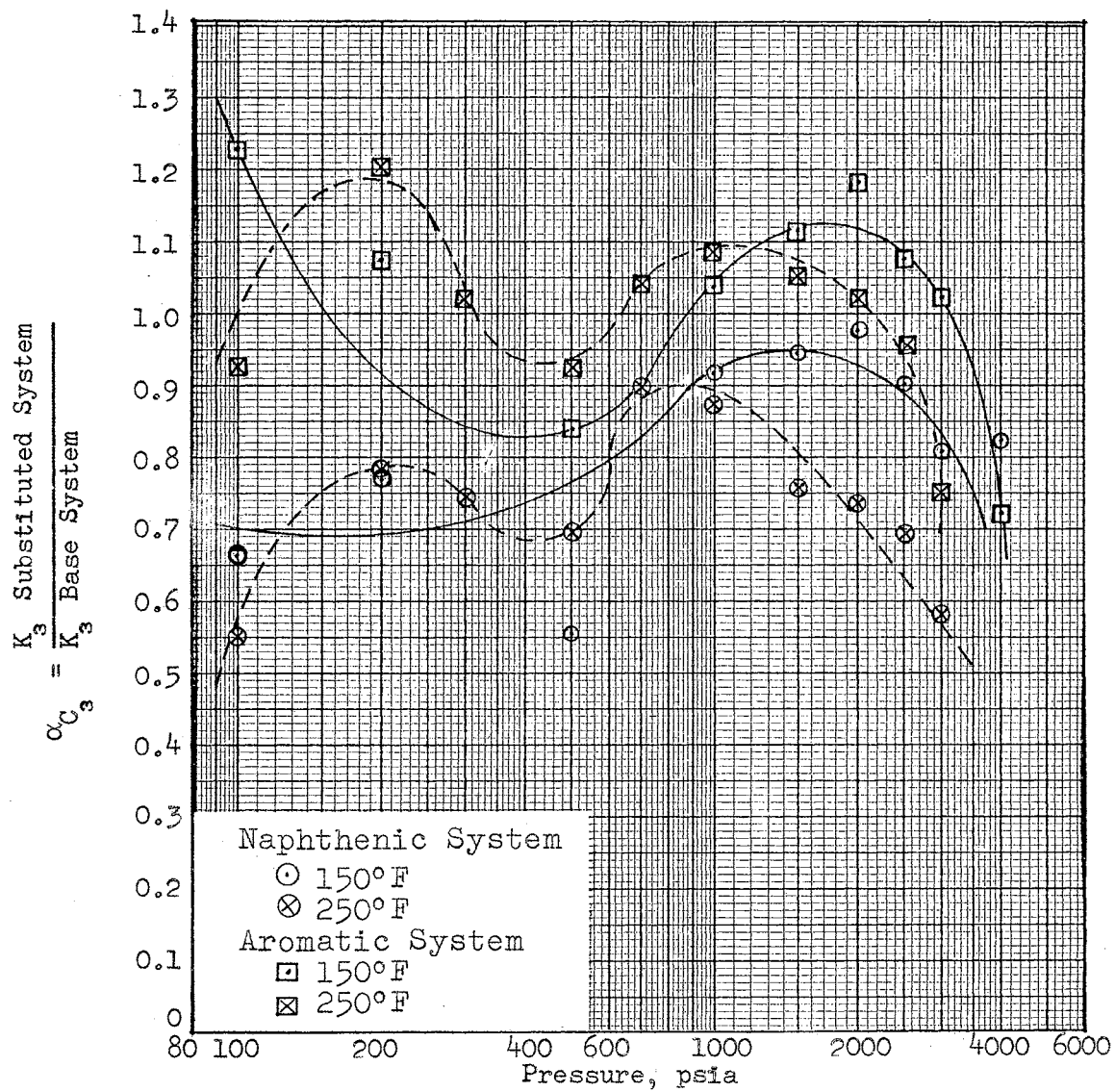


Figure 14. Ratios of Substituted System Propane K-Values to the Base System

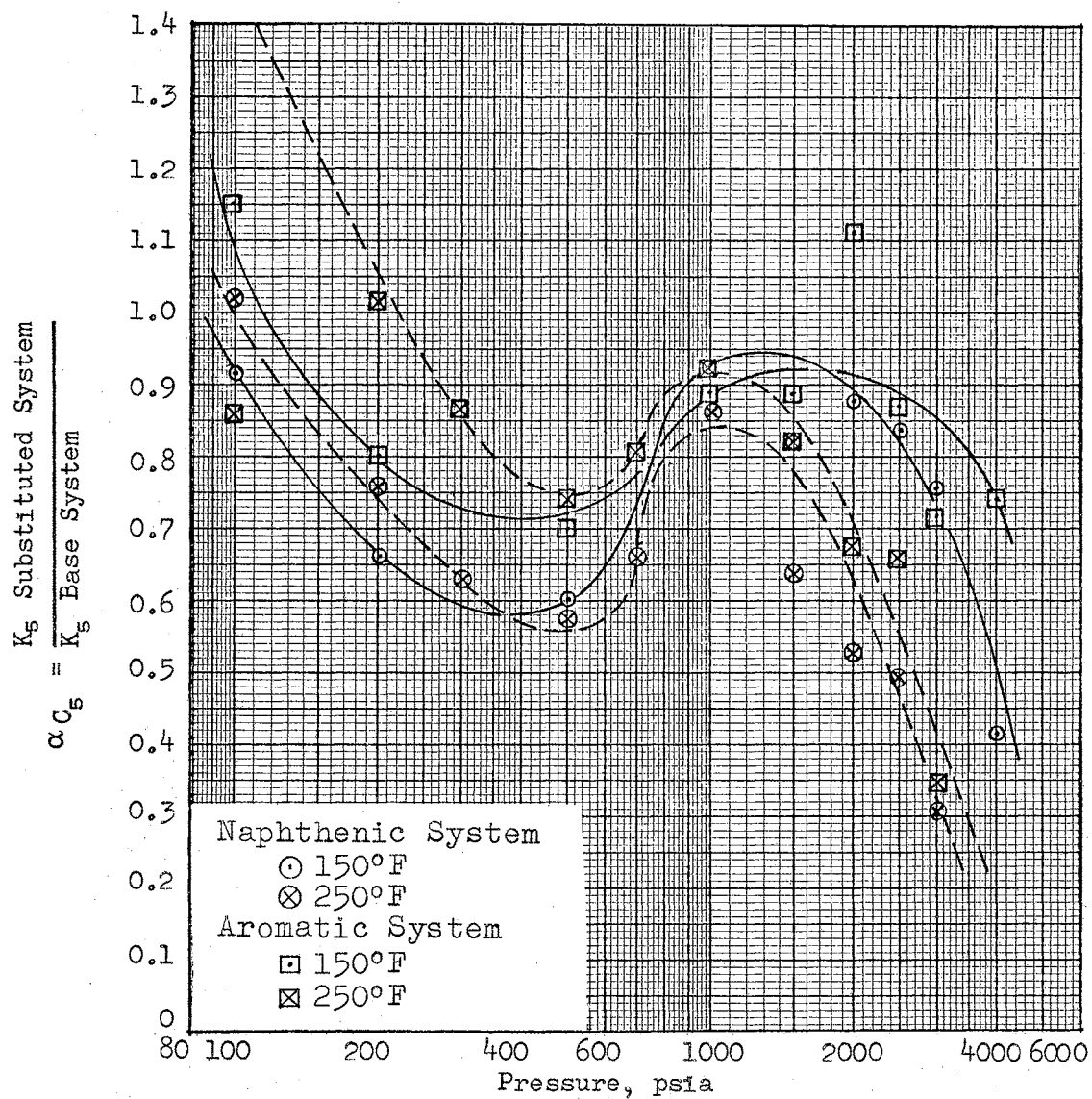


Figure 15. Ratios of Substituted System Pentane K-Values to the Base System

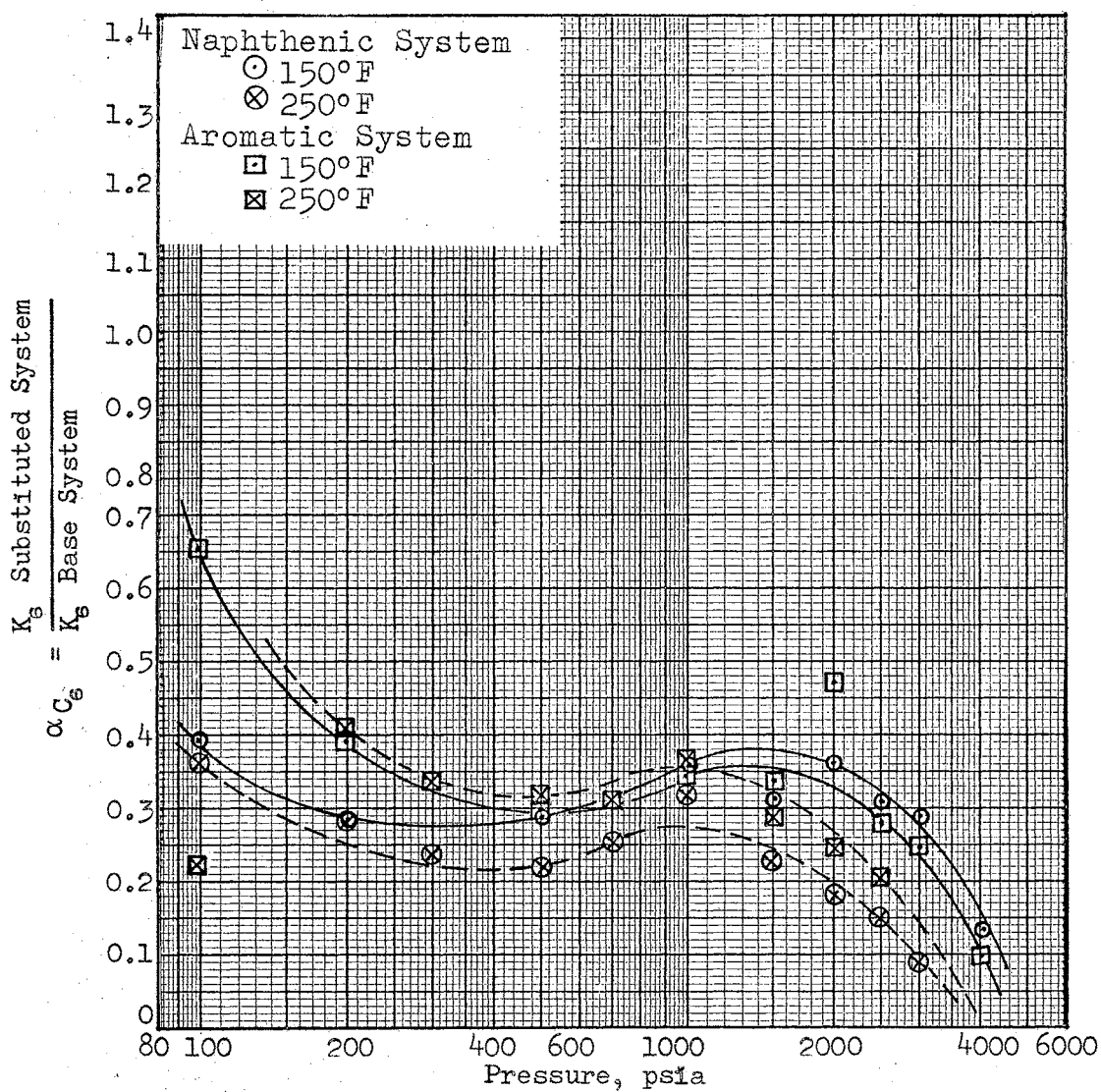


Figure 16. Ratios of Substituted System Hexane K-Values to the Base System

systems. Methane is the only component that has a continuously increasing ratio with pressure. Other components show an increase with pressure initially but a decrease at higher pressures. The ratio increases with temperature below 1000 psia but decreases at higher pressures for all components except methane. Decahydronaphthalene has a greater effect in lowering the lighter component K-values than does 1-methylnaphthalene.

C. Error Analysis

The accuracy of experimental results is related to the magnitude of the error between the observed and true behavior irrespective of precision. Accuracy can be determined by the agreement of measurements made by different methods or, for phase equilibrium, by thermodynamic consistency tests. For these systems, however, neither method can be easily or accurately applied.

Precision, however, can be quite conveniently examined for this system by the method of propagation of errors without the need for duplication of runs. Thus, an analysis of error was made based on possible deviations resulting from the chromatographic analysis of the equilibrium phase compositions.

The derivation is based on Equation (B-1) used to relate the chromatograph peak area ratios to component weight ratios. The basic error equation is:

$$\text{Weight ratio} = (r_i \pm \Delta r_i) \times \frac{(A_i \pm \Delta A_i) \times (t_i \pm \Delta t_i)}{(A_j \pm \Delta A_j) \times (t_j \pm \Delta t_j)} \quad (\text{VI-1})$$

Thus, the largest experimental error in the vapor or liquid composition is given by Equation (VI-2).

$$\Delta x_i = \frac{(A_i t_i \Delta r_i + \Delta A_i t_i r_i + \Delta A_i t_i \Delta r_i) / M_i}{\sum_{j=1}^6 (A_j t_j - \Delta A_j t_j) (r_j - \Delta r_j) / M_j} \quad (\text{VI-2})$$

where

A_i = Integrated area of component i's chromatograph analysis peak.

Δ = Magnitude of error in corresponding quantity.

t_i = Chromatograph attenuation of peak for component i.

r_i = Calibration slope for component i in conversion of chromatograph results to concentrations.

x_i = mole fraction of component i in phase.

M_i = molecular weight of component i.

For the K-value, this expression reduces to

$$\Delta K_i = \frac{y_i \pm \Delta y_i}{x_i \pm \Delta x_i} - \frac{y_i}{x_i} \quad (\text{VI-3})$$

The possible error in the peak areas for the individual components is as follows. For methane, the maximum error is 0.5 area units. For ethane, propane, pentane, and hexane, this value is 1.0. The error is 10.0 for the heavy component. The possible error in the calculation is

0.1 weight ratio to area ratio for methane and 0.01 for the other components.

The main assumption here is that the maximum error for particular quantities does not change with different samples as the run pressure is varied from 100 psia to the convergence pressure. However, this variation cannot be accurately determined so the average values listed earlier were used.

The maximum error band for the experimental data is illustrated in Figures 6 through 11.

CHAPTER VII

CORRELATION WORK

The correlation work involves the use of the generalized BWR equation of state for direct K-value calculation. Modifications of the equation constants and their mixing rules were made after a study of available literature. High pressure binary system literature data were used to optimize this correlation.

A. Use of BWR Equation for K-Value Prediction

The BWR equation of state has been used successfully to calculate vapor-liquid equilibrium K-values directly. Generally, these calculations are performed on systems of light hydrocarbons. Emphasis is normally placed on the equation's ability to fit PVT data for the pure components rather than mixture phase equilibrium K-values. It is evident that the BWR equation performance is poorer at low temperatures and high pressures when used to predict K-values (64).

The deviations can be attributed to certain weaknesses in the BWR equation of state. One major weakness is the inability of the equation to predict the liquid density with an accuracy comparable to that obtained with vapor

phase densities (6). Accurate phase densities are directly related to the accuracy of the K-value as demonstrated by Equation (VII-28).

Another weakness is the need to change the value of the "Co" constant to obtain good predictions of the pure component vapor pressures as suggested by the authors in their original work (8). The usefulness of making "Co" a function of temperature is illustrated by Stotler and Benedict (64) and Starling (63) for phase equilibrium calculations and by Barner and Schreiner (3) for prediction of mixture enthalpies.

The possibility of obtaining improved K-value results by changing the original equation of state constant mixing rules was also shown by Stotler and Benedict (64). Their work concerned the improvement of calculated results by adjusting the interaction constant for the mixture corresponding to " A_0 ". This illustrates the potential for improving the BWR equation not only for mixture property calculations, but also for pure components.

In the past, all equations of state have been subject to use in a generalized form based on the theory of corresponding states. The BWR equation is no exception (9, 38, 66, 25, 21, 13, 18). This work has met with reasonable success, especially with hydrocarbons. The importance of generalization lies in the ability to use the equation rapidly for many different compounds without the need of having extensive tabulations of the equation of state

constants for all compounds of interest. Often, sufficient data are not available to determine the constants for specific compounds. Important in this regard is the success obtained in using the generalized BWR equation for correlating multicomponent, high pressure vapor-liquid equilibria (63).

In this correlation work, generalized BWR constants were evaluated using literature binary system data. These evaluations were made using several different mixing rules for the BWR equation constant " B_0 ". Interaction coefficients are also evaluated on a generalized basis for naphthenic and aromatic components. The numerical values of the new generalized BWR constants and interaction coefficients determined in this investigation are presented in Chapter VIII.

Based on analysis of results available in literature, the following aspects of the BWR equation were examined for K-value calculation.

Generalized BWR Equation

A K-value correlation is more effective and versatile if based on generalized parameters. The range of complexity in equations of state is great. The BWR equation of state at present provides the best accuracy while not being too complex for practical applications. As indicated previously, many generalizations of the BWR equation of state exist. The generalization developed by Edmister,

Vairogs, and Klekers (18) was used in this study. This generalization is only slightly inferior to the original specific component BWR constants when used to calculate pure hydrocarbon P-V-T data. However, it is greatly superior to one of the most recent generalizations, by Su and Viswanath (66).

In this generalization, the P, T, and d terms in Equation (III-9) are replaced by reduced parameters giving us

$$\begin{aligned} \pi = \tau \rho + (B_o' \tau - A_o' - C_o' / \tau^2) \rho^2 + (b' \tau - a') \rho^3 \\ + (a' \alpha') \rho^6 + \frac{c' \rho^3}{\chi^2} (1 + \gamma' \rho^2) \exp(-\gamma' \rho^2) \end{aligned} \quad (\text{VII-1})$$

where

$$P = P_c \pi, \quad T = T_c \tau, \quad \text{and} \quad d = \frac{\rho P_c}{RT_c}.$$

π , τ , and ρ are reduced parameters defined by these substitution relationships.

The reduced, dimensionless constants are defined in terms of the specific components and gas constants as well as the critical properties.

$$B_o = \frac{B_o P_c}{RT_c} \quad (\text{VII-2})$$

$$A_o' = \frac{A_o P_c}{R^2 T_c^2} \quad (\text{VII-3})$$

$$C_o' = \frac{C_o P_c}{R^2 T_c^4} \quad (\text{VII-4})$$

$$b' = \frac{b P_c^2}{R^2 T_c^2} \quad (\text{VII-5})$$

$$a' = \frac{a P_c^2}{R^3 T_c^3} \quad (\text{VII-6})$$

$$\alpha' = \frac{\alpha P_c^3}{R^3 T_c^3} \quad (\text{VII-7})$$

$$C' = \frac{C P_c^2}{R^3 T_c^3} \quad (\text{VII-8})$$

$$\gamma' = \frac{\gamma P_c^2}{R^2 T_c^2} \quad (\text{VII-9})$$

Seven of the reduced constants are given as functions of acentric factor while the product $\alpha'a'$ is treated as a constant

$$\gamma' = 0.052058 - 0.09064\omega + 0.105062\omega^2 \quad (\text{VII-10})$$

$$C' = 0.035694 + 0.185297\omega - 0.230125\omega^2 \quad (\text{VII-11})$$

$$a' = 0.0235866 + 0.290284\omega - 0.295414\omega^2 \quad (\text{VII-12})$$

$$b' = 0.0275404 + 0.131009\omega - 0.134924\omega^2 \quad (\text{VII-13})$$

$$C_o' = 0.098224 + 0.401236\omega - 0.0397262\omega^2 \quad (\text{VII-14})$$

$$A_o' = 0.243258 - 0.127521\omega - 0.509131\omega^2 \quad (\text{VII-15})$$

$$B_o' = 0.113011 + 0.155737\omega - 0.326620\omega^2 \quad (\text{VII-16})$$

$$\alpha'a' = 0.0000875 \quad (\text{VII-17})$$

This generalization gives good results not only for the twelve hydrocarbons originally treated by Benedict, Webb, and Rubin, but also for substances such as benzene and carbon dioxide.

Co Adjustment for Temperature

The original authors of the BWR equation suggested that "Co" should be adjusted from temperature-to-temperature to get a better K-value prediction (8). Several sources illustrate the improvement in accuracy obtained by this adjustment. Most of these adjustments are presented in a tabular or graphic form for specific compounds (77, 3, 64, 36, 8).

Starling, in his generalization of the BWR equation (63), gave "Co" as a linear function of reciprocal temperature.

$$C_{o,i} = C_{o1} + (285688 \times 10^4 - \frac{862754 \times 10^6}{T}) (N_i - 1) + 127881 \times 10^4 (N_i - 1)^2 \quad (\text{VII-18})$$

where

$C_{o,i}$ = C_o for component i

C_{o1} = C_o for methane

N_i = number of carbon atoms in component i.

This relatively simple modification was a successful improvement in his generalization.

A more complex model for C_o was developed by Kaufmann (26)

$$C_o \times 10^{-10} = A_1 + A_2 \tau + A_3 \tau^2 + A_4 \tau^3 + A_5 \tau^4 \quad (\text{VII-19})$$

where

A_i = constants for specific component

T_r = reduced temperature, T/T_c .

This is a simple polynomial expansion in terms of reduced temperature. It gained him an improvement in the results at the cost of introducing four new constants for each component.

The temperature dependence correction for " C_0 " should be such as to produce the maximum improvement in the results with the minimum increase in complexity. Examination of the literature indicated that a linear function of reciprocal temperature would meet these requirements. In this work, Equation (VI-14) was changed to the following form:

$$C_0' = C_1 + C_2\omega + C_3\omega^2 + \frac{C_4}{T} \quad (\text{VII-20})$$

where C_i 's are constants whose values were determined during the course of this work. This model introduces only one extra constant in the BWR generalization.

Constants to be Evaluated

The generalized BWR constants used in this work, Equations (VI-10) through (VI-17) with the exception of B_0 , were evaluated from pure component constants published in the original work (8). However, B_0' was optimized to give the best fit to the P-V-T data using the already determined generalization for the other constants. The generalized form of the BWR equation involves 22 actual constants (18).

The regression of all 22 constants using the limited amount of binary data would require a prohibitive amount of computer time. Also, the constants developed from the PVT data should not be simply discarded since the equation of state should be compatible with both properties.

One constant that must be evaluated again is B_0' . In the original generalization, it was simply regressed to give the best possible fit to the P-V-T data using the other constants. Thus, if an adjustment is made on any other constant, B_0' requires reevaluation.

It was shown earlier that C_0' should be modified for temperature effects to obtain an improved correlation. This requires that C_0' be reevaluated.

In general, B_0 , A_0 , and C_0 make up the second virial coefficient in the BWR equation of state. The second virial coefficient is the major factor in gas phase P-V-T calculation. Thus, to have a realistic scope for this study, only the constants in the second virial coefficient were reevaluated.

$$B(T) = \left(B_0 RT - A_0 - \frac{C_0}{T^2} \right) \quad (\text{VII-21})$$

where $B(T)$ is the second virial coefficient as a function of temperature in the BWR equation when it is expressed in the virial form for pressure.

The evaluation of the B_0 and C_0 constants in the generalized form requires the regression of seven generalized coefficients. A_0 , the constant not associated with

temperature in the second virial coefficient, was not modified.

Mixing Rules

Up to the present time, the mixing rules most frequently used for the A_0 , B_0 , and C_0 BWR constants are the same as those originally proposed (8). These are the square root relationship for all constants except B_0 which uses the linear combination rule. The square root mixing rule is given for the constant A_0 in a mixture as

$$A_0 = \sum_{i=1}^N \sum_{j=1}^N x_i x_j \sqrt{A_{0i}} \sqrt{A_{0j}} \quad (\text{VII-22})$$

where N is the number of components in the mixture and A_{0i} is the BWR constant for the pure component i . The linear mixing rule for B_0 is given as follows:

$$B_0 = \frac{1}{2} \sum_{i=1}^N \sum_{j=1}^N x_i x_j (B_{0i} + B_{0j}). \quad (\text{VII-23})$$

Benedict, Webb, and Rubin suggested the Lorentz mixing rule for B_0 . However, they considered this mixing rule as too complex to use for the slight improvement obtained in the results (7). The Lorentz mixing rule is as follows

$$B_0 = \frac{1}{8} \sum_{i=1}^N \sum_{j=1}^N x_i x_j [(B_{0i})^{1/3} + (B_{0j})^{1/3}]^3. \quad (\text{VII-24})$$

A linear square root combination rule for B_0 was examined because of its usefulness in P-V-T calculations for mixtures (34). This rule is given as:

$$B_0 = \frac{1}{4} \sum_{i=1}^N \sum_{j=1}^N x_i x_j [(B_{0,i})^{\frac{1}{2}} + (B_{0,j})^{\frac{1}{2}}]^2. \quad (\text{VII-25})$$

These four combining rules, the square root, linear, Lorentz, and the linear square root, were investigated in this study for the constant B_0 . The conventional mixing rules were used for all other constants since most questions have centered around the correct mixing rule for this constant.

Interaction Coefficients

Little work has been done up to the present time to develop interaction coefficients for particular components or types of compounds other than the coefficients obtained from the previously mentioned mixing rules. One adjustment was made by Stoller and Benedict (64) for A_0 in the methane-nitrogen system.

$$A_0 = x_1^2 A_{01} + 2.874 x_1 x_2 + x_2^2 A_{02}. \quad (\text{VII-26})$$

Here, 2.874 was used instead of the conventional $2\sqrt{A_{01} A_{02}}$ obtained from the square root mixing rule.

In this investigation, interaction coefficients " θ " were evaluated for the three BWR constants in the second virial coefficient, A_0 , B_0 , and C_0 . Using A_0 for an

example, these coefficients take the following form for a binary system with the square root mixing rule:

$$A_0 = x_1^2 A_{01} + 2x_1 x_2 \theta \sqrt{A_{01} A_{02}} + x_2^2 A_{02} . \quad (\text{VII-27})$$

This " θ " interaction can be applied in a similar fashion to the other mixing rules.

The interaction coefficient " θ " was evaluated for interactions between dissimilar components such as the paraffin-naphthene and paraffin-aromatic interactions. A value of $\theta = 1.0$ will be assigned to the paraffin-paraffin interaction since these systems should behave more ideally than the others.

One goal of this investigation was to determine the amount of improvement that can be obtained in K-value calculations using these generalized interaction coefficients. θ 's for the paraffin-naphthene and paraffin-aromatic interactions were evaluated using binary system phase equilibrium data combined with the various mixing rules for the B_0 constant. In multicomponent systems, the mixing rules used to obtain the mixture constants are simply combinations of the possible binary systems that can exist in the mixture (6, 7, 8). The appropriate interaction coefficient is applied to each of these possible binary combinations in the calculation as illustrated in the computer program in Appendix G.

B. Use of Binary Data

All the new generalized BWR constants and interaction coefficients in this investigation were developed using binary data. The binary system is the simplest case under consideration. However, one can easily see from Equations (VI-22) through (VI-25) that the complexity of the BWR equation increase with the number of components in the system. Since this work involves using experimental data to evaluate the coefficients, the simplicity of the expressions was considered to facilitate calculation. Binary data were found to be more useful due to their simplicity of expression as well as abundance when compared with multicomponent data.

In this investigation, only paraffinic system data were used in the evaluation of the generalized B_0' and C_0' BWR constants with different mixing rules. This corresponds to a $\theta = 1.0$. Next, the interaction coefficients θ were evaluated using these new generalized constants and binary data on paraffin-naphthene and paraffin-aromatic systems.

This study was restricted to systems under temperatures and pressures similar to those used in this experimental investigation and in natural gas condensate processing. Binary data in the range of 100 to 400°F. were used with pressure ranging from 100 to 3500 psia. The analysis was limited to data with K-values of the

heaviest component greater than 0.010 to guarantee that the data used in this evaluation are reliable.

Binary systems with heavy components up to n-decane were available. However, the heaviest naphthenic component was methyl cyclohexane and aromatic was toluene. These are considerably lighter than the compounds used in this experimental investigation. Thus, when the correlation was compared to the multicomponent data, this extrapolation in molecular weight had to be considered. The 182 binary data points used in this study are listed in Appendix H.

C. Correlation Procedure

The generalized BWR equation of state correlation work for phase equilibrium involved two stages. The first was to optimize the generalized B_0' and C_0' BWR equation of state constants with respect to available binary system phase equilibrium data. The second step was to use these new constants and evaluate interaction coefficient for mixtures of dissimilar components for use with the B_0 , C_0 , and A_0 constants. This calculation was performed using binary system phase equilibrium data on paraffinic-naphthenic and paraffinic-aromatic systems. All optimizations required extensive, time consuming, regression calculations on a digital computer. The following is a detailed explanation of the procedures used.

The first part of this correlation involved the

regression of the generalized B_o' and C_o' BWR equation constants using paraffinic binary system data. An example of the computer program used is listed in Appendix G. The calculations were carried out on an IBM 7040 computer at Oklahoma State University.

In this regression, the K-values were calculated using Equation (III-1). This equation is

$$K_i = \frac{d_L \exp(\bar{W}_i L/RT)}{d_V \exp(W_i V/RT)} \quad (\text{VII-28})$$

where

$$\begin{aligned} \bar{W}_i = & (B_o + B_{o,i})RT - 2(A_o A_{o,i})^{\frac{1}{2}} - 2(C_o C_{o,i})^{\frac{1}{2}} T^2 d \\ & + \frac{3}{2} RT (b^2 b_i)^{1/3} - (a^2 a_i)^{1/3} d^2 + \frac{3}{5} a(\alpha^2 \alpha_i)^{1/3} \\ & - (a^2 a_i)^{1/3} d^5 \\ & + \frac{3d^2 (c^2 c_i)^{1/3}}{T^2} \left(\frac{1 - \exp(-\gamma d^2)}{d^2} - \frac{\exp(-\gamma d^2)}{2} \right) \\ & - \frac{2d^2 c}{T^2} \left[\frac{\gamma_i}{\gamma} \right]^{\frac{1}{2}} \left(\frac{1 - \exp(-\gamma d^2)}{\gamma d^2} - \exp(-\gamma d^2) \right. \\ & \left. - \frac{\gamma d^2 \exp(-\gamma d^2)}{2} \right). \end{aligned} \quad (\text{VII-29})$$

Equation (VII-29) is derived for the constant B_o using the linear combination rule (63). The criterion for convergence of the generalized BWR equation constant optimization was the minimum sum of squares of the following error

expressions

$$\text{Dev. } K_i = 1 - (f_i^L/f_i^V) \text{ calc.} \quad (\text{VII-30})$$

for the K-values of all the components of the paraffinic binary systems.

The calculated K_i is based on the experimental phase compositions, temperature, and pressure. The error introduced by the correlation appears in the calculation of the fugacities of different components in the two phases based on this experimental data. This gives

$$K_i = (f_i^L/x_i)/(f_i^V/y_i) \quad (\text{VII-31})$$

where L and V refer to the liquid and vapor phases, respectively. Thus, one can regress a new expression for the generalized B_o' and C_o' BWR constants using the experimental binary system data and minimizing the sum of the deviation functions illustrated in Equation (VII-30). This required the regression of seven distinct constants for C_o and B_o .

$$B_o' = B_1 + B_2\omega + B_3\omega^2 \quad (\text{VII-32})$$

$$C_o' = B_4 + B_5\omega + B_6\omega^2 - \frac{B_7}{T} \quad (\text{VII-33})$$

In this investigation, the calculations were performed using a nonlinear regression program. The computer program used in this study was originally developed by R. M. Bear (4) and modified in this investigation for the specific BWR equation regression.

The nonlinear regression is essentially a method of least squares. Suppose that one has a relationship

$$Z_{n+1}(i) = F(Z_1(i), \dots, Z_n(i), \dots; B_1, \dots, B_m) \quad (\text{VII-34})$$

where $i = 1$ to N sets of data, B_j s are the constants, and $Z_{n+1}(i)$ is the dependent variable with $Z_1(i)$ to $Z_n(i)$ the independent variables. If $\bar{Z}_{n+1}(i)$ is the actual observed value of $Z_{n+1}(i)$. It is simply wished to minimize the sum of squares of the deviation with respect to B_j .

$$S = \sum_{i=1}^N [\bar{Z}_{n+1}(i) - F(Z, (i), \dots; B_1, \dots)]^2 \quad (\text{VII-35})$$

$$\frac{\partial S}{\partial B_j} = 0, \quad j = 1, 2, \dots, m. \quad (\text{VII-36})$$

Using a first order Taylor expansion about a point B_0 with respect to B_j , one obtains

$$F(Z_1, \dots; B_1, \dots) = F(Z_1, \dots; B_1^0, \dots) + \sum_{j=1}^m \frac{\partial F}{\partial B_j} \Delta B_j \quad (\text{VII-37})$$

when $B_j = B_j^0 + \Delta B_j$.

Equations (VII-36) and (VII-37) give one m linear equations in the m unknowns ΔB_j . These equations can be solved for ΔB_j which is used to correct the original B_j . This procedure can be iterated until convergence is obtained.

The actual calculations involved in this regression

can be best illustrated with a brief review of the computer program used. The program consists of eight subroutines called MAIN, GAUSS, SOLV, DERIV, MULLER, DENSTY, YCOMP, and BWRCST.

The section MAIN is simply the input subroutine for the data cards. It is used to read all instruction cards and experimental data to be used in the regression.

Subroutine GAUSS is the heart of the regression procedure. This subroutine handles the logic procedure and calculations involved in the nonlinear regression procedure. The rest of the subroutines simply provide specific calculation of quantities necessary in the regression procedure.

The subroutine SOLV solves the simultaneous linear expressions obtained from Equations VI-36 and VI-37. This calculation is performed only once for each regression cycle.

Subroutine DERIV simply calculates the partial derivatives of the deviation function as illustrated in Equation (VI-36). This calculation is performed by means of incrementation in the independent variable. To obtain the partial derivatives, this calculation must be performed many times. With the BWR equation, this requires many trial and error calculations of the phase densities. This is the step that makes the programs execution time long, requiring several hours of computer time to obtain convergence for a set of generalized B_0' and C_0' constants.

MULLER is a subroutine used to speed up the convergence of this regression calculation by providing a better estimate in the phase density calculation which is a trial and error procedure. This is simply an iteration technique, the Muller method (70), used to solve for roots of an equation requiring three points to give a good estimate of the root.

DENSTY is a subroutine that is time consuming but much used. This subroutine calculates the phase densities using the BWR equation. The roots of this density equation for both the gas and liquid phases are determined using the Muller method mentioned previously. Since the equation cannot be solved directly, a decrease in the number of density calculations required in the course of a regression greatly reduces the time required to carry out this calculation. This subroutine also contains the generalized BWR constant model being regressed.

YCOMP is the subroutine which contains the mathematical expression to be used in the particular regression. In this study, it provides the calculation of the ratio of experimental to calculated K-values in deviation calculation Equation (VI-30).

The last subroutine is BWRCST. This subroutine simply calculates the BWR equation constants that are not being regressed from the generalized expressions as functions of acentric factor for the compounds in question.

This regression procedure gives us the best values

for the generalized B_0' and C_0' BWR constants based on the 102 binary paraffinic K-values. The quality of fit for the particular model in question is also indicated by the results. These regressions using the same binary data were performed using the model for B_0' given in Equation (VII-32). The model used for C_0' was that given by Equation (VII-33) with temperature effects. The mixing rules for all constants except B_0 were the standard square root used by the original authors. For B_0 , however, the linear, square root, linear square root, and Lorentz mixing rules were investigated.

The other part of the regression work involved the evaluation of interaction coefficients " θ " for mixture BWR equation constants B_0 , C_0 , and A_0 . Essentially the same computer program was used to evaluate the interaction coefficients as was used for evaluating the equation of state constants. The interaction constants, θ , were evaluated for binary systems as follows:

$$B_0 = x_1^2 B_{01} + 2x_1 x_2 \theta_{12} B_{012} + x_2^2 B_{02} \quad (\text{VII-38})$$

where B_{012} is calculated by a method depending on the mixing rule used. Similar expressions were used for A_0 and C_0 .

The generalized B_0 and C_0 constants obtained using the paraffinic data were considered as a reference for the interaction with $\theta = 1.0$. Values of θ were evaluated for paraffin-naphthene and paraffin-aromatic binary systems

using the generalized constants developed from paraffinic hydrocarbon system binary data.

The θ regression required only modifications in the program used to regress the equation of state constants. The change was in the subroutine DENSTY where the BWR expressions had to be modified to accomodate the interaction coefficients to be regressed. This regression was considerably faster since only three constants had to be regressed. An example of this modification in DENSTY subroutine can be found in Appendix C.

The interaction coefficients were evaluated for both paraffin-naphthene and paraffin-aromatic interactions using the linear, linear square root, and square root mixing rules for B_0 . These regressions provide information on both the best value for the interaction coefficients as well as their quality of the fit to the data. The results of this work will be discussed in Chapter VIII.

CHAPTER VIII

CORRELATION RESULTS

The generalized BWR equation of state modifications developed in this correlation work for phase equilibrium calculation are evaluated by comparison with experimental binary and multicomponent system K-values. Table VI presents the optimized B_0' and C_0' generalized BWR equation of state constants determined for different B_0 mixing rules based on experimental binary system data listed in Appendix H. Table VII illustrates the interaction coefficients, θ , determined for the optimized BWR equation mixture constants, A_0 , B_0 , and C_0 from paraffinic-naphthenic and paraffinic-aromatic binary system experimental data.

Table VIII presents the absolute per cent deviations in the K-value calculation using the generalized BWR equation of state (18) in its original form with different mixing rules for the B_0 constant and the Redlich-Ackerman R-K equation of state when applied to binary hydrocarbon system data. The results clearly indicate that the generalized BWR equation of state is superior to the Redlich-Ackerman R-K equation of state correlation. The binary system results are not conclusive as to the best mixing rule for the BWR equation constants B_0 due to the

TABLE VI

OPTIMIZATION RESULTS FOR GENERALIZED BWR EQUATION CONSTANTS " B_o' " AND " C_o' "
 BASED ON PARAFFINIC BINARY SYSTEM LITERATURE DATA

" B_o " Mixing Rule Used	Generalized BWR Constants " B_o' " and " C_o' " as Function of Acentric Factor and Reduced Temperature
Linear	$B_o' = 0.0998005 + 0.539138x\omega - 1.20578x\omega^2$ $C_o' = 0.154792 + 0.462707x\omega - 0.387600x\omega^2 - 0.0257257x\tau$
Linear Square Root	$B_o' = 0.0754096 + 0.840782x\omega - 1.58141x\omega^2$ $C_o' = 0.155359 + 0.709310x\omega - 0.713493x\omega^2 - 0.0483684x\tau$
Square Root	$B_o' = 0.103388 + 0.626005x\omega - 1.05564x\omega^2$ $C_o' = 0.151278 + 0.886906x\omega - 0.882247x\omega^2 - 0.0682833x\tau$

TABLE VII
INTERACTION COEFFICIENTS, θ , DEVELOPED FOR THE
OPTIMIZED BWR EQUATION MIXTURE CONSTANTS
BASED ON BINARY SYSTEM LITERATURE DATA

BWR Equation "B ₀ " Constant Mixing Rule Used	Binary System Literature Data (Appendix H) Used to Optimize Interaction Coefficients	Interaction Coefficients, θ , for BWR Equation Constants		
		B ₀	A ₀	C ₀
Linear "	Naphthenic	0.846707	0.949393	0.900416
	Aromatic	1.55697	1.41389	0.737401
Linear Square Root "	Naphthenic	0.510885	0.607272	1.09785
	Aromatic	0.424780	0.510543	1.14951
Square Root "	Naphthenic	-0.0948258	0.13536	1.32980
	Aromatic	-0.204109	0.0327316	1.33388

TABLE VIII
COMPARISON OF GENERALIZED BWR AND REDLICH-ACKERMAN VALUES
AND EXPERIMENTAL LITERATURE BINARY SYSTEM K-VALUES

Equation of State	"B ₀ " Mixing	BWR Constant Rule Used	Average Absolute Deviations of all K-values in Binary System Data Used (Appendix H)		
			Paraffinic	Naphthenic	Aromatic
Generalized BWR					
Equation of State (18)		Linear	26.9	14.1	23.5
" " "		Square Root	18.0	21.9	27.9
" " "		Linear Square Root	21.3	17.9	25.7
" " "		Lorentz	19.8	19.3	26.5
Redlich-Ackerman					
R-K Equation (51)			47.4	27.7	56.1

high percentage deviations involved. However, the linear mixing rule seems to be slightly superior for the naphthenic and aromatic systems while the square root mixing rule is best for paraffinic systems. The generalized BWR results are better for the paraffinic and naphthenic binary data when compared to the aromatic system results.

Table IX illustrates the per cent deviations in the binary system K-values for the developed correlations optimizing the generalized BWR equation constants B_0 and C_0 and interaction coefficients θ . The use of the paraffinic binary data with the linear B_0 mixing rule to regress a new B_0 and C_0 generalization model shows a significant improvement over the original BWR generalization results. Using the different binary system data, interaction coefficient correlations, Table VII, were developed as explained earlier. The introduction of the θ s for the aromatic and naphthenic system interactions did little to improve the average per cent deviation (Table IX) compared to the results obtained for the paraffinic case of $\theta = 1.0$. The correlation regressions were based on a minimum value of the sum of the squares of deviation (see Chapter VII), thus making it possible for the average per cent deviation to be slightly larger in a better fit as shown in Table IX.

The B_0 generalization regression based on the square root mixing rule and paraffinic binary data gives a

TABLE IX

COMPARISON OF OPTIMIZED BWR EQUATION VALUES USING DIFFERENT "B₀" MIXING RULES
WITH INTERACTION COEFFICIENTS AND EXPERIMENTAL LITERATURE
BINARY SYSTEM K-VALUES

Mixing rule used for BWR Equation constant "B ₀ " during optimization using paraffinic binary system literature data	Interaction coefficients used*	Average Absolute Deviation of All K-Values in Binary Systems Data Used (Appendix H)**		
		Paraffinic	Naphthenic	Aromatic
Linear	P	<u>8.5</u>	13.4	21.6
Linear	N	<u>8.4</u>	11.3	18.6
Linear	A	13.4	13.7	<u>19.7</u>
Square Root	P ($\theta = 1$)	<u>7.7</u>	30.9	34.7
Square Root	N	<u>11.1</u>	<u>18.0</u>	28.0
Square Root	A	11.0	21.8	<u>28.7</u>
Linear Square Root	P ($\theta = 1$)	<u>7.2</u>	14.9	24.9
Linear Square Root	N	<u>7.9</u>	<u>9.3</u>	20.0
Linear Square Root	A	8.4	10.2	<u>20.6</u>

*P = Paraffinic-Paraffinic ($\theta = 1.0$)

N = Paraffinic-Naphthenic

A = Paraffinic-Aromatic

**Underlined values are for the data used to optimize the equation and the
interaction coefficients.

smaller average error for the paraffinic data than does the linear mixing rule case. However, the results for the naphthenic and aromatic systems show considerably larger deviations. The regression of interaction coefficients for the aromatic and naphthenic systems does improve their agreement with the binary data. However, the linear B_0 mixing rule results are definitely superior to the square root results for the naphthenic and aromatic systems.

The linear square root mixing rule when used with the B_0 constant regression gives the best agreement for the binary data. Minimum deviations are observed for the paraffinic and naphthenic data when used with their interaction coefficients. The aromatic system results show the least improvement, being comparable in magnitude to results of the linear mixing rule regression.

The results in Table IX show clearly that an improvement is obtained for binary systems when the B_0 generalization is optimized based on vapor-liquid equilibrium data. Also, the interaction coefficient, θ , used to compensate for naphthenic and aromatic effects provides a slight improvement for the respective systems. The best over-all results are given by the linear square root mixing rule used with the B_0 equation of state constant.

Tables X and XI give the average per cent deviation in the vapor phase composition calculation for the multicomponent systems studied in this experimental investigation. The experimental multicomponent data are compared

TABLE X

COMPARISON OF LITERATURE CORRELATION VALUES AND EXPERIMENTAL MULTICOMPONENT
SYSTEM K-VALUES AND SYSTEM PRESSURES
FOR BUBBLE POINT CALCULATIONS

Correlation	Experimental Data	System Pressure	Average absolute % Deviation between calculated and experimental values							
			Vapor Mole Fractions							Heavy Comp y's
			All y's	C ₁ y's	CO ₂ y's	C ₂ y's	C ₃ y's	C ₄ y's	C ₅ y's	
Redlich-Ackerman R-K Equation (51)	P	65.5	39.6	9.2	----	22.1	32.6	51.0	57.9	64.9
	N	68.0	29.8	5.7	----	21.0	26.6	37.1	41.9	44.4
	A	95.5	46.2	7.4	----	22.8	31.2	51.0	60.4	102.4
Chao-Seader (11)	P	23.4	16.3	2.2	----	19.2	12.0	14.5	16.9	32.7
	N	80.2	21.2	1.8	----	8.3	16.1	25.7	31.3	44.1
	A	84.5	32.2	4.2	----	15.8	12.9	42.2	48.8	69.4
	CO ₂	54.8	21.7	5.9	31.3	12.6	9.3	31.2	32.8	38.8
Generalized BWR (18)	P	101.1	30.2	2.7	----	8.9	22.3	34.4	39.1	73.7
	N	85.1	31.9	4.3	----	13.8	21.1	38.7	42.9	61.4
	A	48.0	40.7	5.6	----	9.3	19.7	67.9	78.6	63.1

P = Paraffinic data, n-Decane heavy component (APPENDIX E)
 N = Naphthenic data, Decahydronaphthalene heavy component (APPENDIX E)
 A = Aromatic data, 1-Methylnaphthalene heavy component (APPENDIX E)
 CO₂ = Systems similar to "P" but containing CO₂ (Table XXXIV (68))

TABLE XI

COMPARISON OF OPTIMIZED GENERALIZED BWR EQUATION VALUES AND EXPERIMENTAL
MULTICOMPONENT SYSTEM K-VALUES AND SYSTEM PRESSURES
FOR BUBBLE POINT CALCULATION

BWR Equation "B ₀ " Mixing Rule Used in Optimization	Interaction Coefficient θ	Exp. System Data Pressure	Average absolute % deviation between calculated and experimental								
			Vapor Mole Fractions								Heavy Comp y's
			All y's	C ₁ y's	CO ₂ y's	C ₂ y's	C ₃ y's	C ₄ y's	C ₅ y's	C ₆ y's	
Linear	P-P	P	16.2	19.7	4.6	----	13.4	14.0	19.1	21.8	45.2
	P-P	N	34.2	21.3	4.1	----	11.1	16.8	18.7	19.9	51.1
	P-P	A	22.8	28.4	4.4	----	25.7	32.7	27.0	26.5	54.4
	P-N	N	26.1	51.5	5.6	----	10.0	17.5	76.9	128.9	70.1
	P-A	A*	----	----	---	----	----	----	----	----	----
Linear Square Root	P-P	P	15.8	16.3	4.0	----	6.9	9.4	17.3	21.0	39.4
	P-P	N	20.8	17.7	3.1	----	8.3	10.8	15.4	18.1	50.5
	P-P	A	17.6	26.9	4.3	----	20.3	27.6	29.3	32.6	47.1
	P-P	CO ₂	55.6	38.1	5.8	32.3	10.0	11.7	58.4	84.6	64.0
	P-N	N	25.5	20.4	4.1	----	8.1	11.2	21.9	26.5	50.8
	P-A	A	28.0	36.9	6.1	----	20.3	31.1	51.2	59.8	52.7
Square Root	P-P	P	15.8	15.4	3.6	----	6.7	12.5	15.5	19.4	34.9
	P-P	N	15.6	25.5	3.3	----	8.9	14.1	21.0	26.7	78.9
	P-P	A	21.8	26.6	4.0	----	16.4	22.7	29.4	35.5	51.7
	P-P	N	40.7	41.46	7.9	----	13.3	29.0	68.1	78.8	51.8
	P-P	A*	----	----	---	----	----	----	----	----	----

P = Paraffinic data, n-Decane heavy component

N = Naphthenic data, Decahydronaphthalene heavy component

A = Aromatic data, 1-Methylnaphthalene heavy component

CO₂ = Systems similar to "P" but containing CO₂, Table XXXIV (68)

* = Convergence was not attained in the Linear Reg. and Square Root Reg. with aromatic data

to the results obtained using the various generalized BWR correlations mentioned previously, the Redlich-Ackerman R-K equation of state, and the Chao-Seader Correlation. This comparison involves the calculation of a system pressure and vapor composition based on a given liquid phase composition and system temperature.

From the results it is evident that the best over-all agreement is obtained using the linear square root mixing rule correlation for B_0 without the use of interaction coefficients. It is evident that even though the interaction constant concept proved useful on the binary data from which it was developed, in almost all cases this method gives inferior results with the multicomponent system data.

The interaction constants were developed from binary system data using naphthenic components not heavier than methylcyclohexane and aromatic components not heavier than toluene. The aromatic and naphthenic components present in the multicomponent systems are much heavier. This may account for the coefficient's inability to represent the heavier component interactions satisfactorily. It is evident that the largest disagreement exists in the heaviest component K-value calculation. The generally good results obtained by the use of the paraffinic data to regress the new B_0 generalizations is probably due to the use of binary paraffinic data with n-decane as the

heaviest component which corresponds to the multicomponent systems used in this study.

A comparison between the existing literature numerical phase equilibrium prediction methods and the new BWR correlation using the linear square root mixing rule for B_0 developed in this work is illustrated in Tables X and XI using experimental multicomponent system K-value data. The results show that the new correlation is superior to the Redlich-Ackerman, Chao-Seader and original generalized BWR equation. Of the three comparison techniques, the Chao-Seader correlation provided the best results. However, the optimized BWR equation using the linear square root mixing rule for B_0 shows smaller errors in the predicted K-values and system pressures with the exception of the heaviest component. Here the Chao-Seader correlation performs equally well.

The Chao-Seader Correlation seems to show smaller deviations when applied to the literature multicomponent data containing carbon dioxide. The developed correlation did not use carbon dioxide data and does not seem to be able to account for its effects.

The interaction coefficients, θ , developed from binary data show no improvement for multicomponent system results. In some cases, the use of the interaction coefficient made it impossible to obtain convergence in the bubble point calculation. This was also true for some of

the highest pressure data points in most of the correlation methods.

CHAPTER IX

CONCLUSIONS AND RECOMMENDATIONS

The purposes of this study were:

- (1) to obtain experimental K-value data for multicomponent systems with heavy components having different physical properties.
- (2) to study the use of the BWR equation of state in its generalized form for direct correlation of vapor-liquid equilibrium data.

Experimental data were taken on three six component systems at 150 and 250°F. Pressures ranged from 100 psia to the convergence pressure of the system. All systems contained methane, ethane, propane, n-pentane, and n-hexane. The distinguishing characteristic of the three systems was the use of either n-decane, decahydronaphthalene or 1-methyl naphthalene as the heaviest component.

The study of the generalized BWR equation of state involved the optimization of the B_0 and C_0 constants based on phase equilibrium data and different mixing rules for B_0 . Interaction coefficients were also examined to take into account naphthenic and aromatic component

interactions. Conclusions and recommendations from this investigation are summarized in the following.

A. Experimental

Conclusions

- (1) The vapor recirculation constant volume equilibrium cell is satisfactory for obtaining complex system vapor-liquid equilibrium data.
- (2) Small samples can be removed from the equilibrium cell with minimum system upset for transfer to a chromatograph for analysis.
- (3) Accurate phase analysis can be made using small sample volumes if all components are present in significant concentrations. Different size sample traps are required for phases of different density.
- (4) Over-all system composition is limited in a constant volume cell equilibrium apparatus. Components and their concentration in the gas compressor must be such that no condensation can occur at ambient temperature and limiting system pressures.
- (5) For best sample analysis, chromatograph peaks should be sufficiently wide to provide an accurate area count. Good

proportionation of peak width can be only accomplished with oven temperature programming.

Recommendations

- (1) To maintain sufficiently high concentrations in both phases for accurate analysis, all components charged through the gas compressor should have a relatively high concentration in the charge gas.
- (2) The constant volume equilibrium cell should be replaced with windowed variable volume equilibrium cell. This would make possible the calculation of phase densities and operation at a constant over-all composition.
- (3) Larger sample traps should be used for low pressure vapor samples to improve the accuracy of the analytical results.
- (4) A system should be developed to make direct transfer of phase samples from the equilibrium cell to the chromatograph for analysis. This should be accomplished without the need to remove sample traps which upsets the cell's thermal equilibrium.
- (5) To best study the effect of naphthenic and aromatic components on the paraffin K-values, ternary and corresponding binary systems

should be investigated. Systems of more than three components are not convenient for correlation development, but only for comparison work.

B. Theoretical

Conclusions

- (1) NGPA convergence pressure K-value correlation gives satisfactory results in multicomponent paraffinic systems up to about 2000 psia for all components except n-decane, n-decane NGPA results appear low at both 150 and 250°F.
- (2) Replacement of n-decane in a multicomponent hydrocarbon system with naphthenic and aromatic components of similar molecular weight elevates the system's convergence pressure. The naphthenic component significantly lowers the lighter component K-values while the aromatic had a smaller and similar effect. The aromatic component of the same molecular weight is considerably less volatile.
- (3) The Poettmann correlation seems relatively poor for predicting heavy naphthenic and aromatic component K-values.
- (4) The BWR equation of state as generalized

by Edmister, Vairogs, and Klekers predicts multicomponent phase equilibrium with more accuracy than the Redlich-Ackerman R-K equation of state.

- (5) Significantly improved accuracy for direct K-value calculation can be achieved by optimizing the generalized B_0 and C_0 constants in the BWR equation of state from experimental binary system data. The C_0 constant is also made a function of temperature.
- (6) The best mixing rule for the B_0 constant in the BWR equation of state for K-value calculation is the linear square root model. This is true for both binary and multicomponent systems.
- (7) The interaction coefficient, θ , of the model $B_0 = B_{11} x_1^2 + 2\theta_{12} x_1 x_2 B_{12} + B_{22} x_2^2$, where B_{12} is a specific combination of B_{11} and B_{22} depending on the particular mixing rule used, gives slightly improved results for binary systems when θ 's are determined for paraffinic-naphthenic and paraffinic-aromatic interactions. However, no improvement was observed when these binary system based interaction coefficients were used in the multicomponent calculations. A

reason for this is that the coefficients were developed based on much more volatile naphthenic and aromatic compounds.

- (8) The generalized BWR equation correlation for direct K-value calculation improves with increase in temperature. The accuracy is somewhat lower than that obtained using the NGPA charts. For the totally paraffinic multicomponent systems, the equation of state correlation reproduced the NGPA values for n-decane closer than the experimental results.

Recommendations

- (1) Binary phase equilibrium data should be used to optimize not only the B_0 and C_0 generalized constants, but also other constants. In this investigation, only the second virial coefficient was examined. However, since the density calculation for the liquid phase is involved, higher order interactions must be considered. A major problem involved in more extensive optimization is the excessive computer time required to perform the calculations.
- (2) The θ interaction model should be examined

more extensively. Although this study indicates that this model is not very useful, more binary data on heavier systems and extension of the interaction calculation to other equation of state constants may prove this model to be of practical use. However, the necessary binary data are not available at present for either system with aromatic or naphthenic compounds. Other interaction models should be considered.

- (3) The BWR equation of state has a limited accuracy for high phase density calculation. This puts limit on the accuracy of results that may be attained using it. An equation of state should be developed that is capable of giving both vapor and liquid phase densities with a high level of accuracy.
- (4) The trial and error solutions to the BWR equation of state for density is the limiting step in the speed of the K-value calculation. Valuable computation time could be conserved if an equation could be used to provide molal volumes by a direct calculation.
- (5) Phase densities calculated from the equation

of state used to correlate K-values should be examined. In this study, no thought was given to the accuracy of the calculated density, just to the K-value.

However, to be completely successful, the equation of state must be able to predict the phase density of the mixture as accurately as the K-values.

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NOMENCLATURE

A	-	area
	-	residual work content
	-	coefficient in Equation (VI-21)
	-	constant in the BWR equation of state
a	-	parameter in the R-K equation of state
	-	constant in the BWR equation of state
B	-	2nd virial coefficient
	-	constant in Equations (VI-3) and (VI-37)
b	-	constant in the BWR equation of state
C	-	constant in Equation (VI-22)
	-	constant in the BWR equation of state
c	-	constant in the BWR equation of state
d	-	density
F	-	function
	-	Fahrenheit
f	-	fugacity
H	-	parameter in Equation (A-3)
K	-	vapor-liquid equilibrium distribution ratio, y/x
M	-	molecular weight
N	-	number of components in a mixture
	-	number of carbon atoms in a compound
P	-	pressure

R	-	gas law constant
r	-	parameter in Equation (VI-1)
S	-	sum of squares
	-	parameter in Equation (B-1)
T	-	temperature
t	-	chromatograph peak attenuation
V	-	volume
x	-	liquid mole fraction
y	-	vapor mole fraction
Z	-	parameter in Equation (VI-36)

Greek Symbols

α	-	constant in BWR equation of state
	-	ratio of K-values
γ	-	activity coefficient
	-	constant in BWR equation of state
Δ	-	change in a property
ω	-	acentric factor
π	-	reduced pressure, P/P_c
ν	-	pure component fugacity coefficient
ρ	-	density
	-	ideal reduced volume, $\frac{dRT_c}{P_c}$
ϕ	-	fugacity coefficient
θ	-	interaction coefficient
Σ	-	summation over all N components in a mixture
τ	-	reduced temperature, T/T_c

Subscripts

- 1, 2 - components 1 or 2, respectively
- c - critical property
- i, j - component i or j, respectively
- o - BWR equation of state constant
- r - reduced property

Superscripts

- L - liquid phase
- o - reference state
- V - vapor phase
- ' - generalized BWR constant

APPENDIX A

CALIBRATION OF TEMPERATURE AND PRESSURE MEASURING EQUIPMENT

The temperature measurements in this investigation were made using iron-constantan thermocouples read with a Leeds and Northrop K-3 potentiometer. The pressure below 3000 psia was measured using Heise pressure gauge and above 3000 psia with the Michels pressure balance.

Thermocouple Calibration

Two thermocouples were used to measure the temperature in the air thermostat. The temperature inside the equilibrium cell was measured with a 0.062" O.D. insulated thermocouple placed $3\frac{1}{4}$ " from the top inside the equilibrium cell. This corresponds to a distance of about $\frac{1}{8}$ " to $\frac{1}{4}$ " above the top liquid distributor plate. All thermocouples used were iron-constantan.

These thermocouples were calibrated against a Leeds and Northrup platinum resistance thermometer, Model 8163, Serial No. 1576919. The thermometer was calibrated by the National Bureau of Standards on May 7, 1964. The thermometer resistance was measured with a calibrated Leeds and Northrup Model 8069-B Muller bridge Serial No. 1550042.

A Leeds and Northrup Model 2430 galvanometer was used in conjunction with the Muller bridge. The thermocouples and platinum resistance thermometer were placed in a silicon oil reservoir in an aluminum block thermostat. The reference junction of the thermocouples is inserted in an ice bath in a Dewar flask.

The calibrations were carried out at approximately 150 and 250°F. The resistance of the thermometer was read on the Muller bridge while the emf of the thermocouples was simultaneously determined on the potentiometer to ± 0.001 mv.

The various thermocouples checked to within ± 0.0002 mv. with each other which is a deviation less than 0.1°F . Since the temperature in this investigation was measured to the nearest 0.1°F ., the same calibration equation was used for all thermocouples based on their average readings. A straight line relationship was fitted to the calibration data of $^\circ\text{F}$. versus mv. at both temperatures. The resulting expressions are presented below.

At 150°F .

$$T^\circ\text{F.} = 149.0 + 27.0 (\text{mv} - 3.390) \quad (\text{A-1})$$

At 250°F .

$$T^\circ\text{F.} = 248.0 + 31.3 (\text{mv} - 6.388) \quad (\text{A-2})$$

Pressure Calibration

The majority of pressure measurements (below 3000

psia) were made using a 0-3000 psi Heise gauge. The readings were made to the nearest 1 psia with the gauge having 2 psi division. The Heise gauge was checked with the Michels pressure balance and was in agreement to the nearest 1 psi.

The Michels pressure balance and measuring cylinders used in this investigation were factory calibrated to an accuracy of one part in 10,000. A review of this calibration and a later accuracy check is given by Stuckey (65). The calibrated accuracy of the pressure balance is considerably higher than that required. However, the accuracy of the Michels pressure balance measurement is limited by the accuracy of the oil and mercury head difference measurement in the gas compressor. The gas compressor level indicator was calibrated as a function of the mercury height in the compressor. The calibration was first performed by Thompson (67) and reported in his thesis. However, a new calibration was required since the equipment was since moved.

The gas compressor calibration was performed with the apparatus shown in Figure 17. A manometer was connected to the pressure bench to indicate the mercury position inside the gas compressor. The upper compartment of the gas compressor and one leg of the manometer were left open to the atmosphere. The pressure bench was used to pump the oil into the lower compartment of the gas compressor. The mercury levels in the manometer were read using a

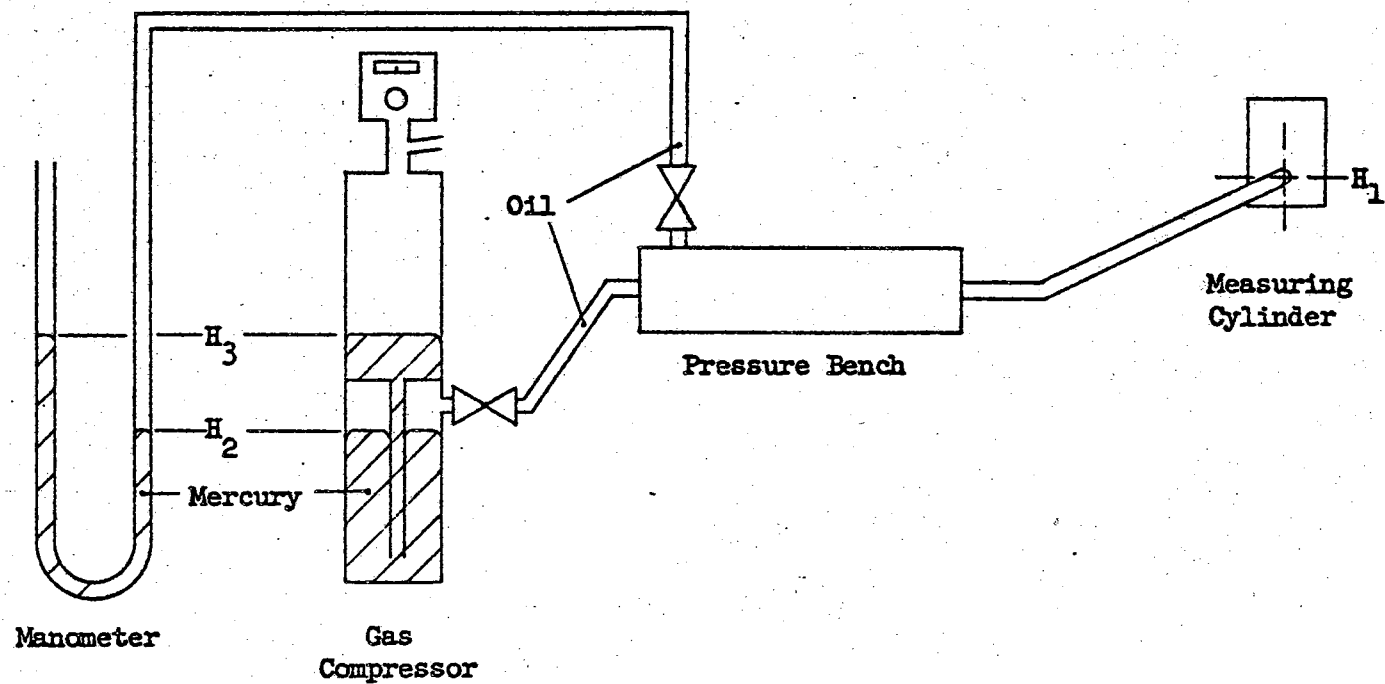


Figure 17. Gas Compressor Level Calibration Apparatus

cathetometer for maximum accuracy. The difference between the pressure at the pressure balance and the surface of the mercury in the gas compressor is seen from Figure 17 to be

$$\Delta P = (H_3 - H_2) \rho_{Hg} - (H_1 - H_2) \rho_{oil} \quad (A-3)$$

where

H = height of interface

ρ_{oil} = density of oil, 0.875 g/cm³

ρ_{Hg} = density of mercury, 13.530g/cm³ at 25.5°C.

Table XII gives the experimental data and the calculated differential pressure.

A plot of P versus the gas compressor level indicator reading indicates a smooth line relationship. A least squares curvefit was performed on this data giving the following as the best relationship.

$$\begin{aligned} \Delta P = & 0.000001902440 \times R^3 - 0.0002795422 \times R^2 \\ & + 0.1141903 \times R + 1.47255 \end{aligned} \quad (A-4)$$

where

ΔP = pressure differential in psi

R = gas compressor level indicator reading.

This equation gives the mean sum of squares of 0.0468524 for the deviations. This represents a mean deviation of about 0.216 psi. Thus, the Michels balance pressure

TABLE XII
EXPERIMENTAL DATA FOR CALIBRATION
OF GAS COMPRESSOR LEVEL

Room Temp

Gas Compressor Level Indicator Reading	Manometer Height in cm.		Calculated ΔP psi
	Low Side	High Side	
36.4	7.405	39.150	5.3098
31.0	8.825	37.660	4.7676
22.8	10.760	35.845	4.0702
25.4	10.180	36.325	4.2669
32.0	8.485	38.105	4.9144
39.2	6.490	40.010	5.6399
44.4	5.110	41.495	6.1740
49.6	3.580	42.965	6.7321
55.6	2.055	44.490	7.3000
59.8	0.755	45.665	7.7600
72.4	39.620	88.625	9.0314
79.4	37.765	90.625	9.7500
87.1	35.460	92.745	10.5727
95.8	33.020	95.375	11.5178
102.6	30.985	97.180	12.2313
109.4	28.600	99.860	13.1761
106.7	29.390	98.825	12.8348
102.3	31.305	97.050	12.1487
92.8	33.680	94.505	11.2316
80.0	37.695	90.575	9.7530
67.9	40.850	87.115	8.5195
60.4	43.110	85.125	7.7300
47.7	46.550	81.660	6.4443
37.5	49.290	78.920	5.4241
25.6	52.525	75.705	4.2233
24.0	52.870	75.425	4.1074
30.2	51.185	77.000	4.7136

Centerline of measuring cylinder oil outlet, 71.525 cm.

readings obtained for the system should be of about the same accuracy as those obtained with the Heise pressure gauge.

APPENDIX B

CHROMATOGRAPH CALIBRATION

The compositions of the vapor and liquid phase samples were analyzed using an F and M Model 810 gas chromatograph. A description of the analytical equipment is given in Chapter VI.

The chromatograph was calibrated using known composition liquid and gas mixtures. Ternary liquid mixtures of n-pentane, n-hexane, and the heavy component were made at four or five different compositions. The heavy components used were n-decane, decahydronaphthalene, and 1 methyl-naphthalene.

These mixtures were prepared in a narrow neck 35 cc. polyethylene bottle. The components were introduced into the bottle in the order of increasing volatility with a glass syringe. This minimized the possibility of loss due to evaporation. The container was weighed on a Metler balance after each addition. The sample bottle was frozen in a block of ice and stored in a freezer.

The analysis was performed on an $0.8\mu\text{l}$ sample injected into the chromatograph. The results are reported in Table XIII as arear ratios of the chromatograph analysis and weight ratios of the different components.

TABLE XIII
CHROMATOGRAPH CALIBRATION DATA

Component Ratio	Flame	
	Ionization Weight Ratio	Results Area Ratio
C_2/C_1	7.4207	8.3244
	1.9016	2.2094
	1.2180	1.4734
	0.4816	0.5322
	0.3746	0.4293
C_3/C_1	4.1932	4.1040
	2.7628	2.8041
	1.8710	1.9549
	0.3170	0.3636
C_5/C_1	3.3234	5.4684
	1.7429	3.0356
	0.8413	1.5015
	0.5032	0.9987
C_6/C_5	1.5529	1.5721
	2.2658	2.2426
	1.1384	1.1437
	0.5296	0.5374
n-Decane/ C_5	16.5517	19.1376
	25.6004	26.6757
	12.0697	12.6856
	5.7338	6.3065
Decahydronaphthalene/ C_5	16.2576	17.8957
	9.8981	11.1180
	14.7575	16.1937
	4.3414	5.6344
1-methylnaphthalene/ C_5	4.9333	5.9936
	15.1648	17.7055
	18.3294	20.9428
	15.3825	17.3325
	10.0827	11.5531

Binary mixtures of the light components were prepared on a volumetric basis. A schematic of this apparatus is illustrated in Figure 18. The apparatus was constructed of glass with spring loaded, Teflon stopcocks. The individual pieces of glass tubing were connected with short pieces of polyethylene tubing. The measuring bomb had a 200 cc volume.

The experimental procedure was to evacuate the entire system and then close off the vacuum pump and sample bomb. Next, the entire system was filled with a gas, say propane, and allowed to achieve thermal equilibrium. The mercury level in the measuring bomb was then raised to its mark, the pressure of the system read on the TI quartz Bourdon tube pressure gauge and the measuring bomb isolated from the rest of the system. The stopcock connecting sample and measuring bombs was then opened and the gas forced into the sample bomb by raising the mercury level. The sample bomb was then sealed off and the mercury drained into its reservoir. Then, the entire system was evacuated and the same process repeated with methane. Complete mixing of the gases was ensured by moving the gas mixture back and forth between the sample and measuring bombs by means of the mercury piston. This procedure was repeated three times in quick succession.

Extra care was exercised in preparing the methane-n-pentane mixtures since the constant temperature air bath was maintained at only 100°F. The vapor pressure of

n-pentane is low at this temperature and it was necessary to insure that the vapor pressure was never exceeded or condensation would occur.

Three to five mixtures of each binary were prepared and analyzed within eight hours. Before withdrawing a sample, the bomb and syringe were heated well above 100°F. to vaporize any components that may have condensed. In the case of the methane-n-pentane mixture, some air was always left in the syringe to provide a dilution volume and, thus, an additional safeguard against condensation. The weight and area percentages are reported in Figure 13

Graphical examination of the results indicated a definite linear relationship between area and weight ratio for a specific component ratio. The following expression was used to fit the calibration results.

$$\text{WEIGHT RATIO } (C_1/C_2) = S_{12} \times \text{Area Ratio } (C_1/C_2). \quad (\text{B-1})$$

S_{12} is the slope of the calibration curve obtained from this experimental data. Values of S_{12} are presented in Table XIV for the various substances used. The reference substance was methane for all gaseous and n-pentane for all liquid samples.

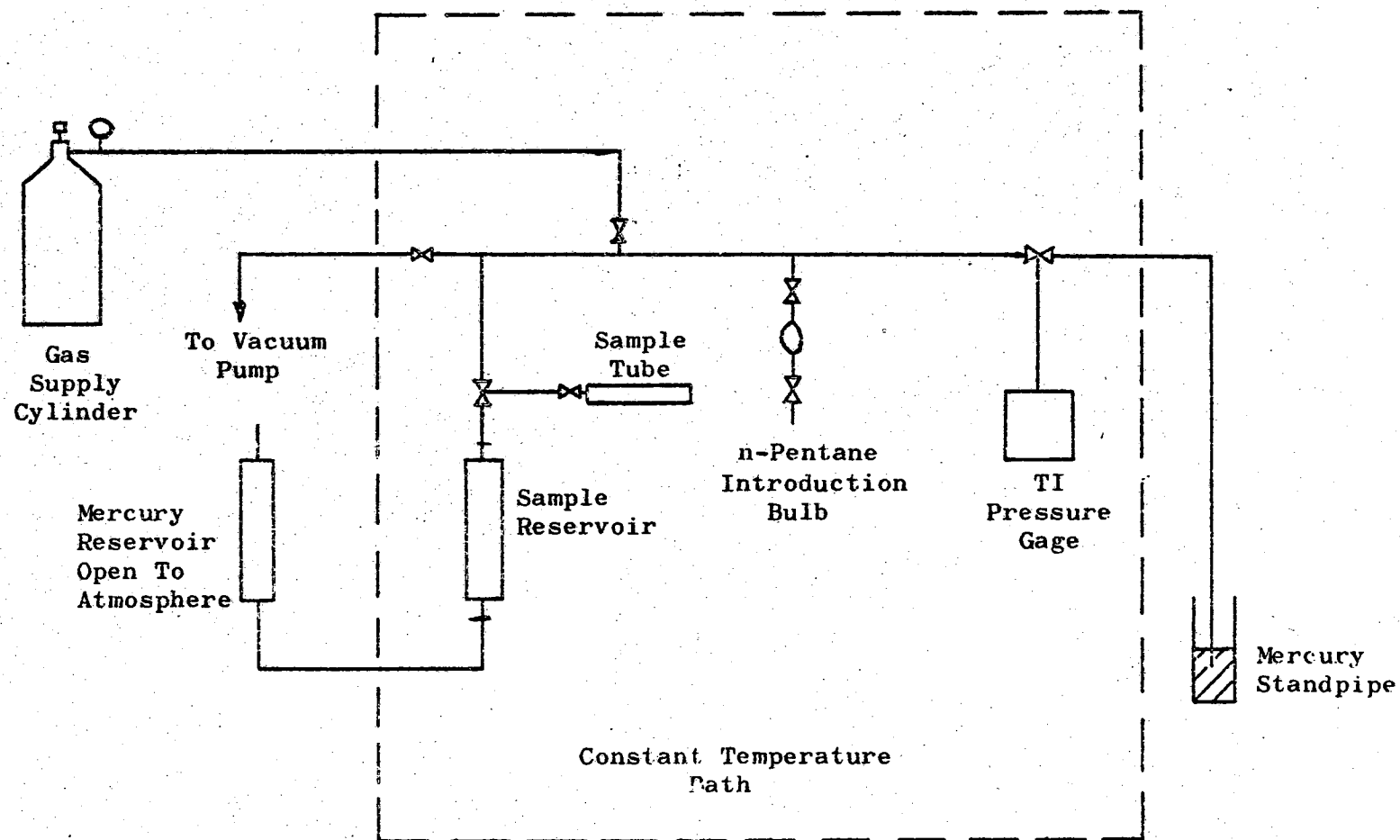


Figure 18. Apparatus for Preparation of Gaseous Calibration Samples

TABLE XIV
CHROMATOGRAPH CALIBRATION CONSTANTS

Ratio C_i/C_1	Slope, S_{ij} for Flame Ionization Detector
C_2/C_1	0.8877
C_3/C_1	1.0024
C_5/C_1	0.5942
C_6/C_5	1.0013
n-Decane/ C_5	0.9299
Decahydronaphthalene/ C_5	0.9014
1-methylnaphthalene/ C_5	0.8716

APPENDIX C

SAMPLE CALCULATIONS OF EXPERIMENTAL DATA

A sample calculation of the temperature and composition is presented in this appendix. The actual calculations of the experimental data were made using an IBM 1620 digital computer. The data used in this sample calculation are those from Run B156.

Temperature

The equilibrium cell temperature was determined using an iron-constantan thermocouple with a potentiometer. The thermocouple calibration is presented in Appendix A. The emf reading during the run was 3.440. Inserting this value in Equation A-1.

$$T^{\circ}\text{F} = 149.0 + 27.0 (3.440 - 3.390) = 150.3^{\circ}\text{F}.$$

This corresponds to a temperature of 150.3°F. This temperature is the value at the time of the sampling.

Pressure

The pressure for the run was taken directly from the Heise gauge reading at 2000 psia where it was maintained. For pressures of 3000 psia and above, the procedure

illustrated by A. N. Stuckey (67) was used to determine the pressure during the run.

Composition

The compositions of the vapor and liquid phases were determined by chromatographic analysis. The weight ratios for the different components were calculated using Equation B-1 with n-pentane as the reference substance. Using the data presented in Table XVIII, one has the following weight ratios for the liquid phase.

$$\begin{aligned}
 \text{weight} \quad \frac{C_1}{C_5} &= \frac{23.4 \times 32 \times 1.68294}{119.1 \times 8.0} = 1.3226 \\
 \text{weight} \quad \frac{C_2}{C_5} &= \frac{50.7 \times 4.0 \times 1.1265}{119.1 \times 8.0} = 0.2398 \\
 \text{weight} \quad \frac{C_3}{C_5} &= \frac{120.4 \times 2.0 \times 0.9976}{119.1 \times 8.0} = 0.2521 \\
 \text{weight} \quad \frac{C_4}{C_5} &= \frac{119.1 \times 8.0 \times 1.0}{119.1 \times 8} = 1.0000 \\
 \text{weight} \quad \frac{C_6}{C_5} &= \frac{148.0 \times 8.0 \times 1.0013}{119.1 \times 8} = 1.2443 \\
 \text{weight} \quad \frac{C_{10}}{C_5} &= \frac{796.5 \times 8.0 \times 0.9299}{119.1 \times 8} = 6.2189 \\
 &\quad \text{Total} = 10.2776
 \end{aligned}$$

The weight fractions X_{wi} of the individual components can be obtained by dividing the individual weight ratios by their total.

The mole fraction of the individual components is given by the following equation:

$$X_i = \frac{X_{w1}/M_{w1}}{\sum_j \left(X_{wj}/M_{wj} \right)} \quad (C-1)$$

The X_{wj}/M_{wj} quantities are given as follows:

$$C_1 = \frac{1.3226}{10.2776 \times 16.042} = 0.0080210$$

$$C_2 = \frac{0.2398}{10.2776 \times 30.068} = 0.0007759$$

$$C_3 = \frac{0.2521}{10.2776 \times 44.094} = 0.0005563$$

$$C_5 = \frac{1.0000}{10.2776 \times 72.146} = 0.0013486$$

$$C_6 = \frac{1.2443}{10.2776 \times 86.17} = 0.0013486$$

$$C_{10} = \frac{6.2189}{10.2776 \times 142.28} = 0.0042528$$

$$\text{Total} = 0.0163606$$

Thus, the mole fractions for each of the components is as follows:

$$x_1 = \frac{0.0080210}{0.0163606} = 0.0474$$

$$x_2 = \frac{0.0007759}{0.0163606} = 0.0474$$

$$x_3 = \frac{0.0005563}{0.0163606} = 0.0340$$

$$x_5 = \frac{0.0013486}{0.0163606} = 0.0824$$

$$x_6 = \frac{0.0013486}{0.0163606} = 0.0859$$

$$x_{10} = \frac{0.0042528}{0.0163606} = 0.2599$$

An identical calculation is performed for the vapor phase. Without showing each step, the vapor phase results are as follows:

$$\begin{array}{lll} y_1 = 0.9201 & y_2 = 0.0413 & y_3 = 0.0156 \\ y_5 = 0.0120 & y_8 = 0.0071 & y_{10} = 0.0038 \end{array}$$

The K-values are calculated as shown in Equation

C-2:

$$K_1 = \frac{y_1}{x_1}. \quad (C-2)$$

The results for this run are:

$$\begin{array}{ll} K_1 = \frac{0.9292}{0.4904} = 1.8767 & K_2 = \frac{0.0413}{0.0474} = 0.8711 \\ K_3 = \frac{0.0156}{0.0340} = 0.4589 & K_5 = \frac{0.0120}{0.0824} = 0.1451 \\ K_8 = \frac{0.0071}{0.0859} = 0.0829 & K_{10} = \frac{0.0038}{0.2599} = 0.0146 \end{array}$$

This example illustrates the calculation steps involved in converting the raw experimental data to the desired P-T-x-y information.

APPENDIX D

RAW EXPERIMENTAL DATA

The raw experimental data used to determine the system pressures, temperatures and phase compositions are presented. Tables XV through XVII present the individual run temperature and pressure data at equilibrium conditions. The Heise gauge and the pressure balance data were used to determine the exact system pressures. Tables XVIII through XXIII present the direct chromatograph data (peak areas and attenuations) used to calculate the phase compositions.

TABLE XV

RAW EXPERIMENTAL DATA: n-DECANE AS
HEAVY COMPONENT

Run No.	Cell Temp. °F	Total Wt. On Balance, kg.		Heise Gauge psia	Oil Level cm.	Gas Compr. Level	Bal. Temp. °F
		Weights lbs.	Wt. grams				
B151	150.5	-----	-----	100.	----	----	----
B175	150.0	-----	-----	200.	----	----	----
B171	150.0	-----	-----	400.	----	----	----
B176	150.0	-----	-----	500.	----	----	----
B178	149.9	-----	-----	1000.	----	----	----
B163	150.1	-----	-----	1250.	----	----	----
B155	149.7	-----	-----	1500.	----	----	----
B156	150.3	-----	-----	2000.	----	----	----
B157	149.9	-----	-----	2500.	----	----	----
B180	149.6	1-2, 12-15	500.	-----	21.6	76.3	80.6
B181	149.9	1-3, 10, 12-15	20.	-----	21.7	93.7	76.0
B251	249.0	-----	-----	100.	----	----	----
B252	248.7	-----	-----	200.	----	----	----
B258	250.3	-----	-----	300.	----	----	----
B253	250.3	-----	-----	500.	----	----	----
B259	249.9	-----	-----	702.	----	----	----
B260	250.0	-----	-----	1000.	----	----	----
B263	250.2	-----	-----	1500.	----	----	----
B264	250.0	-----	-----	2000.	----	----	----
B265	249.6	-----	-----	2500.	----	----	----
B266	249.5	1,2, 12-15	561.0	-----	19.7	88.4	77.0

Measuring cylinder No. 5 used with pressure balance.

TABLE XVI

RAW EXPERIMENTAL DATA: DECAHYDRONAPHTHALENE
AS HEAVY COMPONENT

Run No.	Cell Temp. °F	Total Wt. On Balance, kg.		Heise Gauge psia	Oil Level cm.	Gas Compr. Level	Bal. Temp. °F
		Weights lbs.	Wt. grams				
D166	150.2	-----	-----	100.	----	----	----
D167	150.2	-----	-----	100.	----	----	----
D168	150.5	-----	-----	200.	----	----	----
D169	150.2	-----	-----	200.	----	----	----
D170	150.5	-----	-----	300.	----	----	----
D171	150.2	-----	-----	300.	----	----	----
D172	150.5	-----	-----	700.	----	----	----
D173	150.1	-----	-----	700.	----	----	----
D175	150.1	-----	-----	1000.	----	----	----
D176	150.0	-----	-----	1500.	----	----	----
D177	150.3	-----	-----	2000.	----	----	----
D178	150.1	-----	-----	2500.	----	----	----
D179	150.1	-----	-----	3000.	----	----	----
D163	150.4	1-3, 10, 12-15	0.	----	29.3	84.7	70.0
D164	150.4	11-4, 9, 12-14	375.	----	29.0	86.4	69.5
D165	150.0	1-5, 9-10, 12-14	0.	----	28.8	87.6	75.5
D251	249.4	-----	-----	100.	----	----	----
D252	250.4	-----	-----	200.	----	----	----
D253	250.7	-----	-----	300.	----	----	----
D254	249.9	-----	-----	500.	----	----	----
D255	250.2	-----	-----	700.	----	----	----
D256	250.4	-----	-----	1000.	----	----	----
D257	250.6	-----	-----	1500.	----	----	----

TABLE XVI (Continued)

Run No.	Cell Temp. °F	Total Wt. On Balance, kg.		Heise Gauge psia	Oil Level cm.	Gas Compr. Level	Bal. Temp. °F
		Weights lbs.	Wt. grams				
D258	250.7	-----	-----	2000.	----	----	----
D259	250.5	-----	-----	2500.	----	----	----
D260	249.9	1-2, 12-15	500.	----	26.7	74.7	71.5
D261	250.0	1-2, 9-10, 12-15	250.	----	26.4	82.2	69.5
D263	249.8	1-4, 9, 12-14	740.	----	26.0	88.9	72.0
Measuring cylinder No. 5 used with pressure balance.							

TABLE XVII

RAW EXPERIMENTAL DATA: 1-METHYLNAPHTHALENE
AS HEAVY COMPONENT

Run No.	Cell Temp. °F	Total Wt. On Balance, kg.		Heise Gauge psia	Oil Level cm.	Gas Compr. Level	Bal. Temp. °F
		Weights lbs.	Wt. grams				
M151	149.9	-----	-----	100.	----	----	----
M152	149.9	-----	-----	200.	----	----	----
M153	150.3	-----	-----	300.	----	----	----
M154	150.0	-----	-----	500.	----	----	----
M156	149.7	-----	-----	1000.	----	----	----
M157	149.9	-----	-----	1500.	----	----	----
M158	149.7	-----	-----	2000.	----	----	----
M159	149.7	-----	-----	2500.	----	----	----
M160	150.1	1-2, 12-15	555.	----	22.9	87.1	75.0
M161	150.1	1-2, 9-10, 12-15	285.	----	22.8	93.7	76.0
M164	150.4	1-5, 9-10, 12-14	0	----	22.1	94.4	74.8
M165	149.9	1-6, 9-13	450.	----	22.0	98.1	80.0
M166	149.8	1-8, 12	930.	----	22.8	100.5	82.0
M251	250.2	-----	-----	102.	----	----	----
M252	250.1	-----	-----	200.	----	----	----
M253	250.3	-----	-----	300.	----	----	----
M254	250.0	-----	-----	500.	----	----	----
M255	250.3	-----	-----	700.	----	----	----
M256	250.4	-----	-----	1000.	----	----	----
M257	249.5	-----	-----	1500.	----	----	----
M258	250.1	-----	-----	2000.	----	----	----
M259	250.3	-----	-----	2500.	----	----	----
M260	250.2	1-2, 12-15	555.	----	22.1	85.2	74.0

TABLE XVII (Continued)

Run No.	Cell Temp. °F	Total On Balance, kg.		Heise Gauge psia	Oil Level cm.	Gas Compr. Level	Bal. Temp. °F
		Weights lbs.	Wt. grams				
M261	250.1	1-2, 9-10, 12-15	280.	----	22.1	91.1	74.0
M262	250.8	1-3, 10, 12-15	20.	----	22.3	90.7	76.8
M263	250.6	1-4, 9, 12-14	500.	----	22.1	96.0	77.0
M264	250.2	1-5, 9-10, 12-14	0	----	22.0	101.1	79.6
M266	250.2	1-8, 12	915.	----	21.8	95.4	74.5

Measuring cylinder No. 5 used with pressure balance.

TABLE XVIII

RAW EXPERIMENTAL CHROMATOGRAPHIC COMPOSITION DATA WITH n-DECANE AS HEAVY COMPONENT AT 150°F

C ₁		C ₂		C ₃		C ₄		C ₅		C ₆		C ₁₀		Phase	Run No.
Area	At.	Area	At.	Area	At.	Area	At.	Area	At.	Area	At.	Area	At.		
178.	1.	56.	1.	68.	1.	1511.	8.	1785.	8.	1129.	64.	L	B151		
80.	32.	89.	2.	84.	1.	1560.	1.	713.	1.	188.	1.	V	B151		
582.	1.	192.	1.	267.	1.	1754.	8.	2444.	8.	15886.	8.	L	B175		
229.	16.	297.	1.	137.	1.	1154.	1.	588.	1.	153.	1.	V	B175		
25.9	4.	77.7	1.	127.8	2.	77.3	16.	203.9	8.	1374.8	8.	L	B171		
82.7	8.	132.9	1.	80.1	2.	61.3	2.	71.4	1.	22.8	1.	V	B171		
242.	4.	388.	1.	485.	1.	537.	16.	1480.	8.	8815.	8.	L	B176		
238.	32.	788.	1.	441.	1.	694.	2.	767.	1.	242.	1.	V	B176		
32.7	8.	74.5	1.	70.5	1.	103.2	8.	141.6	8.	929.9	8.	L	B178		
37.6	64.	118.7	2.	96.2	1.	116.5	2.	153.6	1.	136.5	1.	V	B178		
33.9	16.	72.8	2.	174.1	1.	91.0	16.	224.2	8.	1285.5	8.	L	B163		
49.7	64.	142.5	2.	78.1	2.	166.6	2.	104.0	2.	160.5	1.	V	B163		
48.0	16.	125.3	2.	164.4	2.	101.2	16.	129.4	16.	1634.0	8.	L	B155		
33.3	128.	119.1	4.	77.3	4.	103.5	4.	143.8	2.	159.2	1.	V	B155		
23.4	32.	50.7	4.	120.4	2.	119.1	8.	148.0	8.	796.5	8.	L	B156		
48.0	128.	193.1	4.	120.8	4.	75.6	8.	214.8	2.	407.4	1.	V	B156		
78.0	16.	83.5	4.	98.7	4.	72.5	16.	187.1	8.	1112.7	8.	L	B157		
49.4	128.	110.6	8.	164.8	4.	99.4	8.	394.8	2.	1407.8	1.	V	B157		
57.7	16.	183.6	1.	101.1	2.	77.3	8.	223.0	4.	1572.1	4.	L	B180		
69.6	64.	150.4	4.	109.8	4.	88.0	8.	201.5	4.	485.6	8.	V	B180		
258.	32.	815.	2.	1702.	1.	1886.	2.	1293.	4.	9145.	4.	L	B181		
817.	64.	2738.	4.	1381.	8.	3312.	8.	4493.	8.	14403.	16.	V	B181		

TABLE XIX

RAW EXPERIMENTAL CHROMATOGRAPHIC COMPOSITION DATA WITH n-DECANE AS HEAVY COMPONENT AT 250°F

C ₁		C ₂		C ₃		C ₄		C ₅		C ₆		Phase	Run No.
Area	At.	Area	At.	Area	At.	Area	At.	Area	At.	Area	At.		
16.5	1.	4.3	1.	6.2	1.	149.8	8.	188.2	8.	1183.7	8.	L	B251
53.6	2.	11.6	1.	7.5	1.	285.1	1.	195.2	1.	109.9	1.	V	B251
35.5	1.	9.5	1.	14.0	1.	119.7	8.	146.2	8.	947.0	8.	L	B252
78.9	4.	30.6	1.	20.0	1.	84.3	4.	213.4	1.	143.4	1.	V	B252
60.2	1.	20.2	1.	27.2	1.	139.2	8.	184.0	8.	1105.6	8.	L	B258
45.8	8.	46.1	1.	29.7	1.	74.4	4.	201.0	1.	97.3	1.	V	B258
108.7	1.	28.7	1.	39.9	1.	128.8	8.	333.5	4.	1104.2	8.	L	B253
33.0	16.	60.6	1.	41.3	1.	38.0	8.	201.7	1.	101.2	1.	V	B253
56.7	2.	34.6	1.	45.9	1.	103.6	8.	137.3	8.	805.7	8.	L	B259
107.4	8.	107.0	1.	64.3	1.	91.7	4.	129.7	2.	148.0	1.	V	B259
43.6	4.	52.5	1.	67.5	1.	193.6	4.	260.6	4.	1537.0	4.	L	B260
86.1	16.	168.1	1.	120.1	1.	99.9	4.	299.0	1.	264.8	1.	V	B260
97.3	4.	99.6	1.	115.0	1.	127.1	8.	165.0	8.	966.3	8.	L	B263
64.6	32.	128.5	2.	91.3	2.	151.8	4.	246.0	2.	731.5	1.	V	B263
546.	8.	1016.	1.	1154.	1.	949.	8.	2375.	4.	14296.	4.	L	B264
835.	32.	1824.	2.	1399.	2.	1078.	8.	1853.	4.	13041.	1.	V	B264
883.	8.	1416.	1.	1584.	1.	1068.	8.	2674.	4.	17070.	4.	L	B265
1021.	32.	2282.	2.	1799.	2.	1279.	8.	2590.	4.	18399.	2.	V	B265
53.9	16.	103.8	1.	93.8	1.	60.7	4.	61.7	4.	133.7	4.	L	B266
136.8	32.	144.3	4.	127.6	4.	80.4	16.	339.0	4.	752.0	4.	V	B266

TABLE XX

RAW EXPERIMENTAL CHROMATOGRAPHIC COMPOSITION DATA WITH DECAHYDRONAPHTHALENE AS HEAVY COMPONENT AT 150°F

C ₁		C ₂		C ₃		C ₄		C ₅		C ₆		C ₇		Phase	Run No.
Area	At.	Area	At.	Area	At.	Area	At.	Area	At.	Area	At.	Area	At.		
57.8	1.	15.8	1.	17.8	1.	145.0	16.	348.3	8.	2014.9	8.	L	D166		
57.3	8.	31.7	1.	11.8	1.	111.8	2.	113.7	1.	71.7	1.	V	D166		
46.8	1.	11.1	1.	14.7	1.	103.2	16.	264.0	8.	1549.6	8.	L	D167		
62.2	8.	29.4	1.	12.9	1.	115.9	2.	116.4	1.	63.7	1.	V	D167		
52.4	2.	29.5	1.	32.8	1.	103.6	16.	258.0	8.	1554.7	8.	L	D168		
60.6	16.	34.9	2.	12.6	2.	112.2	2.	122.3	1.	137.7	1.	V	D168		
62.3	2.	39.6	1.	38.3	1.	131.9	16.	334.9	8.	2026.1	8.	L	D169		
64.2	16.	68.9	1.	29.8	1.	113.7	2.	113.8	1.	90.2	1.	V	D169		
37.7	4.	47.3	1.	50.1	1.	97.2	16.	247.3	8.	1480.5	8.	L	D170		
51.8	32.	114.4	1.	51.1	1.	120.5	2.	126.5	1.	72.2	2.	V	D170		
48.3	4.	60.8	1.	64.9	1.	126.4	16.	325.4	8.	1945.8	8.	L	D171		
57.0	32.	124.7	1.	59.7	1.	133.3	2.	141.4	1.	137.1	1.	V	D171		
46.1	8.	56.6	2.	60.7	2.	92.0	16.	236.4	8.	1434.0	8.	L	D172		
62.9	64.	335.8	1.	166.5	1.	105.4	4.	226.7	1.	238.4	1.	V	D172		
42.8	8.	112.7	1.	117.2	1.	89.0	16.	227.3	8.	1382.2	8.	L	D173		
54.8	64.	148.5	2.	143.0	1.	83.2	4.	207.2	1.	167.4	1.	V	D173		
62.6	8.	141.5	1.	152.6	1.	193.7	8.	239.1	8.	1284.4	8.	L	D175		
107.8	32.	8.2	32.	164.4	1.	86.1	4.	50.3	4.	130.1	1.	V	D175		
67.7	8.	149.1	1.	156.1	1.	132.0	8.	164.8	8.	1721.0	4.	L	D176		
112.1	128.	350.1	4.	186.3	4.	147.9	8.	193.0	4.	258.5	2.	V	D176		
60.6	16.	125.0	2.	129.1	2.	173.6	8.	214.2	8.	1195.3	8.	L	D177		
57.1	128.	200.9	4.	107.1	4.	165.1	4.	240.3	2.	294.9	1.	V	D177		

TABLE XX (Continued)

C_1		C_2		C_3		C_4		C_5		C_6		C_7		Phase	Run No.
Area	At.	Area	At.	Area	At.	Area	At.	Area	At.	Area	At.	Area	At.		
55.5	16.	213.1	1.	213.9	1.	110.9	8.	285.2	4.	1560.0	4.	L	D178		
93.0	256.	334.6	8.	208.4	8.	163.5	16.	301.0	8.	1820.0	2.	V	D178		
40.4	32.	156.2	2.	155.6	2.	148.8	8.	187.6	8.	2191.1	4.	L	D179		
81.6	128.	159.8	8.	208.7	4.	194.6	8.	201.9	8.	812.9	4.	V	D179		
64.3	16.	207.9	1.	119.6	2.	244.0	4.	159.8	8.	1043.6	8.	L	D163		
137.5	64.	256.5	4.	131.0	8.	145.0	16.	318.8	8.	1618.5	4.	V	D163		
53.8	16.	158.8	1.	92.0	2.	148.1	4.	193.8	4.	1130.5	4.	L	D164		
112.6	64.	260.0	4.	143.8	8.	177.6	16.	209.0	16.	747.1	16.	V	D164		
111.2	32.	145.0	4.	122.0	4.	136.6	8.	315.0	4.	1930.2	4.	L	D165		
232.9	64.	160.0	16.	136.5	16.	145.9	32.	356.2	16.	1875.5	16.	V	D165		

TABLE XXI

RAW EXPERIMENTAL CHROMATOGRAPHIC COMPOSITION DATA WITH DECAHYDRONAPHTHALENE AS HEAVY COMPONENT AT 250°F

C_1		C_2		C_3		C_4		C_5		C_6		C_{10}		Phase	Run No.
Area	At.	Area	At.	Area	At.	Area	At.	Area	At.	Area	At.	Area	At.		
37.5	1.	6.0	2.	5.6	2.	117.6	16.	320.5	8.	1908.8	8.	L	D251		
240.0	2.	47.9	1.	19.8	1.	152.7	8.	200.0	4.	215.5	1.	V	D251		
71.9	1.	12.7	1.	11.2	1.	92.0	16.	247.7	8.	1421.8	8.	L	D252		
87.8	8.	20.8	2.	8.2	2.	64.1	8.	170.6	2.	138.3	1.	V	D252		
70.3	2.	24.8	1.	21.9	1.	116.1	16.	316.0	8.	1850.0	8.	L	D253		
90.4	32.	191.0	1.	74.1	1.	40.1	32.	220.2	4.	293.6	1.	V	D253		
53.3	4.	39.6	1.	34.7	1.	185.0	8.	252.3	8.	1459.3	8.	L	D254		
61.2	32.	136.5	1.	59.1	1.	73.4	8.	202.8	2.	191.1	1.	V	D254		
25.1	8.	31.3	1.	25.8	1.	95.5	8.	260.1	4.	1564.9	4.	L	D255		
54.2	128.	269.3	2.	113.1	2.	97.3	16.	279.6	4.	437.0	1.	V	D255		
54.2	8.	79.0	1.	64.0	1.	170.1	8.	231.3	8.	1365.5	8.	L	D256		
59.3	64.	294.4	1.	136.0	1.	103.7	8.	302.8	2.	383.2	1.	V	D256		
80.6	8.	111.9	1.	85.4	1.	164.1	8.	222.6	8.	1316.4	8.	L	D257		
88.0	64.	219.6	2.	91.3	2.	109.9	8.	348.9	2.	383.0	1.	V	D257		
65.6	16.	182.0	1.	151.7	1.	214.0	8.	289.6	8.	1802.3	8.	L	D258		
74.6	256.	206.9	8.	183.9	4.	87.2	32.	143.0	16.	1607.0	1.	V	D258		
37.8	128.	222.4	4.	182.3	4.	199.9	32.	272.6	32.	1710.8	32.	L	D259		
58.8	32.	159.5	1.	79.0	1.	131.2	2.	234.8	1.	218.2	1.	V	D259		
25.3	32.	134.9	1.	108.8	1.	79.9	8.	206.4	4.	1266.2	4.	L	D260		
108.6	256.	168.3	16.	184.4	8.	141.8	32.	280.1	16.	1985.4	4.	V	D260		

TABLE XXI (Continued)

C_1		C_2		C_3		C_5		C_8		C_{10}		Phase	Run No.
Area	At.	Area	At.	Area	At.	Area	At.	Area	At.	Area	At.		
49.0	32.	255.0	1.	206.7	1.	128.8	8.	172.8	8.	1077.3	8.	L	D261
94.2	128.	153.0	8.	186.6	4.	131.6	16.	274.9	8.	927.0	4.	V	D261
62.4	32.	149.1	2.	125.5	2.	114.5	8.	152.9	8.	1876.8	4.	L	D263
39.0	256.	175.0	8.	300.0	4.	145.5	32.	202.5	32.	1273.3	32.	V	D263

TABLE XXII

RAW EXPERIMENTAL CHROMATOGRAPHIC COMPOSITION DATA WITH 1-METHYLNAPHTHALENE AS HEAVY COMPONENT AT 150°F

C ₁		C ₂		C ₃		C ₄		C ₅		C ₆		C ₁₀		Phase	Run No.
Area	At.	Area	At.	Area	At.	Area	At.	Area	At.	Area	At.	Area	At.		
34.0	1.	8.7	1.	9.3	1.	282.9	8.	261.9	8.	734.5	16.	L	M151		
185.7	4.	71.3	1.	26.4	1.	159.8	4.	163.4	2.	36.5	1.	V	M151		
46.7	2.	27.0	1.	27.8	1.	168.3	16.	189.8	16.	2257.3	8.	L	M152		
68.4	32.	158.4	1.	59.8	1.	89.3	8.	182.4	2.	47.4	1.	V	M152		
56.9	2.	34.2	1.	33.0	1.	217.8	8.	260.0	8.	1534.1	8.	L	M153		
49.9	64.	252.0	1.	92.1	1.	94.4	8.	186.5	2.	60.4	1.	V	M153		
40.0	4.	41.7	1.	38.7	1.	187.4	8.	225.9	8.	1277.3	8.	L	M154		
80.0	64.	190.0	2.	131.0	1.	95.0	8.	198.3	2.	40.0	1.	V	M154		
76.7	4.	90.0	1.	85.1	1.	178.1	8.	220.0	8.	2728.6	4.	L	M156		
80.1	128.	219.5	4.	182.6	2.	68.0	16.	157.1	4.	36.9	1.	V	M156		
55.8	8.	116.9	1.	107.5	1.	166.5	8.	202.2	8.	2264.2	4.	L	M157		
58.2	256.	171.8	8.	151.4	4.	201.3	8.	252.9	4.	62.9	1.	V	M157		
52.4	16.	105.7	2.	216.0	1.	114.2	16.	284.5	8.	1963.7	8.	L	M158		
61.5	128.	198.8	4.	207.2	2.	130.5	8.	198.0	4.	233.0	1.	V	M158		
43.4	16.	171.2	1.	162.3	1.	138.8	8.	179.5	8.	2319.0	4.	L	M159		
95.8	256.	362.7	8.	192.8	8.	109.6	32.	177.7	16.	839.8	1.	V	M159		
71.3	16.	137.8	2.	130.9	2.	200.5	8.	257.2	8.	2050.0	8.	L	M160		
113.4	256.	216.0	16.	131.5	16.	147.4	32.	263.0	16.	1693.6	1.	V	M160		
55.1	16.	100.0	2.	93.2	2.	110.9	8.	288.4	4.	2265.1	4.	L	M161		
101.8	128.	196.2	8.	137.8	8.	160.9	16.	317.6	8.	1278.1	1.	V	M161		

TABLE XXII (Continued)

C_1		C_2		C_3		C_5		C_6		C_{10}		Phase	Run No.
Area	At.	Area	At.	Area	At.	Area	At.	Area	At.	Area	At.		
120.0	16.	180.0	2.	139.5	2.	74.6	8.	169.7	4.	634.4	4.	L	M164
68.7	256.	165.5	16.	229.1	8.	106.0	32.	237.5	16.	864.8	8.	V	M164
117.9	32.	140.0	4.	104.6	4.	195.1	4.	230.5	4.	4173.3	1.	L	M165
77.6	256.	165.4	16.	121.8	16.	217.4	16.	248.2	16.	1143.3	8.	V	M165
44.1	64.	102.4	4.	157.8	2.	134.8	4.	300.3	2.	3000.0	1.	L	M166
162.7	256.	205.8	32.	159.5	32.	131.9	64.	307.7	32.	1492.6	32.	V	M166

TABLE XXIII

RAW EXPERIMENTAL CHROMATOGRAPHIC COMPOSITION DATA WITH 1-METHYLNAPHTHALENE AS HEAVY COMPONENT AT 250°F

C ₁		C ₂		C ₃		C ₄		C ₅		C ₆		C ₁₀		Phase	Run No.
Area	At.	Area	At.	Area	At.	Area	At.	Area	At.	Area	At.	Area	At.		
13.2	1.	2.5	1.	2.5	1.	134.6	8.	150.8	8.	2278.4	4.	L	M251		
78.2	16.	77.0	1.	32.7	1.	296.3	8.	239.7	4.	145.7	1.	V	M251		
51.8	1.	11.0	1.	12.2	1.	94.7	16.	219.9	8.	1642.8	8.	L	M252		
12.9	32.	31.7	1.	17.1	1.	55.0	8.	131.1	2.	49.9	1.	V	M252		
58.1	1.	12.8	1.	13.1	1.	131.8	8.	152.4	8.	2328.9	4.	L	M253		
133.9	32.	340.3	1.	166.4	1.	43.7	64.	101.2	16.	220.6	1.	V	M253		
50.8	2.	21.5	1.	21.7	1.	127.8	8.	293.8	4.	2360.3	4.	L	M254		
59.5	64.	161.6	2.	72.3	2.	97.6	16.	239.9	4.	109.3	1.	V	M254		
52.6	4.	46.0	1.	42.9	1.	173.2	8.	197.5	8.	3107.1	4.	L	M255		
33.1	64.	176.3	1.	84.7	1.	83.6	8.	201.4	2.	46.8	1.	V	M255		
50.9	4.	46.3	1.	44.3	1.	123.0	8.	286.3	4.	2274.9	4.	L	M256		
60.4	128.	181.8	4.	181.3	2.	124.4	16.	321.8	4.	189.6	1.	V	M256		
51.8	8.	90.0	1.	85.6	1.	153.0	8.	190.4	8.	3176.7	4.	L	M257		
77.5	64.	227.6	2.	127.2	2.	132.3	8.	184.5	4.	186.3	1.	V	M257		
53.6	8.	84.7	1.	77.3	1.	112.4	8.	268.0	4.	2189.2	4.	L	M258		
59.1	256.	199.0	8.	107.5	8.	194.2	16.	290.0	8.	644.1	1.	V	M258		
61.8	8.	101.6	1.	93.1	1.	217.4	4.	258.2	4.	2196.1	4.	L	M259		
74.2	256.	258.1	8.	147.0	8.	246.4	16.	192.0	16.	1293.5	1.	V	M259		
53.4	16.	170.3	1.	159.2	1.	146.0	8.	175.8	8.	3016.7	4.	L	M260		
72.2	128.	126.0	8.	164.2	4.	131.8	16.	223.2	8.	1110.5	1.	V	M260		

TABLE XXIII (Continued)

C ₁		C ₂		C ₃		C ₅		C ₆		C ₁₀		Phase	Run No.
Area	At.	Area	At.	Area	At.	Area	At.	Area	At.	Area	At.		
43.7	16.	138.9	1.	125.6	1.	194.5	4.	233.1	4.	2122.4	4.	L	M261
100.2	256.	189.2	16.	29.0	64.0	176.8	32.	305.0	16.	2550.4	2.	V	M261
49.7	16.	154.5	1.	138.9	1.	181.4	4.	218.8	4.	2006.0	4.	L	M262
64.9	256.	132.0	16.	176.1	8.	114.3	32.	211.0	16.	1053.0	4.	V	M262
42.0	32.	125.1	2.	113.5	2.	117.4	8.	280.8	4.	2665.0	4.	L	M263
53.6	256.	213.0	8.	164.4	8.	200.7	16.	199.0	16.	1201.1	4.	V	M263
72.9	16.	213.0	1.	87.9	2.	75.0	8.	178.0	4.	1760.6	4.	L	M264
129.1	256.	290.0	16.	218.2	16.	126.7	64.	262.8	32.	1202.4	16.	V	M264
89.6	32.	112.5	4.	201.4	2.	121.2	8.	280.0	4.	3302.4	4.	L	M266
50.3	256.	129.0	16.	115.0	16.	129.1	32.	295.2	16.	1661.0	32.	V	M266

APPENDIX E

EXPERIMENTAL RESULTS

TABLE XXIV

EXPERIMENTAL xy DATA AND K-VALUES FOR BASE SYSTEM
AT 150°F

Pressure psia		C ₁	C ₂	C ₃	C ₅	C ₆	C ₁₀
100.	y	0.8712	0.0216	0.0062	0.0701	0.0269	0.0040
	x	0.0226	0.0025	0.0019	0.2023	0.2004	0.5703
	K	38.6	8.54	3.32	0.347	0.134	0.0069
200.	y	0.9099	0.0263	0.0073	0.0379	0.0162	0.0024
	x	0.0460	0.0054	0.0046	0.1466	0.1713	0.6261
	K	19.8	4.86	1.61	0.258	0.0944	0.0037
400.	y	0.8602	0.0617	0.0449	0.0211	0.0103	0.0018
	x	0.0852	0.0228	0.0453	0.1344	0.1486	0.5636
	K	10.1	2.70	0.991	0.157	0.0691	0.0032
500.	y	0.9203	0.0340	0.0115	0.0222	0.0103	0.0018
	x	0.1202	0.0172	0.0130	0.1410	0.1629	0.5457
	K	7.65	1.98	0.885	0.157	0.0630	0.0033
1000.	y	0.9370	0.0330	0.0081	0.0120	0.0066	0.0033
	x	0.2612	0.0266	0.0152	0.1089	0.1253	0.4628
	K	3.59	1.24	0.532	0.110	0.0528	0.0071
1250.	y	0.9374	0.0300	0.0099	0.0130	0.0068	0.0029
	x	0.3260	0.0313	0.0226	0.1156	0.1194	0.3851
	K	2.88	0.960	0.440	0.112	0.0568	0.0076
1500.	y	0.9275	0.0370	0.0145	0.0119	0.0069	0.0022
	x	0.3513	0.0409	0.0324	0.0979	0.1049	0.3725
	K	2.64	0.904	0.447	0.122	0.0660	0.0057
2000.	y	0.9202	0.0413	0.0156	0.0120	0.0071	0.0038
	x	0.4903	0.0474	0.0340	0.0824	0.0859	0.2599
	K	1.88	0.871	0.459	0.145	0.0829	0.0146

TABLE XXIV (Continued)

Pressure psia		C ₁	C ₂	C ₃	C ₅	C ₈	C ₁₀
2500.	y	0.8954	0.0447	0.0201	0.0149	0.0124	0.0124
	x	0.5365	0.0513	0.0366	0.0659	0.0713	0.2384
	K	1.67	0.873	0.550	0.226	0.174	0.0520
3000.	y	0.8585	0.0414	0.0183	0.0179	0.0172	0.0466
	x	0.5753	0.0409	0.0272	0.0509	0.0616	0.2441
	K	1.49	1.01	0.672	0.352	0.279	0.191
3999.	y	0.6502	0.0486	0.0296	0.0435	0.0495	0.1785
	x	0.6575	0.0464	0.0292	0.0397	0.0456	0.1815
	K	1.0 (one phase) for all components					

TABLE XXV

EXPERIMENTAL xy DATA AND K-VALUES FOR BASE SYSTEM
AT 250°F

Pressure psia		C ₁	C ₂	C ₃	C ₅	C ₆	C ₁₀
100.	y	0.5986	0.0231	0.0090	0.2103	0.1207	0.0382
	x	0.0177	0.0016	0.0014	0.1694	0.1785	0.6314
	K	33.9	14.1	6.31	1.24	.676	.0605
200.	y	0.7736	0.0268	0.0106	0.1092	0.0579	0.0219
	x	0.0461	0.0044	0.0039	0.1643	0.1682	0.6130
	K	16.8	6.08	2.70	0.665	0.344	0.0357
300.	y	0.8019	0.0360	0.0140	0.0861	0.0487	0.0133
	x	0.0644	0.0077	0.0063	0.1574	0.1745	0.5897
	K	12.4	4.67	2.23	0.547	0.279	0.0224
500.	y	0.8416	0.0345	0.0142	0.0640	0.0356	0.0100
	x	0.1130	0.0107	0.0089	0.1415	0.1536	0.5722
	K	7.45	3.24	1.59	0.452	0.232	0.0175
702.	y	0.8612	0.0383	0.0139	0.0486	0.0288	0.0092
	x	0.1476	0.0161	0.0129	0.1425	0.1583	0.5226
	K	5.84	2.38	1.08	0.341	0.182	0.0176
1000.	y	0.8797	0.0383	0.0165	0.0337	0.0211	0.0105
	x	0.2157	0.0232	0.0180	0.1265	0.1428	0.4737
	K	4.08	1.65	0.919	0.266	0.148	0.0222
1500.	y	0.8691	0.0386	0.0166	0.0337	0.0229	0.0192
	x	0.3212	0.0294	0.0205	0.1109	0.1207	0.3975
	K	2.71	1.31	0.809	0.304	0.190	0.0482
2000.	y	0.8510	0.0415	0.0192	0.0363	0.0261	0.0259
	x	0.4122	0.0342	0.0235	0.0947	0.0993	0.3362
	K	2.06	1.21	0.818	0.383	0.263	0.0769
2500.	y	0.8195	0.0409	0.0195	0.0339	0.0288	0.0575
	x	0.4879	0.0349	0.0236	0.0780	0.0818	0.2938
	K	1.68	1.17	0.825	0.435	0.352	0.196
3001.0	y	0.8416	0.0396	0.0212	0.0327	0.0289	0.0360
	x	0.8518	0.0366	0.0200	0.0317	0.0270	0.0329
	K	1.0 (one phase) for all components					

TABLE XXVI (1 of 2)

EXPERIMENTAL xy DATA FOR BASE SYSTEM WITH
 DECAHYDRONAPHTHALENE SUBSTITUTED FOR
 N-DECANE AT 150°F

Pressure psia		C ₁	C ₂	C ₃	C ₅	C ₈	C ₁₀
100.	y	0.8835	0.0218	0.0049	.0569	.0243	.0086
	x	0.0343	0.0033	0.0023	.1819	.1832	.5950
	K	25.8	6.52	2.15	.313	.133	.0144
100.	y	0.8827	0.0247	0.0083	.0543	.0229	.0070
	x	0.0365	0.0041	0.0042	.1704	.1827	.6021
	K	24.2	6.02	1.99	.319	.125	.0116
200.	y	0.9116	0.0311	0.0086	.0279	.0127	.0081
	x	0.0775	0.0103	0.0088	.1620	.1691	.5722
	K	11.8	3.01	0.976	.172	.0753	.0140
200.	y	0.9180	0.0292	0.0097	.0269	.0113	.0050
	x	0.0716	0.0108	0.0080	.1602	.1705	.5790
	K	12.8	2.71	1.21	.168	.0660	.00866
300.	y	0.9395	0.0232	0.0062	.0180	.0079	.0051
	x	0.1126	0.0126	0.0081	.1534	.1636	.5498
	K	8.35	1.84	0.774	.118	.0485	.00926
300.	y	0.9286	0.0301	0.0111	.0179	.0080	.0043
	x	0.1092	0.0163	0.0134	.1510	.1630	.5472
	K	8.50	1.85	0.829	.119	.0489	.00793
700.	y	0.9412	0.0280	0.0084	.0130	.0059	.0035
	x	0.2375	0.0260	0.0169	.1252	.1349	.4594
	K	3.96	1.08	0.498	.104	.0435	.00754
700.	y	0.9424	0.0285	0.0083	.0118	.0062	.0028
	x	0.2306	0.0271	0.0170	.1267	.1356	.4630
	K	4.09	1.05	0.487	.0932	.0454	.00604

TABLE XXVI (2 of 2)

EXPERIMENTAL xy DATA FOR BASE SYSTEM WITH
DECAHYDRONAPHTHALENE SUBSTITUTED FOR
N-DECANE AT 150°F

Pressure psia		C ₁	C ₂	C ₃	C ₅	C ₆	C ₁₀
1000.	y	0.9439	0.0256	0.0097	.0125	.0061	.0022
	x	0.3054	0.0308	0.0201	.1249	.1292	.3897
	K	3.09	0.832	0.483	.0997	.0471	.00568
1500.	y	0.9388	0.0327	0.0105	.0102	.0056	.0021
	x	0.4035	0.0397	0.0251	.1040	.1088	.3190
	K	2.33	0.825	0.419	.0983	.0514	.00659
2000.	y	0.9314	0.0366	0.0118	.0111	.0068	.0023
	x	0.4656	0.0429	0.0267	.0881	.0911	.2856
	K	2.00	0.853	0.440	.126	.0744	.00818
2500.	y	0.9170	0.0368	0.0138	.0133	.0103	.0087
	x	0.5408	0.0464	0.0281	.0714	.0770	.2364
	K	1.70	0.794	0.493	.186	.133	.0368
3000.	y	0.8952	0.0391	0.0154	.0176	.0153	.0173
	x	0.5525	0.0477	0.0287	.0672	.0710	.2329
	K	1.62	0.821	0.538	.262	.216	.0744
4000.3	y	0.8255	0.0456	0.0359	.0288	.0265	.0378
	x	0.5133	0.0491	0.0435	.0643	.0706	.2591
	K	1.61	0.928	0.824	.447	.375	.146
4995.9	y	0.7501	0.0513	0.0437	.0391	.0386	.0774
	x	0.5943	0.0519	0.0463	.0540	.0593	.1941
	K	1.26	0.987	0.943	.723	.650	.399
5999.6	y	0.7681	0.0471	0.0243	.0318	.0325	.0962
	x	0.7677	0.0447	0.0277	.0312	.0301	.1036
	K	1.0 (one phase) all components					

TABLE XXVII (1 of 2)

EXPERIMENTAL xy DATA FOR BASE SYSTEM WITH
DECAHYDRONAPHTHALENE SUBSTITUTED FOR
N-DECANE AT 250°F

Pressure psia		C ₁	C ₂	C ₃	C ₅	C ₆	C ₁₀
100.	y	0.6276	0.0224	0.0056	0.2110	.1159	.0175
	x	0.0246	0.0028	0.0016	0.1629	.1860	.6221
	K	25.5	7.97	3.53	1.30	.623	.0281
200.	y	0.8340	0.0234	0.0071	0.0804	.0449	.0102
	x	0.0598	0.0050	0.0034	0.1616	.1824	.5878
	K	14.0	4.68	2.09	0.498	.246	.0173
300.	y	0.8867	0.0209	0.0049	0.0520	.0299	.0056
	x	0.0879	0.0055	0.0030	0.1534	.1750	.5752
	K	10.1	3.78	1.66	0.339	.171	.00973
500.	y	0.9091	0.0226	0.0059	0.0360	.0209	.0055
	x	0.1545	0.0102	0.0054	0.1417	.1620	.5261
	K	5.88	2.21	1.09	0.254	.129	.0104
700.	y	0.9207	0.0255	0.0065	0.0273	.0164	.0036
	x	0.2440	0.0136	0.0068	0.1227	.1400	.4730
	K	3.77	1.88	0.958	0.223	.117	.00762
1000.	y	0.9189	0.0255	0.0071	0.0265	.0162	.0058
	x	0.2816	0.0183	0.0090	0.1168	.1331	.4412
	K	3.26	1.39	0.792	0.227	.122	.0130

TABLE XXVII (2 of 2)

EXPERIMENTAL xy DATA FOR BASE SYSTEM WITH
 DECAHYDRONAPHTHALENE SUBSTITUTED FOR
 N-DECANE AT 250°F

Pressure psia		C ₁	C ₂	C ₃	C ₅	C ₆	C ₁₀
1500.	y	0.9197	0.0340	0.0109	0.0190	.0126	.0039
	x	0.3675	0.0302	0.0178	0.0989	.1124	.3733
	K	2.50	1.12	0.613	0.192	.112	.0104
2000.	y	0.9150	0.0376	0.0129	0.0177	.0121	.0048
	x	0.4083	0.0335	0.0215	0.0880	.0998	.3488
	K	2.24	1.12	0.597	0.201	.122	.0137
2500.	y	0.9133	0.0367	0.0140	0.0168	.0126	.0066
	x	0.4504	0.0392	0.0248	0.0787	.0899	.3170
	K	2.03	0.935	0.565	0.214	.140	.207
3001.2	y	0.9064	0.0314	0.0104	0.0195	.0162	.0161
	x	0.5900	0.0351	0.0171	0.0615	.0666	.2296
	K	1.54	0.893	0.607	0.318	.243	.0701
3500.4	y	0.8826	0.0424	0.0199	0.0204	.0178	.0169
	x	0.6056	0.0466	0.0291	0.0526	.0591	.2070
	K	1.46	0.910	0.684	0.387	.302	.0815
4998.7	y	0.6834	0.0342	0.0177	0.0421	.0491	.1734
	x	0.6931	0.0370	0.0188	0.0420	.0470	.1621
	K	1.0 (one phase) all components					

TABLE XXVIII (1 of 2)

EXPERIMENTAL xy DATA FOR BASE SYSTEM WITH
1-METHYLNAPHTHALENE SUBSTITUTED FOR
N-DECANE AT 150°F

Pressure psia		C ₁	C ₂	C ₃	C ₅	C ₆	C ₁₀
100.	y	0.8283	0.0284	0.0063	.0942	.0404	.0024
	x	0.0271	0.0025	0.0016	.2379	.1846	.5463
	K	30.6	11.5	3.98	.396	.219	.00435
200.	y	0.9136	0.0236	0.0054	.0394	.0169	.0012
	x	0.0503	0.0052	0.0032	.1917	.1812	.5684
	K	18.2	4.55	1.67	.206	.0930	.00203
300.	y	0.9262	0.0261	0.0058	.0289	.0120	.0010
	x	0.0868	0.0093	0.0054	.1756	.1758	.5471
	K	10.7	2.80	1.06	.165	.0681	.00187
500.	y	0.9428	0.0250	0.0052	.0185	.0081	.0004
	x	0.1358	0.0126	0.0071	.1681	.1698	.5066
	K	6.94	1.98	0.735	.110	.0476	.000849
1000.	y	0.9440	0.0289	0.0073	.0132	.0064	.0002
	x	0.2226	0.0233	0.0133	.1366	.1414	.4627
	K	4.24	1.24	0.545	.0969	.0453	.000429
1500.	y	0.9401	0.0310	0.0082	.0134	.0071	.0002
	x	0.3198	0.0299	0.0166	.1261	.1284	.3792
	K	2.94	1.04	0.496	.106	.0550	.000611
2000.	y	0.9278	0.0335	0.0105	.0163	.0103	.0016
	x	0.3535	0.0318	0.0196	.1018	.1063	.3870
	K	2.62	1.05	0.536	.160	.0972	.00415

TABLE XXVIII (2 of 2)

EXPERIMENTAL xy DATA FOR BASE SYSTEM WITH
1-METHYLNAPHTHALENE SUBSTITUTED FOR
N-DECANE AT 150°F

Pressure psia		C ₁	C ₂	C ₃	C ₅	C ₈	C ₁₀
2500.	y	0.9178	0.0388	0.0124	.0173	.0118	.0018
	x	0.4238	0.0373	0.0214	.0895	.0971	.3308
	K	2.17	1.04	0.583	.194	.121	.00555
3001.3	y	0.9099	0.0387	0.0142	.0195	.0146	.0031
	x	0.4235	0.0365	0.0210	.0787	.0846	.3557
	K	2.15	1.06	0.679	.248	.173	.00872
3499.8	y	0.8971	0.0386	0.0164	.0234	.0194	.0051
	x	0.4987	0.0404	0.0227	.0663	.0723	.2995
	K	1.80	0.955	0.720	.353	.268	.0172
5998.6	y	0.8706	0.0468	0.0196	.0222	.0208	.0200
	x	0.7963	0.0533	0.0250	.0327	.0312	.0615
	K	1.09	0.878	0.784	.678	.668	.325
6996.2	y	0.8765	0.0417	0.0185	.0203	.0194	.0236
	x	0.8361	0.0443	0.0200	.0229	.0226	.0540
	K	1.048	0.941	0.927	.887	.857	.436
7995.1	y	0.8313	0.0469	0.0220	.0223	.0218	.0557
	x	0.8426	0.0437	0.0203	.0213	.0199	.0523
	K	1.0 (one phase) for all components					

TABLE XXIX (1 of 2)

EXPERIMENTAL xy DATA FOR BASE SYSTEM WITH
1-METHYLNAPHTHALENE SUBSTITUTED FOR
N-DECANE AT 250°F

Pressure psia		C ₁	C ₂	C ₃	C ₅	C ₆	C ₁₀
102.	y	0.7301	0.0160	0.0041	0.1828	.0620	.0050
	x	0.0160	0.0011	0.0007	0.1729	.1623	.6470
	K	45.5	14.8	6.28	1.06	.382	.00768
200.	y	0.7971	0.0219	0.0071	0.1122	.0561	.0056
	x	0.0424	0.0032	0.0022	0.1639	.1595	.6288
	K	18.8	6.8	3.31	0.685	.351	.00895
300.	y	0.8454	0.0318	0.0120	0.0729	.0354	.0025
	x	0.0655	0.0068	0.0054	0.1569	.1521	.6132
	K	12.9	4.66	2.22	0.465	.233	.00415
500.	y	0.8789	0.0353	0.0122	0.0476	.0245	.0015
	x	0.1085	0.0109	0.0084	0.1442	.1390	.5890
	K	8.10	3.25	1.44	0.330	.177	.00250
700.	y	0.8944	0.0353	0.0130	0.0373	.0188	.0012
	x	0.1579	0.0164	0.0117	0.1374	.1314	.5452
	K	5.66	2.16	1.11	0.271	.143	.00212
1000.	y	0.8964	0.0399	0.0153	0.0305	.0165	.0013
	x	0.1976	0.0213	0.0157	0.1262	.1231	.5161
	K	4.54	1.88	0.978	0.242	.134	.00249
1500.	y	0.9017	0.0392	0.0169	0.0254	.0149	.0020
	x	0.2654	0.0273	0.0200	0.1036	.1081	.4756
	K	3.40	1.44	0.843	0.245	.138	.00416
2000.	y	0.8951	0.0446	0.0186	0.0243	.0152	.0022
	x	0.3441	0.0322	0.0226	0.0953	.0953	.4106
	K	2.60	1.39	0.820	0.255	.160	.00542

TABLE XXIX (2 of 2)

EXPERIMENTAL xy DATA FOR BASE SYSTEM WITH
1-METHYLNAPHTHALENE SUBSTITUTED FOR
N-DECANE AT 250°F

Pressure psia		C ₁	C ₂	C ₃	C ₅	C ₆	C ₁₀
2500.	y	0.8902	0.0458	0.0201	0.0244	.0159	.0035
	x	0.3748	0.0365	0.0257	0.0871	.0867	.3891
	K	2.37	1.26	0.781	0.280	.184	.00910
3001.5	y	0.8802	0.0455	0.0228	0.0265	.0188	.0062
	x	0.4254	0.0402	0.0289	0.0768	.0776	.3511
	K	2.07	1.13	0.789	0.345	.243	.0176
3500.0	y	0.8740	0.0489	0.0231	0.0255	.0184	.0102
	x	0.4622	0.0435	0.0303	0.0679	.0683	.3279
	K	1.89	1.12	0.762	0.375	.270	.0309
3999.6	y	0.8849	0.0402	0.0162	0.0257	.0199	.0131
	x	0.5157	0.0358	0.0194	0.0622	.0629	.3041
	K	1.72	1.12	0.833	0.414	.317	.0431
4998.3	y	0.8541	0.0502	0.0299	0.0264	.0220	.0175
	x	0.5561	0.0490	0.0343	0.0513	.0515	.2577
	K	1.54	1.02	0.872	0.514	.426	.0677
5997.4	y	0.8336	0.0554	0.0321	0.0270	.0235	.0284
	x	0.6136	0.0531	0.0337	0.0417	.0415	.2165
	K	1.36	1.04	0.952	0.648	.566	.131
7995.8	y	0.6886	0.0523	0.0359	0.0292	.0280	.1661
	x	0.6744	0.0501	0.0346	0.0301	.0292	.1816
	K	1.0 (one phase) all components					

TABLE XXX

RATIOS OF SUBSTITUTED SYSTEM K-VALUES
TO THE BASE SYSTEM

$$\alpha_1 = \frac{K_1 \text{ in base system with substituted heavy component}}{K_1 \text{ in base system}}$$

	Pressure psia	αC_1				
		C_1	C_2	C_3	C_5	C_8
Decahydronaphthalene system at 150°F	100.	.668	.756	.653	.903	.988
	200.	.652	.556	.761	.653	.703
	500.	.534	.532	.552	.592	.723
	1000.	.862	.670	.906	.908	.896
	1500.	.881	.910	.935	.807	.783
	2000.	1.07	.979	.963	.865	.903
	2500.	1.02	.910	.894	.824	.769
	3000.	1.09	.810	.798	.745	.722
	4000.	1.62	.882	.812	.406	.344
at 250°F	100.	.754	.554	.544	1.04	.922
	200.	.837	.769	.773	.753	.720
	300.	.810	.813	.735	.620	.612
	500.	.790	.687	.685	.562	.557
	700.	.647	.788	.887	.652	.644
	1000.	.800	.844	.861	.852	.824
	1500.	.923	.854	.750	.630	.591
	2000.	1.08	.920	.731	.522	.461
	2500.	1.20	.794	.682	.490	.396
	3000.	1.55	.827	.574	.307	.227
1-methylnaphthalene system at 150°F	100.	.793	1.31	1.21	1.14	1.63
	200.	.918	.932	1.06	.795	.986
	500.	.907	1.00	.828	.699	.754
	1000.	1.18	1.00	1.03	.877	.859
	1500.	1.11	1.15	1.10	.874	.841
	2000.	1.40	1.21	1.17	1.10	1.17
	2500.	1.30	1.19	1.06	.855	.699
	3000.	1.44	1.05	1.01	.705	.618
	4000.	1.82	.912	.713	.322	.247
at 250°F	100.	1.35	1.01	.911	.852	.565
	200.	1.12	1.12	1.19	1.03	1.02
	300.	1.05	1.00	1.01	.856	.840
	500.	1.10	1.02	.915	.736	.768
	700.	.976	.915	1.03	.799	.792
	1000.	1.12	1.14	1.07	.911	.913

TABLE XXX (Continued)

Pressure psia	αC_i				
	C_1	C_2	C_3	C_5	C_6
1500.	1.26	1.10	1.04	.807	.726
2000.	1.26	1.14	1.01	.664	.609
2500.	1.41	1.07	.945	.645	.524
3000.	2.09	1.04	.744	.335	.226

APPENDIX F

THE BWR EQUATION OF STATE

The Benedict-Webb-Rubin (BWR) (6, 7) equation of state was developed on the basis of residual work content, \tilde{A} . \tilde{A} was defined as the difference between the actual molal work content of a substance at a molal density d and absolute temperature T and its work content at the same temperature and pressure in its hypothetical ideal gas state. This is also known as Helmholtz free energy and is expressed as

$$\tilde{A} = A - RT \ln d - \lim_{d \rightarrow 0} (A - RT \ln d). \quad (F-1)$$

This definition for a mixture is the difference between the actual molal work content and hypothetical ideal gas state work content of one mole of mixture at the same temperature, density, and composition.

$$\tilde{A} = A - \sum_i X_i [RT \ln X_i d + \lim_{d \rightarrow 0} (A_i - RT \ln d)]. \quad (F-2)$$

The pressure of a mixture is related to the residual work content as

$$\tilde{A} = \int_0^d \frac{P - RTd}{d^2} \delta d \quad (F-3)$$

or

$$P = RTd + d^2 \frac{\partial \tilde{A}}{\partial d} \Big|_{T, x} \quad (F-4)$$

The fugacity of component i , f_i , in a mixture is related to residual work content as follows:

$$RT \ln f_i = \left(\frac{\partial N\tilde{A}}{\partial n_i} \right)_{T, V, n} + RT \ln (RT d x_i) \quad (F-5)$$

where

n_i = number of moles of the i^{th} component

$$N = \sum_i n_i$$

V = total volume of the mixture.

The empirical expression for the residual work content of pure components with respect to temperature and density was given as (6):

$$\begin{aligned} \tilde{A} = & (B_0 RT - A_0 - C_0/T^2)d + (bRT - a)d^2/2 \\ & + a\alpha d^5/5 \\ & + \frac{cd^2}{T^2} \left[\frac{1 - \exp(-\gamma d^2)}{\gamma d^2} - \frac{\exp(-\gamma d^2)}{2} \right]. \end{aligned} \quad (F-6)$$

Combining Equations (F-4) and (F-6) with proper differentiation, one obtains the pressure form of the BWR equation,

$$\begin{aligned} P = & RTd + (B_0 RT - A_0 - C_0/T^2)d \\ & + (bRT - a)d^3 \end{aligned}$$

$$+ a d^6 + \frac{c d^3}{T^2} (1 + \gamma d^2) \exp(-\gamma d^2). \quad (F-7)$$

Equation (F-4) can also be combined with Equation (F-5) to give the fugacity expression for components in a mixture.

$$\begin{aligned} RT \ln \bar{F}_i &= RT \ln(d RT X_i) \\ &+ \left[(B_o + B_{c,i}) RT - 2(A_o A_i)^{\frac{1}{2}} - 2(C_o C_{o,i})^{\frac{1}{2}}/T^2 \right] d \\ &+ \frac{3}{2} \left[RT(b^2 b_i)^{\frac{1}{2}} - (a^2 a_i)^{\frac{1}{2}} \right] d^2 \\ &+ \frac{3}{6} \left[a(\alpha^2 \alpha_i)^{\frac{1}{2}} + \alpha(a^2 a_i)^{\frac{1}{2}} \right] d^3 \\ &+ \frac{3d^2 (c^2 c_i)^{\frac{1}{2}}}{T^2} \left[\frac{1 - \exp(-\gamma d^2)}{\gamma d^2} - \frac{\exp(-\gamma d^2)}{2} \right] \\ &+ \frac{2d^2 c}{T^2} \left(\frac{\gamma_i}{\gamma} \right)^{\frac{1}{2}} \left[\frac{1 - \exp(-\gamma d^2)}{d^2} \right. \\ &\quad \left. - \exp(-\gamma d^2) - \frac{\gamma d^2 \exp(-\gamma d^2)}{2} \right]. \end{aligned} \quad (F-8)$$

The above expression was derived using the "normal" BWR mixing rules for the constants with B_o using the linear and A_o and C_o the square root combinations. The use of the interaction coefficient θ in the form of Equation (VII-38) modifies the above expression in several ways. The $2(A_o A_{o,i})^{\frac{1}{2}}$ and $2(C_o C_{o,i})^{\frac{1}{2}}$ expressions in Equation (F-8) are replaced by:

$$2 \left(\sum_{j=1}^N \theta_{ij} X_j (A_{o,i} A_{o,j})^{\frac{1}{2}} \right) \quad (F-9)$$

and

$$2 \left(\sum_{j=1}^N \theta_{ij} X_j (B_{0i} B_{0j})^{\frac{1}{2}} \right) \quad (\text{F-10})$$

where

N = number of components in the system

$\theta_{ij} = 1$ when $j = i$.

The term $(B_0 + B_{0i})$ is replaced by

$$2 \left(\sum_{j=1}^N \theta_{ij} X_j (C_{0i} C_{0j})^{\frac{1}{2}} \right) \quad (\text{F-11})$$

for the square root mixing rule, and

$$\sum_{j=1}^N \theta_{ij} X_j (B_{0i} + B_{0j}) \quad (\text{F-12})$$

for the linear mixing rule, and

$$\frac{1}{2} \left(\sum_{j=1}^N \theta_{ij} X_j (B_{0i}^{\frac{1}{2}} + B_{0j}^{\frac{1}{2}})^2 \right) \quad (\text{F-13})$$

for the linear square root mixing rule.

For the special case of a binary system, Equations (F-11) through (F-13) become:

$$2(X_i B_{0i} + X_j \theta (B_{0i} B_{0j})^{\frac{1}{2}}) \quad (\text{F-14})$$

$$2 X_i B_{0i} + X_j \theta (B_{0i} + B_{0j}) \quad (\text{F-15})$$

$$2 X_i B_{0i} + 0.5 X_j \theta (B_{0i}^{\frac{1}{2}} + B_{0j}^{\frac{1}{2}})^2. \quad (\text{F-16})$$

A direct expression for calculating K-values of a component in a mixture using the BWR equation of state is given by Equations (VI-30) and (VI-31). These expressions are obtained by combining Equations (F-8) and (III-32).

APPENDIX G

PROGRAM LISTING

Experimental K-Value Calculation Program

```

3400032007013600032007024902402511963611300102
ZZJOB
ZZDUP
*DFLETKANDXS
ZZZZ
ZZJOB
ZZFOR
*FANDK1010
*LDISKKANDXS.778
C      CALCULATION OF CONCENTRATIONS AND K VALUES FROM CHROMATOGRAPH ANALYSIS.
C      SIX COMPONENTS
      DIMENSION A(6),AT(6),WR(6),X(6),XL(6),XV(6),RK(6),NRUN(3),XW(6),
1      XR(6),WM(6)
100    FORMAT (6(F7.1,F5.0),I2,1X,A5)
101    FORMAT (6F10.6,15,2X,A5)
102    FORMAT (5F9.4,F9.6,F8.2,F9.2,7X,A5,1X,/)
103    FORMAT (3(2X,A5))
104    FORMAT (2X,2A3,25X,F9.3,9X,F7.2, 9X,A5)
99     N1=1
      N2=2
      WM(1)= 16.042
      WM(2)= 30.068
      WM(3)= 44.094
      WM(4)= 72.146
      WM(5)= 86.17
      READ 199, SLOPE1, SLOPE2,SLOPE3,SLOPE5,SLOPE6,WM(6)
199    FOR,IAT (5F11.8,F12.3)
9      K=0
      READ 104,NA,NB,P,T,NRUN(1)
10     IN=K+1+1
      READ 100,A(1),AT(1),A(2),AT(2),A(3),AT(3),A(4),AT(4),A(5),AT(5),
1      A(6),AT(6),NPHASE,NRUN(IN)
      DO 23 I=1,6
23      A(I)=A(I)*AT(I)
      WR(1)=1.0/((A(4)/A(1))*SLOPE1)
      WR(2)=1.0/((A(4)/A(2))*SLOPE2)
      WR(3)=1.0/((A(4)/A(3))*SLOPE3)
      WR(4)=1.000
      WR(5)=A(5)/A(4)*SLOPE5
      WR(6)=A(6)/A(4)*SLOPE6
      WT=WR(1)+WR(2)+WR(3)+WR(4)+WR(5)+WR(6)
      DO 11 I=1,6
11      XW(I)=WR(I)/WT
      TM=0.0
      DO 20 I=1,6
      XR(I)=XW(I)/WM(I)
20      TM=TM+XR(I)
      DO 21 I=1,6
21      X(I)=XR(I)/TM
      IF ( NPHASE-1 ) 999, 12, 13
13      DO 15 I=1,6
15      XV(I)=X(I)
14      K=K+1
      GO TO 16
12      DO 22 I=1,6
22      XL(I)=X(I)
      K=K+1
16      IF ( K-1 ) 999, 10, 17
17      DO 18 I=1,6

```

```
1P RK(I)=XV(I)/XL(I)
PUNCH 101,XL(1),XL(2),XL(3),XL(4),XL(5),XL(6),N1,NRUN(2)
PUNCH 101,XV(1),XV(2),XV(3),XV(4),XV(5),XV(6),N2,NRUN(3)
PUNCH 102,RK(1),RK(2),RK(3),RK(4),RK(5),RK(6),T,P,NRUN(1)
IF (SENSE SWITCH 2) 98, 97
97 PRINT103,NRUN(1),NRUN(2),NRUN(3)
98 IF (SENSE SWITCH 1) 99, 9
999 PRINT 998
998 FORMAT (32H      ERROR IN DATA, START OVER )
9999 CALL EXIT
      END
ZZZZ
```


Regression Program

```

$IBFTC MAIN      DECK
  DIMENSION XL(300),XV(300),TS(300),P(300),TC(300),PC(300),W(300),
  ZNSYST(300),AQ12(300),SA13(300),SH13(300),SC13(300),ALGA(300),
  3ALP13(300),GM12(300),RTLL(2),RTLVL(2),DM(3),YM(3)
  COMMON XL,XV,TS,P,TC,PC,W,NSYST,R,AQ12,SA13,SB13,SC13,ALGA,ALP13,
  1GM12,DL,DV,NQ,RTLL,RTLVL,DM,YM
C  EMBEDDING PROGRAM FOR GAUSS
  DIMENSION B(24), Z(12,300), MM(12)
  COMMON NUMBER,B,Z
  COMMON /COMA/ MM
  COMMON /COMB/ JJ
  1 READ (5,2) (MM(J),J=1,12)
  2 FORMAT (12I6)
  NUMBER=MM(1)
  NSET=MM(2)
  JJ=MM(3)
  IF (NUMBER) 4,4,10
  4 WRITE (6,5)
  CALL EXIT
  5 FORMAT (40H0 GAUSS INPUT ZERO, PROGRAM STOP /1H1)
  10 READ(5,11) (B(J),J=1,24)
  11 FORMAT (6F12.12)
  IF (MM(5)) 15,14,14
  14 MBER=NUMBER-1
  DO 52 N=1,MBER ,2
  READ (5,51) XL(N),XV(N),TS(N),P(N),TC(N),TC(N+1),PC(N),PC(N+1),
  1W(N),W(N+1),NSYST(N)
  XL(N+1)=1.0-XL(N)
  XV(N+1)=1.0-XV(N)
  Z(1,N) =TS(N)
  Z(1,N+1)=TS(N)
  Z(NSET,N)=1.0
  52 Z(NSET,N+1)=1.0
  51 FORMAT (2F6.4,F8.2,F9.2,2F8.2,2F9.2,2F6.4,I5)
  CALL BWRCST
  15 CALL GAUSS
  IF (MM(8)-2) 30,20,30
  20 WRITE (6,21)
  21 FORMAT (40H0 GAUSS CONVERGENCE //)
  MM(8)=1
  30 MM(11)=MM(11)-1
  IF (MM(11)) 1,1,14
  END

```

DECK0010
 DECK0020
 DECK0030
 DECK0040
 DECK0050
 DECK0060
 DECK0070
 DECK0080
 DECK0090
 DECK0100
 DECK0110
 DECK0120
 DECK0130
 DECK0140
 DECK0150
 DECK0160
 DECK0170

DECK0190
 DECK0200
 DECK0201
 DECK0210
 DECK0220
 DECK0230
 DECK0240
 DECK0250

*IBFIC GAUSS DECK		
SUBROUTINE GAUSS		GAUS0030
DIMENSION XL(300),XV(300),TS(300),P(300),TC(300),PC(300),W(300),		
ZNSYST(300),A012(300),SA13(300),SP13(300),SC13(300),ALGA(300),		
3ALP13(300),GM12(300),PTLL(2),RTLV(2),DM(3),YM(3)		
COMMON XL,XV,TS,P,TC,PC,W,NSYST,R,A012,SA13,SP13,SC13,ALGA,ALP13,		
IGM12,DL,DV,NQ,RTLL,RTLV,DM,YM		
DIMENSION A(20,21),B(24),BMIN(20),BSTART(20),C(20,1),X(20,1),		GAUS0040
X Z(12,300),DFL(20),E(20),MM(12),RECORD(100),CY(300),FP(20,300)		GAUS0050
COMMON NUMBER,B,Z		GAUS0060
COMMON /COMA/ MM		GAUS0061
COMMON /COMB/ JJ		GAUS0062
COMMON /COMC/ CY		GAUS0063
COMMON /COMD/ FP		GAUS0064
COMMON /COME/ A,C,M		GAUS0065
EQUIVALENCE (A,X)		GAUS0070
C	SECTION 0. IDENTIFICATION OF CONTROL VARIABLES	GAUS0100
C	B(1)-B(20) PARAMETERS TO BE DETERMINED	GAUS0120
C	B(21) = TOLERANCE	GAUS0130
C	B(22) = CONTROL FOR DIFFERENT YCOMPS	GAUS0140
C	B(23) = SCALE FACTOR FOR B(J) VECTOR. USUALLY UNITY.	GAUS0150
C	MM(1) = NUMBER OF DATA POINTS	GAUS0170
C	MM(2) = INDEX OF DEPENDENT VARIABLE	GAUS0180
C	MM(3) = NUMBER OF PARAMETERS	GAUS0190
C	MM(4) = LIMIT ON NUMBER OF ITERATIONS	GAUS0200
C	MM(5) IS USED BY THE EMBEDDING PROGRAM, WHEN NEGATIVE IT SKIPS	GAUS0210
C	READING OF THE Z(J,K)	GAUS0220
C	MM(6) = -1 GIVES INTERMEDIATE RESULTS AT EACH ITERATION	GAUS0240
C	MM(6) = 0 GIVES NO INTERMEDIATE RESULTS	GAUS0250
C	MM(6) = 1 GIVES INTERMEDIATE RESULTS AT FIRST ITERATION ONLY	GAUS0260
C	MM(7) = 1 GIVES STRAIGHT GAUSS	GAUS0280
C	MM(7) = 0 GIVES PARABOLIC GAUSS (RECOMMENDED)	GAUS0290
C	MM(8) = -1 UPON RETURN MEANS OVERFLOW OR SINGULARITY OF MATRIX	GAUS0310
C	MM(8) = -2 UPON RETURN MEANS THAT ITERATION LIMIT IS EXCEEDED	GAUS0320
C	MM(8) = 1 GIVES THE BACK SOLUTION AT THE OUTSET OF THE PROGRAM	GAUS0330
C	MM(8) = 2 SIGNALS THAT CONVERGENCE HAS OCCURRED	GAUS0340
C	MM(9) = 1 RECORDS INPUT DATA ON TAPE 6	GAUS0360
C	MM(9) = 0 BYPASSES THIS RECORDING	GAUS0370
C	MM(10) = -1 RECORDS THE MATRICES AT EACH ITERATION	GAUS0390
C	MM(10) = 0 BYPASSES RECORDING OF MATRICES	GAUS0400
C	MM(10) = 1 RECORDS THE MATRICES AT FIRST ITERATION ONLY	GAUS0410
C	MM(11) = NUMBER OF PROBLEMS TO BE FED THE EMBEDDING PROGRAM	GAUS0430
C	MM(12) WHEN NEGATIVE NULLIFIES ALL PROGRAM	GAUS0440
C	IT IS SUGGESTED THAT B(20) BE USED TO GIVE THE FUNCTION CHOICE	GAUS0470
C	IN YCOMP, WHEN THERE ARE MULTIPLE FUNCTIONS TO BE TESTED.	GAUS0480
	NUMBER = MM(1)	GAUS0490
	NSFT = MM(2)	GAUS0500
	JJ = MM(3)	GAUS0510
	LIMIT = MM(4)	GAUS0520
	NULL = MM(12)	GAUS0530
	MM(12) = MM(12) + 1	GAUS0540
	IDNTFC = MM(12)	GAUS0550
	TZERO = 1.0	GAUS0570
	SCALE 1 = 0.2	GAUS0580
	SCALE 2 = 1.5	GAUS0590

SCALE 3 = 1.0	GAUS0600
TOL1 = B(21)	GAUS0610
X NORM = 0.0	GAUS0620
MARK P = 0	GAUS0640
KKPATH = -1	GAUS0650
NDOWN = 0	GAUS0660
NN = 0	GAUS0670
NNPARA = 0	GAUS0680
NPATH = 1	GAUS0690
NTZERO = -1	GAUS0700
SUMSQ = 0.0	GAUS0710
T = 0.0	GAUS0720
X3 = 3.0	GAUS0730
X2 = 2.0	GAUS0740
Y2 = 2.0	GAUS0750
Y3 = 3.0	GAUS0760
IF (LIMIT - 100) 2,47,47	GAUS0780
2 IF (TOL1) 420,420,1	GAUS0790
1 DO 4 J=1,JJ	GAUS0810
BMIN(J) = B(J)	GAUS0820
BSTART(J) = B(J)	GAUS0830
X NORM = X NORM + B(J)**2	GAUS0840
DEL(J) = 0.05*ABS (B(J))	GAUS0850
IF (DEL(J)) 4,3,4	GAUS0860
3 DEL(J) = 0.05	GAUS0870
4 CONTINUE	GAUS0880
WRITE (6,5)	GAUS0900
5 FORMAT (51H1 GAUSSIAN PARAMETER SUBROUTINE Z(12,300))	GAUS0910
WRITE (6,412) (MM(1), L=1,12)	GAUS0930
WRITE (6,108) (B(J), J = 1,24)	GAUS0940
IF (MM(9)) 400,6,400	GAUS0960
6 IF (MM(8) - 1) 7,80,7	GAUS0980
7 IF (B(23)) 8,8,430	GAUS1000
8 JPARA = -1	GAUS1010
MPATH = -1	GAUS1020
T = 0.0	GAUS1030
MM(8) = 2	GAUS1040
WRITE(6,59)	GAUS1050
DO 9 J=1,JJ	GAUS1060
9 BSTART(J) = B(J)	GAUS1070
10 SQLAST = SUMSQ	GAUS1090
SUMSQ = 0.0	GAUS1100
NTZERO = NTZERO + 1	GAUS1110
NN = NN+1	GAUS1120
IF (NN - LIMIT) 12,12,11	GAUS1130
11 MM(8) = -2	GAUS1150
GO TO 80	GAUS1160
12 CALL YCOMP	GAUS1180
DO 17 N= 1,NUMBER	GAUS1181
YC = CY(N)	GAUS1190
DELY = YC - Z(INSET,N)	
SUMSQ = SUMSQ + DELY**2	GAUS1210
IF (NULL) 17,13,13	GAUS1220
13 IF (MM(6)) 14,17,14	GAUS1230
14 IF (N-1) 16,15,16	GAUS1240

15	WRITE (6,410)	GAUS1250
16	WRITE (6,18) N,YC,Z(INSET,N),DELY	GAUS1260
	MARK P = 1	GAUS1270
17	CONTINUE	GAUS1280
	RECORD(NN) = SUMSQ	GAUS1290
18	FORMAT (16,4E18.7)	GAUS1300
	GO TO 440	GAUS1310
19	IF (NN - 1) 20,22,30	GAUS1330
20	IF (SUMSQ-SQMIN) 21,21,27	GAUS1360
21	NDOWN = 1	GAUS1370
22	SQMIN = SUMSQ	GAUS1380
	DO 24 J=1,JJ	GAUS1390
24	BMIN(J) = B(J)	GAUS1400
25	IF (MPATH) 301,200,38	GAUS1410
27	IF (NDOWN) 28,28,29	GAUS1430
28	NDOWN = -1	GAUS1440
29	IF (MPATH) 301,200,36	GAUS1450
30	IF (MM(6)) 32,32,31	GAUS1470
31	MM(6) = 0	GAUS1480
32	IF (MM(10)) 20,20,33	GAUS1490
33	MM(10) = 0	GAUS1500
	GO TO 20	GAUS1510
36	TZERO = TZERO*SCALE1	GAUS1530
	NTZERO = -1	GAUS1540
38	DO 39 J=1,JJ	GAUS1560
	B(J) = BMIN(J)	GAUS1570
39	BSTART(J) = BMIN(J)	GAUS1580
	Y1 = SQMIN	GAUS1600
	X1 = 0.0	GAUS1610
	JPARA = -1	GAUS1620
	MPATH = -1	GAUS1630
	GO TO 301	GAUS1640
40	SUM2 = SUM1	GAUS1660
	SUM1 = SUMSQ	GAUS1670
	NNPARA = 0	GAUS1680
	IF (SUM1 - SUM2) 19,45,19	GAUS1690
45	TZERO = SCALE1*TZERO	GAUS1710
	NDOWN = 0	GAUS1720
	T = 0.0	GAUS1730
	GO TO 8	GAUS1740
47	LIMIT = 99	GAUS1760
	GO TO 2	GAUS1770
49	$T = -0.5 * ((X1 * X1 - X2 * X2) * (Y1 - Y3) - (X1 * X1 - X3 * X3) * (Y1 - Y2)) /$	GAUS1800
	$X \quad ((X1 - X3) * (Y1 - Y2) - (X1 - X2) * (Y1 - Y3))$	GAUS1810
	MPATH = 1	GAUS1830
	JPARA = -1	GAUS1840
	NNPARA = 1	GAUS1850
	NDOWN = 0	GAUS1860
	GO TO 366	GAUS1870
53	WRITE (6,54)	GAUS1890
54	FORMAT (24H0 OVER-UNDERFLOW //)	GAUS1900
	MM(8) = -1	GAUS1910
	MM(10) = -1	GAUS1920
	GO TO 301	GAUS1930
56	WRITE (6,57)	GAUS1960

57	FORMAT (24H0 MATRIX IS SINGULAR //)	GAUS1970
	MM(8) = -1	GAUS1980
	MM(10) = -1	GAUS1990
	GO TO 301	GAUS2000
59	FORMAT (114H0CYCLE SUM OF SQUARES *****//)	GAUS2020
	X***** PARAMETERS *****//)	GAUS2030
58	FORMAT (16, F18.5, 5E18.6/(E42.6,4E18.6))	GAUS2040
60	DO 66 J=1,JJ	GAUS2090
	BTEST = B(J)-BSTART(J)-DEL(J)	GAUS2100
	IF (BTEST) 63,63,62	GAUS2110
62	B(J) = BSTART(J) + DEL(J)	GAUS2120
63	CONTINUE	GAUS2130
	BTEST = B(J) - BSTART(J) + DEL(J)	GAUS2140
	IF (BTEST) 65,65,66	GAUS2150
65	B(J) = BSTART(J)-DEL(J)	GAUS2160
66	CONTINUE	GAUS2170
	MPATH = -1	GAUS2190
67	DO 69 J=1,JJ	GAUS2200
69	BSTART(J) = B(J)	GAUS2210
	GO TO 10	GAUS2220
80	IF (NULL) 1000,82,82	GAUS2260
82	AV = 0.0	GAUS2270
	AV1 = 0.0	GAUS2280
	AV2 = 0.0	GAUS2290
	YMAX = 0.0	GAUS2300
	ZMAX = 0.0	GAUS2310
	ZZMAX = 0.0	GAUS2320
	DO 81 J=1,JJ	GAUS2330
81	B(J) = BMIN(J)	GAUS2340
	N = 1	GAUS2350
	DO 90 J=1,JJ	GAUS2360
90	WRITE (6,91) J,B(J)	GAUS2370
91	FORMAT (4H B 12, F14.5)	GAUS2380
	WRITE (6,100)	GAUS2390
92	WRITE (6,93)	GAUS2410
93	FORMAT (82H0NUMBER Y OBSERVED Y CALCULATED	GAUS2420
	X DELTA Y PCT DEVIATION ///)	GAUS2430
94	CALL YCOMP	GAUS2450
98	YC = CY(N)	GAUS2451
	DELY = YC - Z(NSFT,N)	
	RATIO = 100.0*(DELY/Z(NSFT,N))	
	ABSRAT = ABS (RATIO)	GAUS2480
	AV = AV + DELY	GAUS2490
	AV1 = AV1 + RATIO	GAUS2500
	AV2 = AV2 + ABSRAT	GAUS2510
	WRITE (6,95) N,Z(NSFT,N),YC,DELY,RATIO	GAUS2520
95	FORMAT (15,E23.5,E17.5,2E19.5)	GAUS2530
	ABSVAL = ABS (DELY)	GAUS2540
	IF (YMAX - ABSVAL) 96,96,97	GAUS2550
96	YMAX = ABSVAL	GAUS2560
	YYMAX = DELY	GAUS2570
	MARK = N	GAUS2580
97	IF (ZMAX-ABSRAT) 971,971,972	GAUS2590
971	ZMAX = ABSRAT	GAUS2600
	ZZMAX = RATIO	GAUS2610

	MARK1 = N		GAUS2620
972	N = N+1		GAUS2630
	IF (N - NUMBER) 98,98,99		GAUS2640
99	D = NUMBER		GAUS2660
	AV = AV/D		GAUS2670
	AV1 = AV1/D		GAUS2680
	AV2 = AV2/D		GAUS2690
	RTMNSQ = SQRT (SUMSQ/D)		GAUS2700
	WRITE (6,100)		GAUS2710
100	FORMAT(118H0*****//GAUS2720		
	X*****//GAUS2730		
	X/)		GAUS2740
	WRITE (6,101) AV,AV1,AV2		GAUS2750
101	FORMAT (30H0 AVERAGE DEVIATION E14.5,		GAUS2760
X	20H AVERAGE PCT DEV E14.5,		GAUS2770
X	20H AVE ABS PCT DEV E14.5)		GAUS2780
	WRITE (6,103) YYMAX,MARK		GAUS2790
103	FORMAT (30H0 MAXIMUM DEVIATION E14.5,I6)		GAUS2800
	WRITE (6,104) ZMAX,MARK1		GAUS2810
104	FORMAT (30H0 MAXIMUM PCT DEV E14.5,I6)		GAUS2820
	WRITE (6,105) RTMNSQ		GAUS2830
105	FORMAT (30H0 ROOT MEAN SQUARE DEVIATION E14.5)		GAUS2840
107	FORMAT (21H0 AT ITERATION I3, 24H, THE SUM OF SQUARES IS		GAUS2860
X	E16.7/ 22H0 FOR PARAMETER VALUES /1H0/(6E20.7))		GAUS2870
108	FORMAT (5F20.5)		GAUS2880
109	FORMAT (//)		GAUS2890
110	FORMAT (I20, F20.8)		GAUS2900
	WRITE (6,5)		GAUS2910
	IF (MM(8) + 2) 114,111,114		GAUS2920
111	WRITE (6,112)		GAUS2930
112	FORMAT (30H0 EXCEEDED ITERATION LIMIT //)		GAUS2940
	GO TO 999		GAUS2950
114	IF (MM(8) - 1) 999,8,999		GAUS2970
200	IF (NDOWN) 201,201,202		GAUS2990
201	T = T*SCALE1		GAUS3000
	GO TO 203		GAUS3010
202	T = T*SCALE2		GAUS3020
203	MPATH = 0		GAUS3030
	JPARA = JPARA + 1		GAUS3040
	GO TO 366		GAUS3050
301	MPATH = 0		GAUS3070
	NDOWN = 0		GAUS3080
	DO 305 M=1,JJ		GAUS3090
	C(M,1) = 0.0		GAUS3100
302	DO 305 N=1,JJ		GAUS3110
305	A(M,N) = 0.0		GAUS3120
	CALL DERIV		GAUS3170
	CALL YCOMP		GAUS3160
	DO 313 N = 1,NUMBER		GAUS3210
	DO 313 K = 1,JJ		GAUS3220
	C(K,1) = C(K,1) + FP(K,N) * (Z(NSSET,N) - CY(N))		GAUS3230
	DO 313 J = K,JJ		GAUS3240
313	A(K,J) = A(K,J) + FP(K,N) * FP(J,N)		GAUS3250
	IF (NTZFRD) 318,318,317		GAUS3300
317	TZFRD = 1.0		GAUS3310

318	T = TZERO	GAUS3320
	DO 316 I=2,JJ	GAUS3340
	II=I-1	GAUS3350
	DO 316 J=1,II	GAUS3360
316	A(I,J) = A(J,I)	GAUS3370
	IF (MM(10)) 319,331,319	GAUS3390
319	WRITE (6,320) NN	GAUS3410
320	FORMAT (19H0 MATRIX, ITERATION I3)	GAUS3420
	MMPATH = 0	GAUS3430
322	DO 323 I=1,JJ	GAUS3440
323	WRITE (6,324) (A(I,J), J=1,JJ)	GAUS3450
324	FORMAT (9E13.5)	GAUS3460
	DO 328 I=1,JJ	GAUS3480
328	WRITE (6,324) C(I,1)	GAUS3490
	IF (MMPATH) 350,331,350	GAUS3500
331	DO 340 I=1,JJ	GAUS3520
	DENOM = ABS (A(I,1))	GAUS3530
	DO 336 J=2,JJ	GAUS3540
	IF (DENOM-ABS (A(I,J))) 335,336,336	GAUS3550
335	DENOM = ABS (A(I,J))	GAUS3560
336	CONTINUE	GAUS3570
	DO 338 K=1,JJ	GAUS3580
338	A(I,K) = A(I,K)/DENOM*SCALE3	GAUS3590
340	C(I,1) = C(I,1)/DENOM*SCALE3	GAUS3600
	MMPATH = 1	GAUS3620
	IF (MM(10)) 322,350,322	GAUS3630
350	DO = 1.0	GAUS3650
	IF (MM(8)) 999,354,354	GAUS3660
354	CALL SOLV	GAUS3670
	GO TO (351,53,56), M	GAUS3680
351	IF (MM(6)) 352,363,352	GAUS3690
352	WRITE (6,353) (X(J,1), J=1,JJ)	GAUS3700
353	FORMAT (13H0 DELTA B(J) / (9E13.5))	GAUS3710
363	Y NORM = 0.0	GAUS3730
	DO 364 J=1,JJ	GAUS3740
364	Y NORM = Y NORM + X(J,1)**2	GAUS3750
	IF (Y NORM - X NORM) 366,366,365	GAUS3770
365	T = 0.5*SQRT (X NORM)/SQRT (Y NORM)	GAUS3780
	X1 = T	GAUS3790
366	DO 367 J=1,JJ	GAUS3800
367	R(J) = BSTART(J) + T*X(J,1)	GAUS3810
371	DO 376 J=1,JJ	GAUS3820
	IF (B(J)) 372,374,372	GAUS3830
372	XX = ABS ((B(J) - BSTART(J))/B(J))	GAUS3840
	GO TO 375	GAUS3850
374	XX = ABS (B(J) - BSTART(J))	GAUS3860
375	IF (XX-TOL1) 376,376,378	GAUS3870
376	CONTINUE	GAUS3880
	MM(8) = 2	GAUS3890
	GO TO 80	GAUS3900
378	IF (MM(7)) 60,379,60	GAUS3920
379	IF (NDOWN) 10,10,380	GAUS3940
380	IF (JPARA) 10,10,49	GAUS3960
400	IF (NULL) 6,401,401	GAUS3980
401	WRITE (6,100)	GAUS3990

IF (MM(5)) 406,403,403	GAUS3991
403 WRITE (6,402)	GAUS4000
402 FORMAT (15H OBSERVATIONS//)	GAUS4010
DO 404 N=1,NUMBER	GAUS4030
404 WRITE (6,405) N, (Z(J,N), J=1,12)	GAUS4040
405 FORMAT (14,RE14.5/(E18.5,7E14.5))	GAUS4050
406 WRITE (6,5) IDNTFC	GAUS4060
GO TO 6	GAUS4070
410 FORMAT (60H0 DATA Y COMP Y OBS DIFFE	GAUS4080
XRENCE)	GAUS4090
411 FORMAT (16,F20.7)	GAUS4100
412 FORMAT (12I6)	GAUS4110
420 TOL1 = 0.0001	GAUS4130
GO TO 1	GAUS4140
430 IF (B(23) - 1.0) 431,8,8	GAUS4160
431 T ZERO = B(23)	GAUS4170
WRITE (6,433) TZERO	GAUS4180
433 FORMAT (30H0 VECTOR SCALE FACTOR = B(23), E12.4//)	GAUS4190
GO TO 8	GAUS4200
440 IF (NULL) 446,441,441	GAUS4220
441 N SPIN = N SPIN + 1	GAUS4230
442 IF(MARK P) 444,443,444	GAUS4240
443 IF (N SPIN - 15) 445,444,444	GAUS4250
444 N SPIN = 0	GAUS4260
WRITE (6,59)	GAUS4270
445 WRITE (6,58) NN, SUMSQ, (B(J), J=1,JJ)	GAUS4280
446 X3 = X2	GAUS4290
X2 = X1	GAUS4300
X1 = T	GAUS4310
Y3 = Y2	GAUS4320
Y2 = Y1	GAUS4330
Y1 = SUMSQ	GAUS4340
IF (NNPARA) 40,19,40	GAUS4350
999 WRITE (6,991)	GAUS4360
DO 990 J=1,NN	GAUS4370
990 WRITE (6,405) J, RECORD(J)	GAUS4380
991 FORMAT (28H0 RECORD OF SUM OF SQUARES //)	GAUS4390
993 FORMAT (24H0 MINIMIZING PARAMETERS //)	GAUS4400
WRITE (6,993)	GAUS4410
WRITE (6,108) (BMIN(J), J=1,JJ)	GAUS4420
1000 RETURN	GAUS4450
END	GAUS4460


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$IBFTC SOLV DECK
SUBROUTINE SOLV
  DIMENSION XL(300),XV(300),TS(300),PI(300),TC(300),PC(300),W(300),
  ZNSYST(300),AD12(300),SA13(300),SB13(300),SC13(300),ALGA(300),
  3ALP13(300),GM12(300),RTLL(2),RTL(2),DM(3),YM(3),
  COMMON XL,XV,TS,P,TC,PC,W,NSYST,R,AD12,SA13,SB13,SC13,ALGA,ALP13,
  1GM12,DL,DV,NQ,RTLL,RTL,DM,YM
  DIMENSION A(20,21), C(20,1), LOC(20), CK(20)
  COMMON /COMB/ JJ
  COMMON /COMF/ A,C,M
  M = 1
  NP = JJ+ 1
  DO 11 I = 1,JJ
    CK(I) = 0.
  11 A(I,NP) = C(I,1)
  DO 50 I = 1,JJ
    IP = I + 1
  C***** FIND MAX ELEMENT IN I' TH COLUMN.
    AMAX = 0.
    DO 2 K = 1,JJ
      IF (AMAX - ABS(A(K,I))) 3,2,2
    C***** IS NEW MAX IN ROW PREVIOUSLY USED AS PIVOT
    3 IF (CK(K)) 4,4,2
    4 LOC(I) = K
      AMAX = ABS(A(K,I))
    2 CONTINUE
      IF (ABS(AMAX).LE.1.E-7) GO TO 99
  C***** MAX ELEMENT IN I' TH COLUMN IS A(L,I)
    5 L = LOC(I)
      CK(L) = 1.
  C***** PERFORM ELIMINATION. L IS PIVOT ROW, A(L,I) IS PIVOT ELEMENT.
    DO 50 J = 1,JJ
      IF (L-J) 6,50,6
    6 F = -A(J,I) / A(L,I)
      DO 40 K = IP,NP
    40 A(J,K) = A(J,K) + F * A(L,K)
    50 CONTINUE
      DO 200 I = 1,JJ
        L = LOC(I)
    200 A(I,1) = A(L,NP) / A(L,I)
      RETURN
  99 M = 3
      RETURN
      END

```

SOLV0010
 SOLV0020
 SOLV0030
 SOLV0040
 SOLV0050
 SOLV0060
 SOLV0070
 SOLV0080
 SOLV0090
 SOLV0100
 SOLV0110
 SOLV0120
 SOLV0130
 SOLV0140
 SOLV0150
 SOLV0160
 SOLV0170
 SOLV0180
 SOLV0190
 SOLV0200
 SOLV0210
 SOLV0220
 SOLV0230
 SOLV0240
 SOLV0250
 SOLV0260
 SOLV0261
 SOLV0262
 SOLV0270
 SOLV0280
 SOLV0290
 SOLV0300
 SOLV0310
 SOLV0320
 SOLV0330
 SOLV0340
 SOLV0350
 SOLV0360

\$IBFTC DERIV DECK

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SUBROUTINE DERIV
  DIMENSION XL(300),XV(300),TS(300),P(300),TC(300),PC(300),W(300),
  ZNSYST(300),AO12(300),SA13(300),SB13(300),SC13(300),ALGA(300),
  3ALP13(300),GM12(300),RTLL(2),RTLVL(2),DM(3),YM(3)
  COMMON XL,XV,TS,P,TC,PC,W,NSYST,R,AO12,SA13,SB13,SC13,ALGA,ALP13,
  1GM12,DL,DV,NQ,RTLL,RTLVL,DM,YM
  DIMENSION B(24),Z(12,300),CY(300),FP(20,300),H(20),Y(300)
  COMMON NUMBER,B,Z
  COMMON /COMB/ JJ
  COMMON /COMC/ CY
  COMMON /COMD/ FP
  IF (B(22)) 20,1,20
1 B(22) = 1.
  DO 7 J = 1,JJ
    TEST = ABS(B(J))
    IF (TEST - 0.001) 5,6,6
5 H(J) = 0.001
  GO TO 7
6 H(J) = 0.0001 * TEST
7 CONTINUE
20 DO 22 J = 1,JJ
  TEMP = B(J)
  B(J) = TEMP + H(J)
  CALL YCOMP
  DO 21 N = 1,NUMBER
21 Y(N) = CY(N)
  B(J) = TEMP - H(J)
  CALL YCOMP
  B(J) = TEMP
  DO 22 N = 1,NUMBER
22 FP(J,N) = (Y(N) - CY(N))/(2. * H(J))
  RETURN
END

```

DERIV010

DERIV020

DERIV030

DERIV040

DERIV050

DERIV060

DERIV070

DERIV080

DERIV090

DERIV100

DERIV110

DERIV120

DERIV130

DERIV140

DERIV150

DERIV160

DERIV170

DERIV180

DERIV190

DERIV200

DERIV210

DERIV220

DERIV230

DERIV240

DERIV250

DERIV260

DERIV270

DERIV280

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$IRFTC MULLER DECK
SUBROUTINE MULLER
  DIMENSION XL(300),XV(300),TS(300),P(300),TC(300),PC(300),W(300),
  ZNSYST(300),AQ12(300),SA13(300),SB13(300),SC13(300),ALGA(300),
  3ALP13(300),GM12(300),RTLL(2),RTLX(2),X(3),Y(3)
  COMMON XL,XV,TS,P,TC,PC,W,ZNSYST,R,AQ12,SA13,SB13,SC13,ALGA,ALP13,
  1GM12,DL,DV,NQ,RTLL,RTLX,X,Y
  X13=X(1)-X(3)
  X23=X(2)-X(3)
  Y13=Y(1)-Y(3)
  Y23=Y(2)-Y(3)
  YX1=Y13/X13
  YX2=Y23/X23
  X12=X(1)-X(2)
  A=(YX1-YX2)/X12
  B=(X13*YX2-X23*YX1)/X12
  C=Y(3)
  D=B*B-4.0*A*C
  IF (D) 1,2,3
1  D=-D
  GO TO 3
2  D=-2.0*C/B
  GO TO 9
3  IF (B) 4,4,5
4  D=-2.0*C/(B-SQRT(D))
  GO TO 9
5  D=-2.0*C/(B+SQRT(D))
9  YMAX=0.0
  DO 11 K=1,3
  IF (ABS(Y(K)) - YMAX) 11,111,10
10 YMAX = ABS(Y(K))
  MAX=K
11 CONTINUE
  X(MAX)=X(3)
  Y(MAX)=Y(3)
  7 X(3)=X(3)+D
13 RETURN
111 X(3)=(X(1)+X(2))/2.0
  GO TO 13
  END

```

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*IBFIC DENSITY .NODECK
SUBROUTINE DENSITY
  DIMENSION XL(300),XV(300),TS(300),X(300),TC(300),PC(300),W(300),
  ZNSYST(300),AO12(300),SA13(300),SB13(300),SC13(300),ALGA(300),
  3ALP13(300),GM12(300),BO1(300),CO12(300),RTL(2),RTL2(2),RTLNF(2),
  4 O(300),DM(3),YM(3)
  COMMON XL,XV,TS,Q,TC,PC,W,NSYST,R,AO12,SA13,SB13,SC13,ALGA,ALP13,
  1GM12,DL,DV,N,RTL,RTL2,DM,YM
  DIMENSION B(24), Z(12,300), MM(12)
  COMMON NUMBER,B,7
  COMMON /COMA/ MM
  COMMON /COMB/ JJ
  P=Q(N)
  T=TS(N)
  DV = .1
  DL = 1.
  DO 77 I=1,2
    K=N+I-1
    BO1( K) =B(1)+B(2)*W( K)+B(3)*W( K)*W( K)
    BO1( K) =BO1( K) *R*TC( K)/PL( K)
    77 CO12( K)= SQRT(CO12( K)*R*R*TC( K)**4/PC( K))
    MMM=0
    M = 1
    GO TO 22
  23 M = 0
  22 IF (M) 24,24,25
  25 DO 26 K=1,2
    I=N+K-1
    26 X(I) = XV(I)
    GO TO 27
  24 DO 1 K=1,2
    I=N+K-1
    1 X(I) = XL(I)
  110 CONTINUE
  27 XBO = 0.
  XAO = 0.
  XCO = 0.
  XSB = 0.
  XSA = 0.
  XSC = 0.
  XALP = 0.
  XGM = 0.
  DO 16 K=1,2
    I=N+K-1
    XBO = X(I)*BO1(I) + XBO
    XAO = X(I)*AO12(I) + XAO
    XCO = X(I)*CO12(I) + XCO
    XSB = X(I)*SB13(I) + XSB
    XSA = X(I)*SA13(I) + XSA
    XSC = X(I)*SC13(I) + XSC
    XALP = X(I)*ALP13(I) + XALP
  16 XGM = X(I)*GM12(I) + XGM
  BO = XBO
  17 AO = XAO*XAO

```

DECK0020
DECK0030
DECK0040
DECK0050

REF. 1+

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19 C0 = XC0*XC0
29 S3 = XSH**3
   SA = XSA**3
   SC = XSC**3
   ALP = XALP**3
21 GM = XGM*XGM
30 CONTINUE
   IF (M) 97,97,96
97 MN=0
   AINCR= .01
   D=0.
92 EXDG= EXP(-GM*D*D)
   GMD2= GM*D*D
   DT03= D**3
   DT05= D**5
   DT06= D**6
   AKD = R*T*D + (B0*R*T-A0-C0/(T*T))*D*D + (SB*R*T-SA)*DT03
1   + SA*ALP* DT06 + SC* DT03 *EXDG/(T*T)
2   + SC*GM*EXDG* DT05 /(T*T) - P
   IF (AKD) 90,91,91
90 IF (MN) 93,93,94
93 D=D+AINCR
   GO TO 92
91 MN=1
   IF (D-3.0) 93,95,95
95 GO TO 96
94 AINCR = 0.05
   GO TO 34
96 D=0.
   AINCR = 0.05
34 EXDG = EXP(-GM*D*D)
   GMD2 = GM*D*D
   DT03 =D**3
   DT05 =D**5
   DT06 =D**6
   AKD = R*T*D + (B0*R*T-A0-C0/(T*T))*D*D + (SB*R*T-SA)*DT03
1   + SA*ALP* DT06 + SC* DT03 *EXDG/(T*T)
2   + SC*GM*EXDG* DT05 /(T*T) - P
   IF(AKD)31,432,33
31 DP=0
   AKDP=AKD
   D=D+AINCR
   GO TO 34
33 DM(1)=DP
   DM(2)=D
   DM(3)=(DP+D)/2.0
   YM(1)=AKDP
   YM(2)=AKD
   YP=DM(1)
   GO TO 371
38 YP=DM(3)
371 EXDG= EXP(-GM*DM(3)*DM(3))
   GMD2= GM*DM(3)*DM(3)
   DT03= DM(3)*DM(3)*DM(3)
   DT05= DM(3)**5

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DT06= DM(3)**6
YM(3)=R*T*DM(3) + (B0*R*T-A0-C0/(T*T))*DM(3)*DM(3) + (SB*R*T-SA)*
1 DT03 + SA*ALP*DT06 + SC*DT03*EXDG/(T*T)
2 + SC*GM*FXDG* DT05 /(T*T) - P
CALL MULLER
IF ( ABS(DM(3)-YP)-0.00001 ) 39, 38, 38
39 D=DM(3)
432 DO 41 K=1,2
I=N+K-1
FU2A= (B0+B01(I))*R*T
FU2B= 2.*XA0*AO12(I)
FU2C= 2.*XCO*CO12(I)/(T*T)
FU2= (FU2A-FU2B-FU2C)*D
FU3A= R*T*XS*XS*SB13(I)
FU3B= XSA*XSA*SA13(I)
FU3C= FU3A-FU3B
FU3= 1.5*FU3C*D
FU4A= SA*XALP*XALP*ALP13(I)
FU4B= ALP*XSA*XSA*SA13(I)
FU4C= FU4A+FU4B
FU4= 0.6*FU4C*D*D*D
FXDG= EXP(-GM*D)
GMD2= GM*D
FU5A= (1.-EXDG)/GMD2
FU5B= FXDG/2.
FU5C= FU5A-FU5B
FU5= 3.*D*D*XSC*XSC*SC13(I)*FU5C/(T*T)
FU6A= FU5A
FU6B= EXDG
FU6C= GMD2*EXDG/2.
FU6D= FU6A-FU6B-FU6C
FU6= 2.*D*D*SC*GM12(I)*FU6D/(T*T*XGM)
RTLNF(K)= FU2+FU3+FU4+FU5-FU6
IF (M) 60,60,61
61 RTLV(K)=RTLNF(K)
GO TO 41
60 RTLL(K)=RTLNF(K)
41 CONTINUE
IF (M) 70,70,42
42 DV=D
GO TO 23
70 DL=D
48 CONTINUE
RETURN
END

```

```

$IBFTC YCOMP  NONFCK
SUBROUTINE YCOMP
DIMENSION XL(300),XV(300),TS(300),P(300),TC(300),PC(300),W(300),
ZNSYST(300),AD12(300),SA13(300),SB13(300),SC13(300),ALGA(300),
3ALP13(300),GM12(300),RTLL(2),RTLTV(2),DM(3),YM(3)
COMMON XL,XV,TS,P,TC,PC,W,NSYST,R,AD12,SA13,SB13,SC13,ALGA,ALP13,
1GM12,DL,DV,N,RTLL,RTLTV,DM,YM
DIMENSION B(24),Z(12,300),CY(300)
COMMON NUMBER,B,Z
COMMON /COMC/ CY
NUMBER=NUMBER-1
DO 1 N=1,NUMBER,2
CALL DENSTY
RT=R*Z(1,N)
CY(N) =(DL* EXP((1.0/RT)*RTLL(1)))/(DV* EXP((1.0/RT)*RTLTV(1)))
CY(N) =CY(N)/(XV(N)/XL(N))
CY(N+1)=(DL* EXP((1.0/RT)*RTLL(2)))/(DV* EXP((1.0/RT)*RTLTV(2)))
1 CY(N+1)=CY(N+1)/(XV(N+1)/XL(N+1))
RETURN
END

```

YCOMP010

YCOMP020

YCOMP030

YCOMP040

YCOMP200

YCOMP210

518FTC RWRCST N0DECK

SUBROUTINE RWRCST

DIMENSION XL(300),XV(300),TS(300),P(300),TC(300),PC(300),W(300),
ZNSYST(300),A012(300),SA13(300),SB13(300),SC13(300),ALGA(300),
BALP13(300),GM12(300),RTLL(2),RTLX(2),DM(3),YM(3)

COMMON XL,XV,TS,P,TC,PC,W,ZNSYST,R,A012,SA13,SB13,SC13,ALGA,ALP13,
GM12,DL,DV,NQ,RTLL,RTLX,DM,YM

DIMENSION B(24), Z(12,300), MM(12)

COMMON NUMBER,B,Z

COMMON /COMA/ MM

COMMON /COMR/ JJ

DECK0020

DECK0030

DECK0040

DECK0050

MBER=NUMBER-1

DO 10 N=1,MBER ,2

DO 10 I=1,2

K=N+I-1

A012(K) =0.3432582-0.1275206*W(K)-0.5091306*W(K)*W(K)

SA13(K) =0.02358656+0.2902838*W(K)-0.2954134*W(K)*W(K)

SB13(K) =0.02754038+0.1310085*W(K)-0.1349244*W(K)*W(K)

SC13(K) =0.03569403+0.1852974*W(K)-0.2301246*W(K)*W(K)

ALGA(K) =0.0000875

ALP13(K)=ALGA(K)**0.33333333/SA13(K)

GM12(K)=0.05205804-0.09063990*W(K)+0.1050599*W(K)*W(K)

R=10.7335

A012(K)=SQRT(A012(K)*R*R*TC(K)*TC(K)/PC(K))

SA13(K)=(SA13(K)*R*R*R*TC(K)**3/PC(K)**2)**0.33333333

SB13(K)=(SB13(K)*R*R*R*TC(K)**2/(PC(K)*PC(K)))**0.33333333

SC13(K)=(SC13(K)*R*R*R*TC(K)**5/PC(K)**2)**0.33333333

ALGA(K)=ALGA(K)*R**6*TC(K)**6/PC(K)**5

ALP13(K)=ALGA(K)**0.33333333/SA13(K)

GM12(K)=SQRT(GM12(K)*R*R*TC(K)*TC(K)/(PC(K)*PC(K)))

10 CONTINUE

RETURN

END

APPENDIX H

BINARY SYSTEM DATA USED IN CORRELATION DEVELOPMENT

TABLE XXXI
PARAFFIN DATA

Methane - n-Heptane (49)			
Temp °F	Pressure psia	Mole Fraction	
		Vapor y_1	Liquid x_1
100.	200.	0.9866	0.0640
100.	800.	0.9911	0.2340
100.	1500.	0.9881	0.3963
100.	2750.	0.9620	0.6400
220.	200.	0.8942	0.0492
220.	1000.	0.9558	0.2410
220.	2500.	0.9280	0.5450
280.	200.	0.7481	0.0405
280.	1000.	0.9100	0.2290
280.	2250.	0.8900	0.4880
400.	200.	0.2060	0.0132
400.	1000.	0.6930	0.2290
400.	1500.	0.6940	0.3060

Methane - n-Decane System (45)			
Temp °F	Pressure psia	Mole Fraction	
		Vapor y_1	Liquid x_1
100	4000.	0.9837	0.6871
220.	200.	0.9890	0.0543
220.	3750.	0.9716	0.6442
280.	200.	0.9665	0.0496
280.	1000.	0.9870	0.0130
280.	3500.	0.9608	0.6168
400.	400.	0.8970	0.0927
400.	1000.	0.9358	0.2257
400.	2750.	0.9137	0.5427

TABLE XXXI (Continued)

Ethane - n-Heptane System (27)			
Temp °F	Pressure psia	Mole Fraction	
		Vapor y_2	Liquid x_2
100.	100.	0.982	0.170
200.	200.	0.921	0.158
200.	400.	0.950	0.359
200.	800.	0.9585	0.623
300.	200.	0.692	0.062
300.	600.	0.851	0.3415
300.	1000.	0.854	0.5635
400.	200.	0.192	0.0105
400.	400.	0.501	0.1035
400.	800.	0.636	0.338
Ethane - n-Decane System (46)			
Temp °F	Pressure psia	Mole Fraction	
		Vapor y_2	Liquid x_2
220.	1100.	0.9902	0.7098
220.	1300.	0.9846	0.7987
220.	1500.	0.9586	0.8986
280.	500.	0.9833	0.3164
280.	1000.	0.9810	0.5567
280.	1600.	0.9353	0.7987
400.	500.	0.9097	0.2357
400.	1000.	0.9138	0.4529
400.	1600.	0.8389	0.6967
Propane - n-Pentane System (56)			
Temp °F	Pressure psia	Mole Fraction	
		Vapor y_3	Liquid x_3
190.	200.	0.716	0.339
190.	450.	0.968	0.876
220.	125.	0.247	0.064
220.	300.	0.721	0.413
220.	500.	0.897	0.759
280.	250.	0.253	0.093
280.	350.	0.452	0.231
280.	500.	0.635	0.437
310.	300.	0.164	0.065
310.	400.	0.358	0.184

TABLE XXXII
NAPHTHENE DATA

Methane - Cyclopentane (12)			
Temp °F	Pressure psia	Mole Fraction	
		Vapor y_1	Liquid x_1
150.	100.	0.755	0.107
150.	200.	0.868	0.038
150.	800.	0.942	0.161
150.	2250.	0.919	0.451

Methane - Cyclohexane (50)			
Temp °F	Pressure psia	Mole Fraction	
		Vapor y_1	Liquid x_1
100.	200.	0.9793	0.0414
100.	400.	0.9860	0.0820
100.	100.	0.9885	0.1977
100.	3000.	0.9539	0.5365
160.	200.	0.9380	0.0365
160.	400.	0.9616	0.0740
160.	1000.	0.9709	0.1812
160.	3000.	0.9370	0.5180
220.	200.	0.8437	0.0318
220.	600.	0.9249	0.1028
220.	1250.	0.9417	0.2134
220.	2750.	0.9109	0.4610
280.	200.	0.6520	0.0248
280.	600.	0.8464	0.0951
280.	1250.	0.8939	0.2054
280.	2500.	0.8690	0.4134
340.	200.	0.3653	0.0148
340.	600.	0.7236	0.0870
340.	1250.	0.8019	0.1984
340.	2250.	0.7886	0.3697

TABLE XXXII (Continued)

Methane - Cyclohexane (60)			
Temp °F	Pressure psia	Mole Fraction	
		Vapor y_1	Liquid x_1
104.	284.4	0.952	0.0715
104.	568.8	0.981	0.126
104.	853.2	0.983	0.182
104.	1422.	0.982	0.297
212.	284.4	0.870	0.055
302.	568.8	0.891	0.093
302.	853.2	0.925	0.151
302.	1422.	0.923	0.267

Methane - Cyclohexane (12)			
Temp °F	Pressure psia	Mole Fraction	
		Vapor y_1	Liquid x_1
150.	100.	0.927	0.018
150.	200.	0.965	0.037
150.	800.	0.979	0.150
150.	3000.	0.951	0.535

Methane - methylcyclohexane (12)			
Temp °F	Pressure psia	Mole Fraction	
		Vapor y_1	Liquid x_1
150.	100.	0.948	0.022
150.	200.	0.968	0.043
150.	800.	0.983	0.171
150.	3000.	0.952	0.569

TABLE XXXII (Continued)

Ethane - Cyclohexane (28)			
Temp °F	Pressure psia	Mole Fraction	
		Vapor y_2	Liquid x_2
100.	100.	0.9374	0.1250
100.	200.	0.9700	0.2695
100.	400.	0.9858	0.5579
150.	100.	0.8850	0.0876
150.	200.	0.9351	0.1841
150.	400.	0.9659	0.3715
150.	600.	0.9819	0.5643
200.	100.	0.7852	0.0577
200.	200.	0.8800	0.1304
200.	600.	0.9516	0.4174
200.	800.	0.9386	0.5521
250.	100.	0.5842	0.0330
250.	200.	0.7808	0.0903
250.	600.	0.8940	0.3251
250.	1000.	0.9082	0.5606
300.	100.	0.2175	0.0095
300.	200.	0.5892	0.0556
300.	600.	0.8044	0.2620
300.	1000.	0.8375	0.4602
350.	200.	0.2974	0.0242
350.	400.	0.5889	0.1178
350.	800.	0.7241	0.2980
350.	1000.	0.7335	0.3944
400.	400.	0.3786	0.0656
400.	600.	0.5293	0.1594
400.	800.	0.5838	0.2432

TABLE XXXIII
AROMATIC DATA

Methane - Benzene System (19)			
Temp °F	Pressure psia	Mole Fraction	
		Vapor y_1	Liquid x_1
150.	100.	0.925	0.075
150.	200.	0.957	0.030
150.	600.	0.980	0.090
150.	3000.	0.956	0.400

Methane - Benzene System (60)			
Temp °F	Pressure psia	Mole Fraction	
		Vapor y_1	Liquid x_1
104.	284.4	0.988	0.045
104.	568.8	0.994	0.108
104.	853.2	0.990	0.151
104.	1422.	0.920	0.221
212.	284.4	0.950	0.040
302.	284.4	0.875	0.035
302.	568.8	0.918	0.081
302.	853.2	0.931	0.120
302.	1422.	0.929	0.192

Methane - Toluene System (19)			
Temp °F	Pressure psia	Mole Fraction	
		Vapor y_1	Liquid x_1
150.	100.	0.973	0.017
150.	300.	0.987	0.052
150.	700.	0.990	0.120
150.	3000.	0.976	0.452

TABLE XXXIII (Continued)

Methane - Toluene System (60)			
Temp °F	Pressure psia	Mole Fraction	
		Vapor y_1	Liquid x_1
212.	284.4	0.959	0.045
302.	284.4	0.945	0.042
302.	568.8	0.965	0.078
302.	853.2	0.966	0.114
302.	1422.	0.965	0.207
Ethane - Benzene System (29)			
Temp °F	Pressure psia	Mole Fraction	
		Vapor y_1	Liquid x_1
122.	300.	0.9700	0.2519
122.	400.	0.9775	0.6225
122.	600.	0.9835	0.3580
212.	300.	0.8824	0.1476
212.	400.	0.9054	0.1986
212.	600.	0.9212	0.3144
212.	1000.	0.9206	0.5754
302.	300.	0.6671	0.0905
302.	400.	0.7252	0.1304
302.	800.	0.8114	0.2908
302.	1000.	0.8112	0.3808
392.	300.	0.2584	0.0305
392.	400.	0.3957	0.0646
392.	800.	0.6008	0.2016
392.	1000.	0.6284	0.2686

TABLE XXXIII (Continued)

Propane - Benzene System (20)			
Temp °F	Pressure psia	Mole Fraction	
		Vapor y_3	Liquid x_3
160.	150.	0.9273	0.3210
160.	300.	0.9844	0.8069
220.	150.	0.7895	0.1668
220.	350.	0.9185	0.5151
220.	500.	0.9600	0.7805
280.	100.	0.3340	0.0332
280.	200.	0.6462	0.1322
280.	400.	0.8087	0.3511
280.	600.	0.8636	0.5989
340.	150.	0.1326	0.0181
340.	300.	0.5446	0.1323
340.	500.	0.6971	0.2942
340.	650.	0.7417	0.4218
400.	300.	0.2319	0.0491
400.	400.	0.3821	0.1090
400.	600.	0.5357	0.2382
400.	700.	0.5786	0.3105

Propane - Toluene System (33)

Temp °F	Pressure psia	Mole Fraction	
		Vapor y_3	Liquid x_3
122.	157.2	0.973	0.600
122.	225.5	0.980	0.917
167.	158.	0.960	0.356
167.	235.	0.964	0.554
167.	301.9	0.978	0.759
202.3	141.	0.969	0.217
248.	235.2	0.894	0.278
248.	355.5	0.891	0.441
248.	515.5	0.928	0.684
264.2	380.	0.905	0.403
264.2	535.8	0.921	0.606

APPENDIX I

CARBON DIOXIDE SYSTEM DATA

TABLE XXXIV

EXPERIMENTAL xy DATA: LOW CO₂ AT 150°F (68)

P, psia		C ₁	CO ₂	C ₂	C ₃	C ₅	C ₈	C ₁₀
200.	y	0.8253	0.1170	0.0243	0.0053	.0175	.0076	.0030
	x	0.0542	0.0162	0.0055	0.0037	.1513	.1530	.6161
	K	15.2	7.21	4.43	1.44	.116	.0496	.0048
300.	y	0.8307	0.0905	0.0399	0.0127	.0168	.0070	.0024
	x	0.0901	0.0178	0.0160	0.0126	.1449	.1461	.5726
	K	9.22	5.09	2.49	1.00	.116	.0478	.0042
500.	y	0.8370	0.0911	0.0397	0.0132	.0122	.0051	.0018
	x	0.1370	0.0257	0.0209	0.0161	.1340	.1352	.5311
	K	6.11	3.54	1.89	0.817	.0913	.0379	.0033
1000.	y	0.8046	0.1318	0.0367	0.0101	.0100	.0053	.0015
	x	0.2784	0.0793	0.0365	0.0235	.1092	.1149	.3583
	K	2.89	1.66	1.01	0.431	.0912	.0462	.0042
1500.	y	0.8402	0.0848	0.0469	.0110	.0094	.0057	.0021
	x	0.3535	0.0570	0.0448	.0308	.0836	.0862	.3441
	K	2.38	1.49	1.05	.355	.113	.0658	.0060
2000.	y	0.8201	0.0921	0.0504	0.0197	.0079	.0052	.0046
	x	0.4996	0.0808	0.0654	0.0457	.0485	.0513	.2088
	K	1.64	1.14	0.770	0.431	.163	.102	.0220
2500.	y	0.8113	0.0948	0.0513	0.219	.0083	.0063	.0061
	x	0.5609	0.0808	0.0591	0.0395	.0404	.0430	.1763
	K	1.45	1.17	0.868	0.554	.206	.146	.0346
3001.		One Phase						

TABLE XXXV

EXPERIMENTAL xy DATA: LOW CO₂ at 250°F (68)

[illegible]

EXPERIMENTAL xy DATA: HIGH CO₂ AT 150°F (68)

APPENDIX J

PHYSICAL CONSTANTS

TABLE XXXVIII

CALCULATION CONSTANTS FOR PURE COMPONENTS

Component	Critical Temp °R	Critical Pressure psia	Acentric Factor ω	Molecular Weight
Methane	343.13	669.7	0.0130	16.043
Ethane	549.77	708.3	0.1050	30.070
Propane	665.68	616.3	0.1520	44.097
n-Pentane	845.08	487.3	0.2520	72.151
n-Hexane	913.14	436.6	0.2899	86.178
n-Heptane	972.25	397.5	0.3520	100.206
n-Decane	1111.7	304.	0.4869	142.287
Cyclopentane	921.17	654.7	0.2050	70.134
Cyclohexane	995.23	591.5	0.2030	84.163
Methylcyclohexane	1029.83	504.4	0.2420	98.190
Decahydronaphthalene	1207.17	370.81	0.3527	138.164
Benzene	1012.70	714.	0.2150	78.108
Toluene	1069.2	590.	0.2518	92.142
1-methylnaphthalene	1384.47	517.55	0.3603	142.190
Carbondioxide	547.43	1071.	0.1060	44.010

VITA

Andris John Klekers

Candidate for the Degree of

Doctor of Philosophy

Thesis: THE PHASE BEHAVIOR IN SIX COMPONENT SYSTEMS
CONTAINING METHANE, ETHANE, PROPANE, N-PENTANE,
N-HEXANE, N-DECANE, DECAHYDRONAPHTHALENE, AND
1-METHYLNAPHTHALENE

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