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VAPOR-LIQUID EQUILIBRIUM RATIOS IN HYDROGEN HYDROCARBON MIXTURES

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NOMENCLATURE

A_N	constant in Chao's equation
A,B	constants in Redlich-Kwong Equation of State
A,B	constants in Van Laar Equation
B(T)	second virial coefficient
C(T)	third virial coefficient
D	vapor product stream flow rate
E	internal energy
F	feed stream flow rate
F.	Fahrenheit
G	Gibbs Free Energy
H	enthalpy
K	vapor-liquid equilibrium composition ratio
K.	Kelvin
L	liquid product stream flow rate
N	number
P	pressure
P.E.	probable error
R	gas constant
S	entropy
T	temperature
V	volume
a,b	constants in van der Waal's Equation of State
a,b	constants in the Redlich-Kwong Equation of State
n	moles

x	mole fraction in the liquid phase
y	mole fraction in the vapor phase
z	compressibility factor
Δ	difference
Λ	constant in hydrogen second virial coefficient quantum mechanical correlation
α	coefficient of thermal expansion
δ	solubility parameter
γ	liquid activity coefficient
Θ	function relating virial coefficients to volume
ν	pure component liquid fugacity coefficient
ρ	density
σ	standard deviation
φ	vapor phase fugacity coefficient
ω	accentric factor
ω'	pseudo-accentric factor

Subscripts

B	second virial coefficient
C	critical property
F	property of feed stream
M	mixture
Mix	mixing
N	component designation
V	vaporization
i,j,k	component designation

r	reduced property
-	molar quantity

Superscripts

L	liquid
V	vapor
-	partial molal quantity
o	pure component property

ABSTRACT

This research was undertaken for the purpose of providing vapor-liquid equilibrium composition data in multi-component mixtures of hydrogen and hydrocarbons of varying molecular structure. The experimental results have been used to evaluate the applicability of one of the more promising current analytical correlations, based on experimental vapor-liquid equilibrium data for binary systems, for use in predicting equilibrium compositions in multi-component systems.

Experimental equipment was built to operate at pressures to 5000 psi and at temperatures to 400° F. The equilibrium cell was internally agitated and had sample ports through which samples of multi-component liquid phase and vapor phase were withdrawn for analysis on a mass spectrometer.

Compounds studied in this work were hydrogen, benzene, cyclohexane and hexane. Data was taken on three ternary systems and on one quaternary system at temperatures of 100° and 200° F. and at pressures of 500 and 1000 psi. All systems contained hydrogen. A total of 170 vapor and 170 liquid samples, representing 28 different equilibrium mixtures, was obtained.

The correlation evaluated in this work was modified to improve the prediction of experimentally obtained hydrogen equilibrium composition ratios. The modified equation gave results comparable to existing correlations for hydrocarbon equilibrium composition ratios. Parameters used in this correlation were evaluated from pure component data as well as from experimental data on binary systems which had been reported in the literature. The vapor-liquid equilibrium composition ratios of all components in the multi-component mixtures were predicted to within approximately 20% of the measured ratios despite the relatively low hydrogen liquid and hydrocarbon vapor concentrations encountered in this work. This suggests that correlations developed from binary vapor liquid equilibrium data can be applied to multicomponent data. However, further efforts in this area are indicated in order to reduce the deviation of the predicted from the measured equilibrium ratios.

INTRODUCTION

At present, engineers are utilizing vapor-liquid equilibrium composition ratios obtained from such generalized correlations as the NGAA K-Value charts(15) and the Kellogg Charts(30) for design work. These charts are the culmination of over thirty years work, which began with the recognition that a combination of Raoult's and Dalton's Laws were inadequate to describe a vapor-liquid system in equilibrium over ranges of pressure and temperature of interest.

A basic parameter in the NGAA charts is a parameter called "convergence pressure." The concept of convergence pressure evolved through a realization that the phase rule variables in two component systems are completely defined by the specification of two of the variables generally known to the design engineer -- namely, the system temperature and pressure. Further, it was recognized that there is a unique critical point locus for any two component system. This led to an attempt to classify any multi-component system as a pseudo-binary system consisting of a pseudo-light and a pseudo-heavy component. It was found that the composition of the pseudo-binary system could be specified with satisfactory accuracy if the system temperature and pressure were extrapolated along a constant temperature line to the critical locus of the system, rather than along a constant composition line. The intersection of this isothermal extension of the system pressure and temperature with the critical locus is used as a correlating pressure, called the convergence pressure.

The NGAA charts are based on experimental data for aliphatic hydrocarbons, and as the physical properties of this homologous group happen to have a definite regularity, this correlation method seemed to meet with success. However, Solomon(56) has shown that these charts may give results in error by as much as 250% for hydrocarbon mixtures containing aromatics. Further, as more experimental data has become available, it has been found that these charts are less and less reliable as the convergence pressure parameter increases. For example, the convergence pressure of close boiling mixtures such as toluene and hexane may be less than 500 psi, whereas the convergence pressure for wide boiling mixtures such as hydrogen and hexane will generally be greater than 10,000 psi.

The concept of convergence pressure has always been a difficult concept to apply. In order to improve the usefulness of the existing NGAA charts, a considerable amount of effort has been expended on improving the prediction of convergence pressures. Lenoir and White(36,37) developed an empirical method of estimating convergence pressures using effective boiling temperatures and weighting factors. They found that each component contributed to the effective boiling points of the pseudo-binary components, and proposed the use of weighting factors to account for the fact that the lightest component in the mixture contributed more to the effective boiling temperature of the pseudo-light component than some intermediate component, whereas the heaviest component had the greatest effect on the pseudo-heavy component boiling point. This method presupposes a knowledge of liquid phase composition.

In order to improve the predictability of wide boiling mixtures, Lenoir and Hipkin(35) developed a generalized convergence pressure correlation for systems containing hydrogen and aliphatic hydrocarbons. This correlation was based on the data existing at the time of their paper, but failed to predict experimental convergence pressures for the system hydrogen-hexane that were later reported by Nichols, Reamer and Sage.(41)

Another set of charts currently in use is the "Kellogg Charts"(30), developed from the Benedict-Webb-Rubin Equation of State(1,2,3) by Benedict, Webb, Rubin and Friend(4,5). These charts utilize the molal average boiling point for each phase as the composition parameter. Vapor-liquid equilibrium values for 12 aliphatic hydrocarbons, from methane to heptane, are represented on 324 charts, including pressures between 14.7 and 3600 psi and temperatures from -100° to 400°F.

However, these charts do not include aromatic compounds, and interpolation is tedious and often inaccurate. DePriester(13) has attempted to consolidate the charts to show the effect of all the variables continuously. He has reduced the number of graphs required for each hydrocarbon to two, while retaining almost the same accuracy contained in the original charts.

At present, further efforts are being made to develop vapor-liquid equilibrium correlations based on the use of equations of state. These correlation techniques may be programmed for a modern computer, or they may be drawn up in the form of nomographs and charts. However, most of the work thus far is based on experimental data from binary systems.

This research has been undertaken to provide vapor-liquid equilibrium data on wide-boiling, multi-component mixtures. The light component studied is hydrogen, while the heavy components are hydrocarbons with relatively similar physical properties, but different molecular structure; namely, benzene, cyclohexane and hexane. The data thus obtained has been used to evaluate the applicability of one of the more promising current analytical correlation methods to multi-component mixtures, and an attempt has been made to improve this correlation.

EXPERIMENTAL CONDITIONS OF STUDY

Ternary and quaternary mixtures of hydrogen, benzene, cyclohexane and hexane have been studied at 100° and 200°F. and at pressures of 500 and 1000 psi.

The equipment built to study these systems was theoretically capable of operating at pressures to 5,000 psi and at temperatures to 400°F. The equipment was statically pressure tested to 7500 psi.

Although the experimental apparatus was located near large windows in the laboratory, there was no means provided for holding and venting fumes directly from the temperature control bath. As glycerine, the heat transfer medium, gives off heavy vapors at elevated temperatures, the operating temperatures in this experiment were arbitrarily limited to 200°F.

A gas compressor unit was incorporated into this equipment, but in this experiment, hydrogen was used directly from the high pressure supply cylinders. The maximum operating pressure studied was approximately 1100 psi.

MATERIALS USED IN STUDY

The hydrocarbons used in this study were obtained from the stock of the Chemistry Department at the University of Michigan. Hydrogen was obtained through the University Plant Department. The manufacturers of these raw materials and the approximate purity of the components, as measured by means of a mass spectrometer, are tabulated below.

TABLE I

PURITY OF MATERIALS

Component	Manufacturer	Analyzed Purity
Benzene	Phillips Petroleum Co., Pure	99.5%
Cyclohexane	Merck Chemical Co., Reagent Grade	99.67%
Hexane	Eastman Kodak Co., Red Label	99.54%
Hydrogen	Mathieson Co., Electrolytic, water pumped	99.5%

EQUIPMENT DESIGN

As a first step in the study of vapor-liquid equilibrium in systems containing hydrogen, attention was directed to the many different types of experimental apparatus that might be used. The initial criteria used in examining possible designs was that the equipment be simple and that analysis of the sample be relatively fool-proof.

A glass bubble-point dew-point apparatus, similar to that used by Professor Webster B. Kay at Ohio State University, was first considered, as this is probably one of the less complex types of apparatus, and the analysis of vapor and liquid samples is simple and accurate. The apparatus is described in detail by Kay(27,28). However, the utility of such apparatus for determining vapor-liquid equilibrium is limited to binary mixtures for which complete phase diagrams may be drawn. Further, the entire scheme is dependent upon the fact that the composition of the sample charged to the cell be known accurately at all times.

Professor Kay has pointed out that hydrogen is difficult to contain within a glass system at high temperatures.(29) Soft glass seems to be best, but it is also the least able to withstand large temperature variations. If a component, such as hydrogen, should leak out of this apparatus during the run, the data obtained would be worthless.

After considering the limitations of this type of apparatus and considering the fact that multi-component systems would be of interest, attention was directed to systems in which samples could be withdrawn and analyzed independently of the equilibrium apparatus. Here, the choice was between a dynamic type of system, perhaps similar to a recirculating type still, and a static type system, in which samples would be withdrawn from the cell itself, after they had come to equilibrium.

Little effort was devoted to investigating a dynamic type equilibrium cell, because of the questionability of attaining true equilibrium in such apparatus. Generally, the maintenance of steady state conditions in a dynamic type cell over a period of time is considered to be equivalent to the attainment of equilibrium. Yet the process of flow itself suggests that potentials exist within the system. Entrainment also appears to be a major problem in such systems. Therefore, attention was directed toward a static type equilibrium cell.

Considering the equipment that was available within the University for use on this project, the choice of an equilibrium cell narrowed to a decision between a rocking bomb apparatus, and an Autoclave Engineering Magne-Dash cell, which was designed by Standard Oil Co. of Indiana. Because of possible problems with moving parts and connections at the high pressures anticipated for the rocking bomb, and because the Magne-Dash cell lends itself to use with a liquid temperature control bath, the decision was made to use the Magne-Dash cell as the equilibrium cell in the vapor-liquid equilibrium equipment.

DESCRIPTION OF THE EQUIPMENT

The system finally decided upon may logically be divided into three main parts; a feed system, an equilibrium section, and a sampling system. These are shown in the schematic diagram in Figure 1.

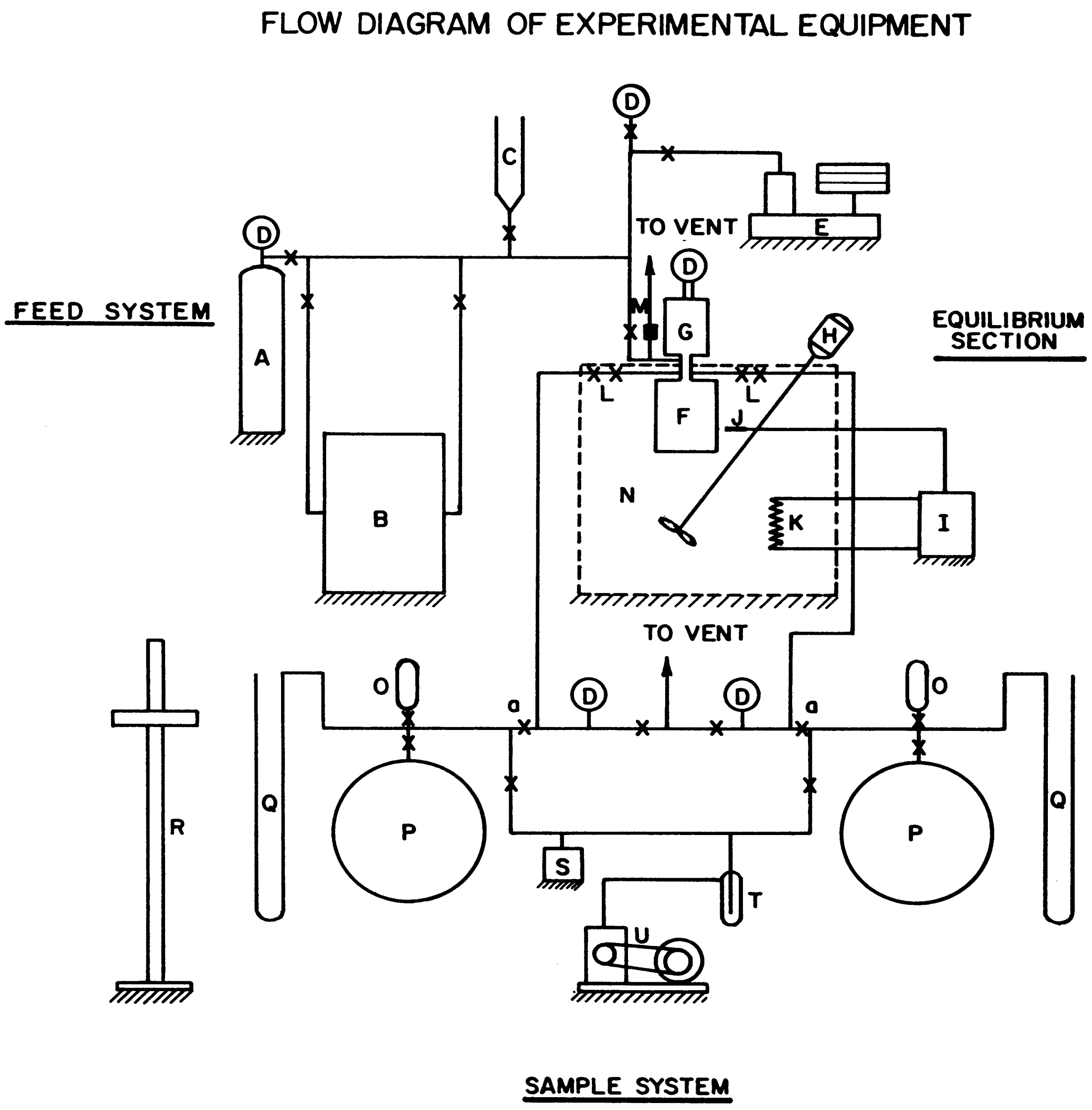
Feed System

The feed system consisted of a source of high pressure gas and a means of compressing gas to pressures above those available in the source cylinder. It also contained a gravity flow feed tank, through which liquid hydrocarbons were introduced.

The compressor was designed and built by H. J. Aroyan and Riki Kobayashi. It has been described in detail by Benham(6) and by Cosway.(10)

Equilibrium Section

The equilibrium cell consisted of an Aminco Micro Reaction Vessel, made of type 316 stainless steel, modified to contain the stirring mechanism provided by an Autoclave Magne-Dash stirrer. The approximate volume of the cell was 200 cubic centimeters. Agitation of the cell contents was produced by the reciprocating motion of the dasher assembly, shown in Figure 2. This motion was made possible by the thrust induced on a magnetic core, when the solenoid surrounding this core was energized. By the use of two coils, a positive thrust in either direction was possible. This action was controlled by a timer which regulated the current flow to both coils, energizing them alternately.



LEGEND

A. HIGH PRESSURE GAS CYLINDER
B. COMPRESSOR
C. GRAVITY FLOW FEED TANK
D. PRESSURE GAUGE
E. DEAD WEIGHT TESTER
F. EQUILIBRIUM CELL
G. SOLENOID HOUSING
H. MIXER
I. TEMPERATURE CONTROLLER
J. THERMISTOR SENSOR
K. IMMERSION HEATER
L. HIGH PRESSURE LOCK
M. RUPTURE DISC.
N. TEMPERATURE CONTROL BATH
O. SAMPLE BOTTLE
P. EXPANSION BOTTLE
Q. MERCURY MANOMETER
R. CATHETOMETER
S. MERCURY McLEOD GAUGE
T. COLD TRAP
U. VACUUM PUMP

Figure 1. Flow Diagram of Experimental Equipment.

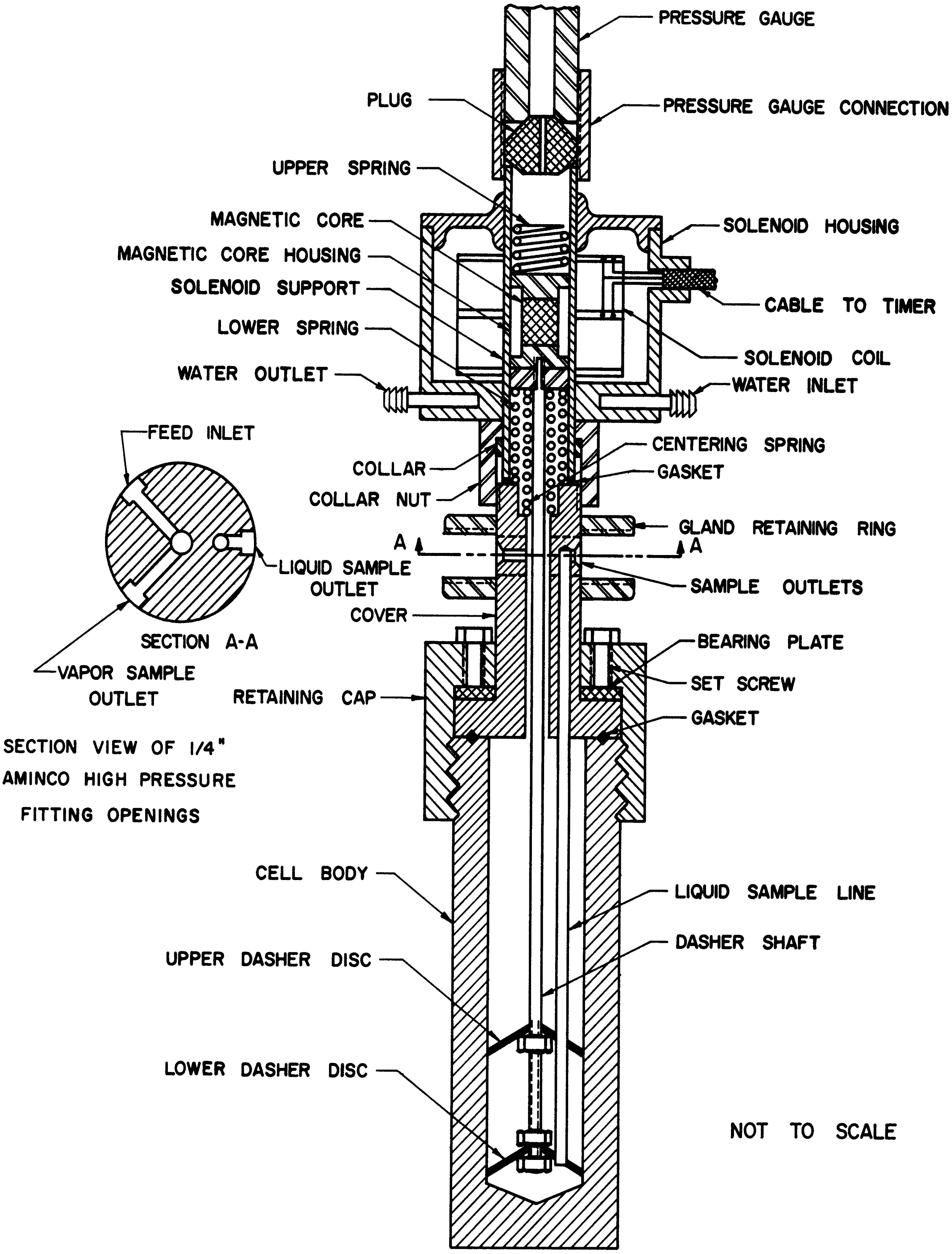


Figure 2. Sketch of Equilibrium Cell and Magne-Dash Shaker Assembly.

The duration of each stroke and hence the degree of agitation was controlled by the rheostats on the timer. This action could be regulated from about 4 cycles per second to one cycle approximately every 4 seconds. The dasher moved back and forth over a linear distance of approximately 1 1/2-inches to accomplish the required agitation. The agitation could be further modified by changing the position of the disks on the dasher shaft, by adding disks, or by using perforated disks.

The upper and lower springs acted as stops for the magnetic core. The centering spring positioned the dasher assembly, supported the weight of the magnetic core, and aided the lower spring on the upward stroke.

The magnetic coils were contained within a water jacket, which was used to remove excess heat from the coils during operation of the agitator.

This cell was immersed up to the top of the retaining cap in a temperature control bath. Insulated heating tapes were wrapped around those portions of the equilibrium cell that protruded above the bath, up to the solenoid housing. The temperature of the glycerine, the heat transfer medium, was controlled by means of a Fenwal Thermistor Temperature Indicating Control Unit. A thermistor sensor, which had a resistance that was extremely sensitive to temperature, was used in a simple bridge circuit. This controller was supplied with three modes of control; on-off control, on-off control with fully adjustable differential, and proportional control with broadly adjustable proportional band limits. The unit was insensitive to stray magnetic fields, vibration and shock, and contact potential in the thermistor leads. Heat was supplied to the bath by means of a set of General Electric hairpin type electric immersion heaters.

In addition to the temperature indicated by this control unit, a series of chromel-alumel thermocouples were placed at various strategic positions on the apparatus, both in the equilibrium section and in the sampling section. The feed inlet line and the sample outlet lines from the cell were wrapped with heavy-duty electrical heating tapes.

Pressure within the cell was indicated by means of a pressure gauge located above the Magne-Dash shaker assembly, and was measured by means of a pressure gauge tester, No. D3-13, supplied by the Chandler Engineering Company. A monel rupture disc, rated at 3175 psi at 72° F., was used in this section.

Sampling System

Both vapor and liquid samples were withdrawn through pressure locks, each consisting of two high-temperature, high-pressure Aminco valves made of super alloy N-155. This alloy consisted of 20% nickel, 21% chromium, 3% molybdenum, 2% tungsten, 20% cobalt, 0.15% carbon, with the balance iron. The valves were designed to operate at temperatures to 1000° F. and at pressures to 25,000 psi. The pressure on the samples was reduced from elevated cell pressure to subatmospheric pressures in these locks, which were totally immersed in the temperature control bath.

The sampling system up to the valves marked "a" in Figure 1 had a volume of approximately 20 cc. and was constructed of stainless steel. This section was provided with pressure gauges and a means of venting the sample, should the high pressure lock system fail. From valves "a" on, the system was made of pyrex glass. Expansion bottles were used to receive the sample expanded from the high pressure lock. Sample bottles were attached to the sample system by means of tapered glass joints. Mercury manometers and a mercury McLeod Gauge were used to measure the pressure within the sample system. A Central Scientific Company Cathetometer was used to measure the height of the mercury legs in the manometers.

Heating tapes and heating lamps provided temperature differentials within the sample system in order to provide convective currents for mixing of the samples.

PROCEDURE

The experimental procedure followed in this work can be divided into three parts -- feeding components to the cell, approaching equilibrium, and sampling.

Feeding Components

Liquid hydrocarbons were first introduced into a clean equilibrium cell at atmospheric conditions. Approximately 150 ml. of a mixture of hydrocarbons were mixed thoroughly in the feed tank, and 10 to 20 ml. of this solution were allowed to flow by gravity into the equilibrium cell. The cell was then valved off, and the hydrocarbon in the cell was evacuated into the cold trap.

When the pressure in the equilibrium cell had been less than 0.05 mm. of mercury for at least two hours, the cell was considered to be flushed and clean. Approximately 120 ml. of solution were then admitted to the cell. Next, hydrogen was introduced to raise the pressure, and heat was applied to the temperature control bath to raise the temperature of the cell to the desired operating levels.

If the pressure in the cell appeared to be too high after the operating temperature had been reached, hydrogen was bled from the cell through the high pressure valve lock system. The Magne-Dash stirrer was then activated.

Equilibrium

It was felt that equilibrium should be reached within two or three hours after operating conditions had been attained. However, to insure that equilibrium was reached, the sampling schedule followed was conservative.

The Magne-Dash stirrer was set for approximately one stroke per second, and was allowed to operate for a minimum of 12 hours. At the end of this period, at least three liquid and three vapor samples were taken in order to flush out the sample lines. Generally, hydrogen vapor was found present in the liquid sampling line.

This operation reduced the pressure in the equilibrium cell. In order to counteract this pressure drop, the contents of the cell were then allowed to remain without agitation in the equilibrium cell, including the high pressure lock, for periods ranging from two to twelve hours. Each time a sample was taken thereafter, this same procedure was followed.

Sampling

Before any sample was withdrawn from the equilibrium cell, the sampling system was evacuated. The pressure in the sampling system was less than 0.05 mm. of mercury at this time.

The first step in sampling, after the vacuum had been attained, was to close the inner valve, closest to the equilibrium cell in the high pressure lock system, and to allow the sample trapped within the lock to expand into the all metal safety volume. If the total pressure in the safety system did not increase with time, the sample was then allowed to expand into the glass portion of the sampling system.

The total pressure in the sampling system after the sample had been expanded into the glass expansion bottles was approximately 3 cm. of mercury as measured on a manometer by means of a cathetometer. This pressure was approximately 25% of the vapor pressure of the heaviest hydrocarbon present at room temperature.

The expanded sample was then allowed to mix by diffusion for periods ranging from three to twelve hours. During some runs, convection currents were set up in the sampling system by applying heat to spots on the outer surface of the system, in an attempt to determine if any improvement in sample mixing took place.

At the end of the mixing period, the sample was allowed to expand further into a 15 ml. sample bottle for a period of ten minutes. The sample bottle and the glass expansion bottle were then valved off, and the sample bottle was removed from the system.

A second sample bottle was placed in the system and evacuated to a pressure less than 0.05 mm. of mercury. The remaining 97% of the original sample that had been held in the glass expansion bottle was then allowed to re-expand up to the second sample bottle. At the end of one to three hours, the second sample bottle was opened for ten minutes.

The entire procedure was repeated at least three times. Hydrogen was then added to or removed from the equilibrium cell in order to establish a new pressure level, and the temperature of the cell was readjusted. The same sampling techniques were then repeated after the mixture had been allowed to come to a new equilibrium.

After samples had been taken at 100° and 200°F., and at 500 and 1000 psi, the equilibrium cell was cleaned and a new hydrocarbon mixture was added. A total of 170 vapor and 170 liquid samples, representing 28 different equilibrium mixtures, was obtained.

ANALYSIS

The samples obtained from this work were analyzed on a Consolidated Engineering Company 21-103B Mass Spectrometer. The theory and routine operation of this instrument have been discussed in great detail by Benham(6) and by Cosway.(10)

All hydrogen-rich vapor samples were run in a group before the hydrocarbon-rich liquid samples were run. This reduced the effect of possible molecular adsorption from one sample and desorption into the next sample in the mass spectrometer. Sample standards were run at least once during each set of analyses. The sensitivity of the instrument to these standards was found to vary not only from day to day, but also to vary during the same day.

Efforts were made to establish the best method of introducing the sample into the mass spectrometer in order to eliminate a possible throttling effect. It was feared that as a result of the wide molecular weight difference in the components to be analyzed, throttling would cause a certain amount of separation between the molecules. No one method of introducing the sample into the mass spectrometer appeared to give better results than any other method.

Several samples were analyzed at least twice -- some during the same day, and others on different days. The spread in the results of the analysis of the same sample was at least as great as the spread between different samples of the same set.

DISCUSSION OF ERRORS

Two groups of errors were involved in this experiment. The first group involved the measurement of the conditions under which equilibrium was attained, while the second group involved the sampling procedure and analysis of the equilibrium samples.

Measurement of Temperature and Pressure

The reported temperature of the glycerine bath was measured by means of a chromel-alumel thermocouple used in conjunction with a Leeds-Northrup portable type potentiometer. This system was calibrated against mercury thermometers which had previously been calibrated by the U.S. Bureau of Standards. The temperature-EMF relationship for this thermocouple was found to be:

$$E = -0.69005 + 0.0213531T + 6.59597T^2 \times 10^{-6}$$

where T is the temperature in degrees Fahrenheit. The temperature of the bath was known to within approximately 0.1°F.

The annulus between the Magne-Dash dasher shaft and the solenoid support and equilibrium cell cover, the feed line and portions of the sample lines were outside of the temperature control bath. This accounted for approximately 3% of the total volume of the equilibrium cell. All lines that protruded above the bath level, except for the annulus beneath the solenoid housing and the bourdon tube in the pressure gauge above the cell, were wrapped with a heavy duty heating tape. The temperature of the wrapped lines was measured by means of a second thermocouple, and was maintained approximately 1°F. above the bath temperature in order to reduce condensation of hydrocarbons in the vapor-phase.

Pressure in the cell was measured by means of a Chandler Engineering Company pressure gauge tester, No. D3-13. This instrument had an absolute accuracy of ± 3 psi, in the pressure range studied here.

Sampling Errors

The most significant errors involved in this work consisted of those errors which occurred in the sampling and in the analysis of the equilibrium sample. The effect of these errors could not be measured individually, but appeared as a total error found in running duplicate samples.

A 1% expansion of the equilibrium cell was introduced when samples were admitted to the high pressure valve lock system. During the experiment, the time during which the sample was allowed to remain in this lock under pressure from the unagitated equilibrium cell was varied from two to twelve hours. However, analyses did not indicate that the composition of the phases was effected by this change in length of time. The pressure composition diagram of the binary hydrogen systems also indicated that the change in pressure experienced during sampling would produce a composition change beyond the accuracy of the analysis.

The possibility of selective adsorption within the sample system also was investigated. Experimentally, no adsorption effect could be found. This finding was confirmed by data measured by

Van Voorhis.(61) At 25° C., Van Voorhis found that hexane, cyclohexane and benzene were physically adsorbed on silica in an amount asymptotically approaching zero at pressures below one-half the vapor pressure of the hydrocarbon. To insure that selective adsorption would not occur in this work, the pressure in the sample system was maintained at one-third the vapor pressure of the heaviest component in the mixture, or lower.

Lack of complete mixing of samples withdrawn from the equilibrium cell was also a possible source of error. The liquid sample was withdrawn as a liquid, and had to evaporate and mix in the sample system. Evaporation of the liquid sample was followed as a pressure increase by measuring heights of the mercury legs in the sample system manometers, and was completed within one hour.

A simplified mathematical model of the system indicated that at the pressures involved, essentially complete mixing by diffusion would have occurred within one hour after the sample had been completely vaporized. Samples were therefore allowed to mix by diffusion for periods ranging from 2 1/2-hours to one week. No effect of mixing time could be found from the results of the analysis. As one further attempt to study the effect of mixing, heat was applied at points to the sample system. This should have caused further mixing by means of heat convection, but did not affect the results.

The main source of error in running duplicate samples has been experimentally determined to be in the analysis obtained from the mass spectrometer. Duplicate analyses of the same sample bottle showed as much variation as the analyses of six different sample bottles. With such large variations in the mass spectrometer results, possible errors from the sources already discussed have been masked.

It is believed that the reason for this discrepancy in the analyses of duplicate samples from the same sample bottle may be attributed to the extreme size variation in the molecules being analyzed. Several different experiments were attempted in an effort to eliminate this source of error, but the only successful method was to run a minimum of six samples for each pressure-temperature-composition point studied. These results have been analyzed statistically, and the results of this type of analysis are summarized in the discussion of the data.

It is believed that the maximum probable error found occurred in the analysis of the hydrogen in both the liquid and the vapor phases, and is less than 0.5 mole per cent. The average spread in the results of analyses for all components is approximately 1 mole per cent.

SMOOTHED EXPERIMENTAL DATA

Ternary and quaternary equilibrium mixtures of hydrogen, benzene, cyclohexane and hexane have been studied at temperatures of 100° and 200°F., and at pressures of 500 and 1000 psi. At least six samples of each phase have been obtained at each pressure-temperature-composition point studied. A material balance and statistical techniques have been used in order to eliminate gross errors from the results reported here.

Since of the approximately one mole of liquid hydrocarbon added to the equilibrium cell, only 0.001 to 0.005 moles vaporized, it seemed reasonable to assume that the composition of the liquid phase on a hydrogen-free basis might be the same as the composition of the hydrocarbon mixture added to the equilibrium cell. Further, approximately 20% or less of the liquid hydrocarbon charged to the cell was removed during sampling over the complete temperature and pressure range studied. The possibility that there was no significant change in the hydrogen-free liquid compositions between additions of hydrocarbon to the cell was examined statistically. It was found that this assumption was valid within a 99% confidence level. Scattered data points that fell outside this limit have been deleted from the results reported here.

A similar analysis of the vapor phase results revealed that there was no significant difference in its hydrocarbon composition on a hydrogen-free basis. These results imply that over the range of conditions studied, the relative volatilities of the hydrocarbons were constant for a given hydrogen-free mixture.

The results of this analysis are summarized in Table II.

The analyses of the hydrogen compositions did not allow the use of a similar statistical treatment. In this case, solubility data on the three binary hydrogen-hydrocarbon systems was used to reject obvious errors. Hydrogen in the liquid phase appeared to follow Henry's Law over the entire range of conditions studied. This permitted the interpolation of hydrogen concentrations in the liquid phase from hydrogen binary data reported by different experimentalists. However, at these relatively low pressures, the vapor phase hydrogen concentrations in binary mixtures did not appear to lie on a straight line between the results of different authors. Thermodynamic calculations confirmed this hypothesis. Consequently, only the system hydrogen-hexane could be used as an estimate of the hydrogen solubility in the vapor phase.

The results of hydrogen analyses from the mass spectrometer have been examined by means of small sample statistical techniques. These techniques are based on the number of samples, the sample mean, and the range between the lowest and the highest sample values.(62) The reported values of hydrogen compositions are based on a combination of experimental results, statistical analyses and data from the literature.

Analysis of the final results indicated that an azeotrope reported at 0.502 mole fraction benzene in the benzene-cyclohexane system at atmospheric pressure has been shifted to lower benzene concentrations at higher pressures(57,65) in the presence of hydrogen.

Tables III and IV summarized the smoothed experimental results obtained in this work. Hydrogen solubility in the liquid phase at constant temperature is plotted in Figure 3. Complete experimental results are appended.

TABLE II

SUMMARY OF EXPERIMENTAL RESULTS
(Hydrocarbon Analysis on a Hydrogen Free Basis)

	Liquid Phase						Vapor Phase					
	Mole Fraction$^{(1)}$						Mole Fraction$^{(1)}$					
Runs	BZ	CX	HX	N$^{(2)}$	$\sigma^{(3)}$	P.E.$^{(4)}$	BZ	CX	HX	N$^{(2)}$	$\sigma^{(3)}$	P.E.$^{(4)}$
18,19,20,21	.219			13	.0078	.0015	.239			21	.0182	.0026
22,23,24,25			.217	10	.0055	.0013			.250	11	.0169	.0036
30,31,32,33		.200		15	.0023	.0004		.200		20	.0051	.0008
34,35,36,37			.179	20	.0128	.0020			.258	22	.0518	.0078
40,41,42,43	.299			23	.0065	.0009	.298			22	.0100	.0015
44,45,46,47		.139		14	.0086	.0016		.157		14	.0133	.0024
50,51,52,53	.500			35	.0317	.0037	.455			33	.0456	.0054
50,51,52,53		.173		35	.0176	.0020		.168		33	.0266	.0031
50,51,52,53			.327	35	.0279	.0032			.377	33	.0547	.0065

NOTES:

(1) Mole fraction of hydrocarbon solute on hydrogen free basis
(2) Number of samples
(3) Standard deviation, $\sigma = \sqrt{(x-\overline{x})^2/(N-1)}$
(4) Probable error, P.E. = $0.674\sigma/\sqrt{N}$

TABLE III

SUMMARY OF EXPERIMENTAL RESULTS AT 100°F.

		Mole Fraction									
		In Liquid Phase					In Vapor Phase				
Run	Press. (psia)	BZ	CX	HX	H_2	P.E.(1)	BZ	CX	HX	H_2	P.E.(1)
18	567	.210		.751	.039	.002	.004		.011	.985	.002
22	580	.763		.211	.026	.004	.010		.003	.987	.001
21	1100	.203		.724	.072	.004	.003		.008	.989	.001
25	1102	.741		.205	.053	.005	.006		.002	.992	.001
30	577		.193	.771	.036	.003		.003	.013	.984	.005
32	1060		.188	.750	.062	.005		.002	.006	.992	.005
34	563		.803	.175	.022	.001		.007	.002	.991	.002
35	1106		.783	.171	.046	.002		.004	.001	.994	.001
40	582	.293	.686		.021	.002	.004	.010		.986	.001
44	588	.845	.136		.019	.004	.008	.002		.990	.005
41	1122	.286	.670		.044	.005	.002	.005		.993	.001
45	1088	.836	.135		.029	.004	.005	.001		.994	.003
50	544	.487	.168	.318	.027	.001	.005	.002	.004	.989	.001
51	1074	.471	.163	.308	.058	.005	.004	.002	.004	.990	.001

NOTE:

(1) Probable error of hydrogen analysis, based on small sample statistics

TABLE IV

SUMMARY OF EXPERIMENTAL RESULTS AT 200°F.

		Mole Fraction									
		In Liquid Phase					In Vapor Phase				
Run	Press. (psia)	BZ	CX	HX	H_2	P.E.(1)	BZ	CX	HX	H_2	P.E.(1)
19	588	.209		.745	.046	.002	.014		.046	.940	.005
20	1057	.201		.717	.082	.004	.010		.030	.960	.003
23	570	.756		.209	.035	.003	.042		.014	.944	.005
24	1067	.732		.203	.066	.005	.022		.007	.970	.004
31	568		.191	.763	.046	.002		.012	.047	.941	.005
33	1089		.183	.734	.082	.001		.007	.028	.965	.003
36	1067		.762	.166	.072	.003		.022	.008	.970	.002
37	574		.787	.172	.041	.001		.033	.012	.955	.006
43	579	.289	.676		.035	.001	.012	.028		.960	.005
47	589	.841	.136		.024	.005	.034	.006		.960	.005
42	1076	.279	.655		.066	.002	.008	.018		.974	.003
46	1108	.822	.133		.045	.002	.019	.006		.975	.002
52	1085	.460	.159	.300	.081	.005	.012	.004	.010	.974	.002
53	541	.482	.167	.315	.036	.002	.027	.010	.023	.940	.001

NOTE:

(1) Probable error of hydrogen analysis, based on small sample statistics

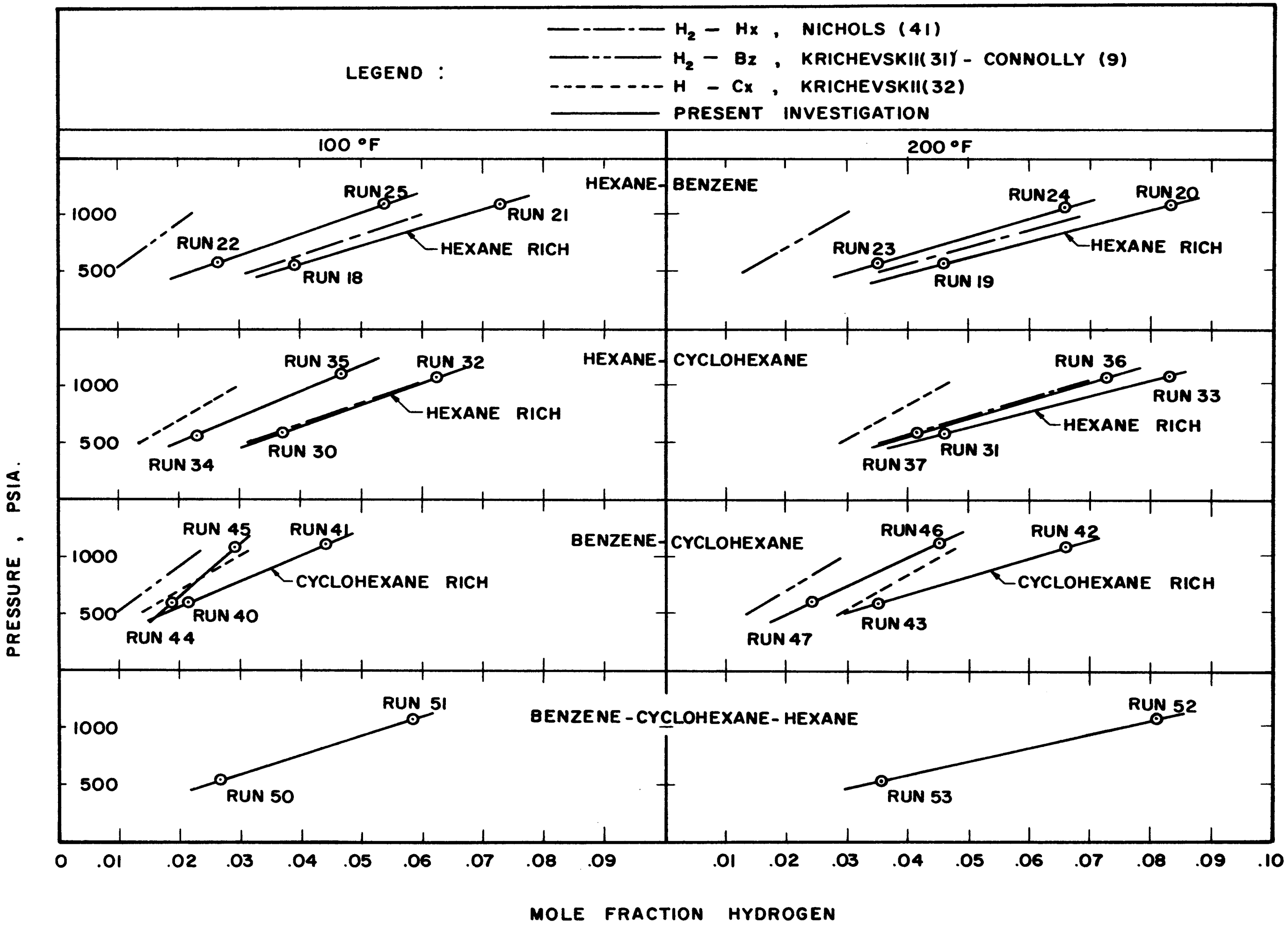


Figure 3. Solubility of Hydrogen in the Liquid Phase at Constant Temperature.

CORRELATION

Introduction

In developing any method of correlating experimental variables, much insight can be gained by making use of theoretical models. Theory must be judged, however, on how well it represents actual data. But it can provide direction to an experimentalist, and it can insure that the maximum amount of utility is obtained from the experimental data.

In the field of vapor-liquid equilibrium, a considerable amount of theory does exist, which should be accounted for by any correlation. From the second law of thermodynamics, it can be shown that for a constant temperature process:

$$\Delta G = \int_{\text{State 1}}^{\text{State 2}} V dP$$

$$= RT \ln \frac{f_2}{f_1}$$

At equilibrium, there should be no available work between the liquid phase, state 1, and the vapor phase, state 2. This condition is satisfied if the difference in the Gibbs Free Energy, ΔG, between the states is zero.

The Gibbs Free Energy can be evaluated directly from the second law of thermodynamics, if some relationship between pressure, volume and temperature is known. The relationship may be in the form of experimental data, or it may be in the form of an equation of state.

The equation of state has the advantage of providing an analytical tool for the evaluation of the free energy of the state.

Equations which relate pressure, volume and temperature for the vapor phase have been studied extensively. Most of these equations have been developed in studying single component systems. The same forms of the equations are used to predict properties of mixtures of gases, although the methods of predicting mixture coefficients have remained substantially empirical.

Equations of state contain parameters that are generally evaluated from experimental data. In order to eliminate the necessity of having experimental data available before the equation can be used for a specific component, considerable attention has been directed toward generalizing these equation coefficients. The theory of corresponding states has been developed to the point that experimental data for one component can be used with relative confidence to predict the coefficients in an equation of state for a different, but similar, pure component.

Although equations of state have been rather highly developed to predict the behavior of vapors, they are of questionable validity when applied to the liquid state. Knowledge of the liquid state is limited. For example, although the shear strength of a liquid is more nearly like that of a vapor than of a solid, its compressibility and its density are more nearly like that of a solid. Neither a theoretical model based entirely on a solid model nor a theoretical model based entirely on the vapor will predict all the aspects of the liquid phase.

Single Equation of State Methods

A method of predicting vapor-liquid equilibrium ratios that is again receiving attention is the single equation of state method.

One equation is used to predict the Gibbs Free Energy in both the vapor and the liquid phases. This method is limited, however, to the range of the validity of the equation of state. One of the better equations of state, the Benedict-Webb-Rubin Equation(1,2,3), is valid only up to twice the critical density of the component being studied. This equation is the basis of the Kellogg Charts.(30)

A major limitation to an equation of state as involved as the Benedict-Webb-Rubin equation has been that experimental data was required before it could be applied to a specific component. Opfell, Sage and Pitzer(42) made a definite contribution to the elimination of this problem by showing that a three parameter theory of corresponding states could be used to define reduced Benedict-Webb-Rubin coefficients. However, although the reduced coefficients predicted thermodynamical properties of pure components as well as the specific coefficients for the same components, neither set of coefficients was as satisfactory in predicting properties as the compressibility factors tabulated by Pitzer.(45) This indicated a need for a more precise analytical representation of the P-V-T behavior of pure components. A generalized equation of state proposed by Hirschfelder, Buehler, McGee and Sutton(21) has been proposed to fill this need.

Other equations of state, such as the Redlich-Kwong Equation of State(50), are more easily applied than the Benedict-Webb-Rubin Equation with reduced coefficients, in that their empirical coefficients are given directly in terms of reduced physical properties. In their present form, however, these latter equations have a range of applicability that is limited to densities less than half of the critical density of the component of interest.

The Redlich-Kwong Equation of State is:

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

Constants for this equation are readily derivable from a knowledge of the critical properties of the component, and are given by the following relationships:

$$A^2 = \frac{a}{R^2T^{2.5}} = 0.4278 \frac{T_C^{2.5}}{P_C T^{2.5}}$$

$$B = \frac{b}{RT} = 0.0867 \frac{T_C}{P_C T}$$

where P_C is given in atmospheres.

For mixtures:

$$A_M = \sum_i x_i A_i$$

and

$$B_M = \sum_i x_i B_i$$

It can be shown that at a constant temperature, the fugacity coefficient of a component in a mixture is given rigorously by the equation$^{(52)}$:

$$RT\ln \frac{\bar{f}_i}{x_i P} = \int_V^{\infty} [(\frac{\partial P}{\partial n_i})_{P,T,n_j} - \frac{RT}{\underline{V}_M}]\, d\underline{V}_M - RT\ln \frac{P\underline{V}_M}{RT}$$

Redlich and Kwong show that the integration of the above equation, using their relationship, gives the result:

$$\log \frac{\bar{f}_i}{x_i P} = 0.4343(z-1)\frac{B_i}{B_M} - \log(z-B_M P) - \frac{A_M^2}{B_M}\left[\frac{2A_i}{A_M} - \frac{B_i}{B_M}\right]\log\left(1 + \frac{B_M P}{z}\right)$$

where the compressibility factor, z, is defined by the relationship:

$$z = \frac{P\underline{V}_M}{RT}$$

At moderate pressures, Redlich and Kwong find that:

$$\ln \frac{\bar{f}_i}{x_i P} = [B_i - A_i^2 + (A_i - A_M)^2]\, P$$

Upon substitution of assumed compositions of one phase into the integrated equation, the value of the fugacity of the component of interest is found. This may be compared with the fugacity of that same component in the second phase, calculated in a similar manner. The assumed initial phase compositions are adjusted until the difference in these fugacities is as small as desired.

An equation of state that is theoretically capable of being used under all conditions is the Virial Equation of State. A sufficient number of virial coefficients can be used to describe the properties of a substance to any desired density. However, data on coefficients greater than the second is limited.

The Virial Equation of State can be written in the form:

$$\frac{P\underline{V}_M}{RT} = 1 + \frac{B_M(T)}{\underline{V}_M} + \frac{C_M(T)}{\underline{V}_M^2} + \cdots$$

where the second virial coefficient of the mixture, $B_M(T)$, is given by the equation:

$$B_M(T) = \sum_{i,j} x_i x_j B_{ij}(T)$$

and the third virial coefficient of the mixture, $C_M(T)$, is given by the equation:

$$C_M(T) = \sum_{i,j,k} x_i x_j x_k C_{ijk}(T) \quad .$$

The first term in this infinite series can be considered to represent the kinetic energy contributions of the molecules to the equation of state. For an ideal gas, in which there are no forces of attraction or repulsion between molecules, the equation may be terminated after the first term.

The second virial coefficient accounts for potential force interactions between pairs of molecules. At densities less than half the critical density, the Virial Equation of State terminated after the second virial coefficient adequately represents the behavior of real gases. Third and higher virial coefficients represent simultaneous potential force interactions between three or more molecules.

The Virial Equation of State can be integrated at constant temperature to give:

$$\ln \frac{\overline{f}_i}{x_i P} = \frac{2}{\underline{V}_M} \sum_j x_j B_{ij}(T) + \frac{3}{2\underline{V}_M^2} \sum_{j,k} x_j x_k C_{ijk}(T) + \cdots\cdots - \ln \frac{P\underline{V}_M}{RT}$$

Several equations of state can be derived by expressing the second virial coefficient analytically, and then substituting the resulting expression into the Virial Equation of State. For example, van der Waal's equation:

$$P = \frac{RT}{\underline{V}-b} - \frac{a}{\underline{V}^2}$$

is equivalent to assuming that :

$$B(T) = b - \frac{a}{RT}$$

The Redlich-Kwong Equation is equivalent to assuming that:

$$B(T) = 0.0867 \frac{RT_C}{P_C} [1.0 - 4.93 (\frac{T_C}{T})^{1.5}]$$

Thus, a study of the interaction coefficients in mixtures, using the Virial Equation of State, should yield results that are directly applicable to other equations of state.

Two Equations of State Method

Chao, Edmister and Prausnitz(49) have suggested that two equations of state be used in predicting vapor-liquid equilibrium. This method has the advantage of requiring a relatively simple equation of state for predicting fugacity coefficients in the vapor phase, since this phase is generally at a relatively low density as compared to the liquid phase. The proposed correlation has the form:

$$K_i = \frac{y_i}{x_i} = \frac{\gamma_i}{\varphi_i} \nu_i$$

where γ_i is the liquid activity coefficient, and is defined:

$$\gamma_i = \bar{f}_i^L / x_i f_i^o$$

The parameter φ_i is the vapor-phase fugacity coefficient, and is defined:

$$\varphi_i = \bar{f}_i^V / y_i P$$

while ν_i is the pure component liquid fugacity coefficient, and is defined:

$$\nu_i = f_i^o/P$$

The activity and fugacity coefficients required to evaluate K-values using this correlation will be discussed in the following sections.

Vapor Phase Fugacity Coefficient

In certain areas of general interest, the density of the vapor phase is less than half the critical density of the component being considered. Consequently, in this case the two equations of state method does not place extreme limitations on the exact vapor phase equations of state to be used. In this work vapor densities were relatively low, so that the integrated form of the Redlich-Kwong Equation for moderate pressures:

$$\ln \varphi_i = [B_i - A_i^2 + (A_i - A_M)^2]\, P$$

as well as the integrated form of the Virial Equation of State through the second virial:

$$\ln \varphi_i = \frac{2}{\underline{V}_M^V} \sum_j y_j B_{ij}(T) - \ln \frac{P\underline{V}_M^V}{RT}$$

has been used to evaluate vapor phase fugacity coefficients.

Using the Theory of Corresponding States, Pitzer and Curl(45) have developed a generalized correlation for pure component second virial coefficients, of the form:

$$B_{ii}(T) = B_{ii}^{(o)}(T) + \omega B_{ii}^{(1)}(T)$$

where

$$B_{ii}^{(o)}(T) = \frac{RT_C}{P_C}(0.073 + 0.46/T_r - 0.50/T_r^2 - 0.097/T_r^3 - 0.0073/T_r^8)$$

and

$$B_{ii}^{(1)}(T) = \frac{RT_C}{P_C}(0.1445 - 0.330/T_r - 0.1358/T_r^2 - 0.0121/T_r^3)$$

The acentric factor, ω, is defined by the relationship:

$$\omega \equiv -\log_{10} P_r(\text{Saturated at } T_r = 0.7) - 1.00$$

and is a measure of the forces that contribute to the nonideality of a gas. The acentric factor is related, through the Clausius-Clapeyron Equation, to the entropy of vaporization of a component. If nonideal forces exist between molecules of a component, these forces should tend to have an orienting effect, which will show up directly in the entropy of the component.

Prausnitz has extended this form of correlation to interaction virial coefficients.(47) He assumes that the critical volume of a mixture is the arithmetic average critical volume of the components:

$$\underline{V}_{C_{ij}} = 1/2\,(\underline{V}_{C_i} + \underline{V}_{C_j})$$

and that the characteristic acentric factor is the arithmetic average of the component acentric factors:

$$\omega_{ij} = 1/2\,(\omega_i + \omega_j)$$

He also presents rules which correct for the deviation from the geometric mean critical temperature of the actual critical temperature of the mixture:

$$T_{C_{ij}} = k_{ij}(T_{C_i} T_{C_j})^{1/2}$$

where k_{ij} is a function of the properties of the interacting molecules. For the hydrocarbons studied here, k_{ij} is essentially unity, while for the hydrogen-hydrocarbon interactions, k_{ij} is approximately equal to 0.85. Prausnitz tabulates the function θ_B, where:

$$\frac{B_{ij}}{\underline{V}_{C_{ij}}} = \theta_B \left(\frac{T}{T_{C_{ij}}}, \omega_{ij} \right)$$

The generalized pure virial coefficients predicted by using the method of Pitzer and Curl have been compared to experimental data. This work is shown on Figure 4, 5 and 6. Figure 7 shows virial coefficients for hydrogen that were used in this work. Prausnitz's correlation compares favorably with experimental data for the system benzene-cyclohexane as shown on Figure 8. However, an attempt was made to calculate second virial interaction coefficients for hydrogen and hydrocarbons from data obtained in this work for further verification of Prausnitz's correlations. Unfortunately, the accuracy of the variables assumed to be known quantities in these calculations is apparently insufficient to provide a definite check on his correlation for molecules of widely differing sizes. Results of this calculation are summarized in Table V. Hydrogen-hydrocarbon interaction virial coefficients predicted by Prausnitz's correlation are shown in Figure 9.

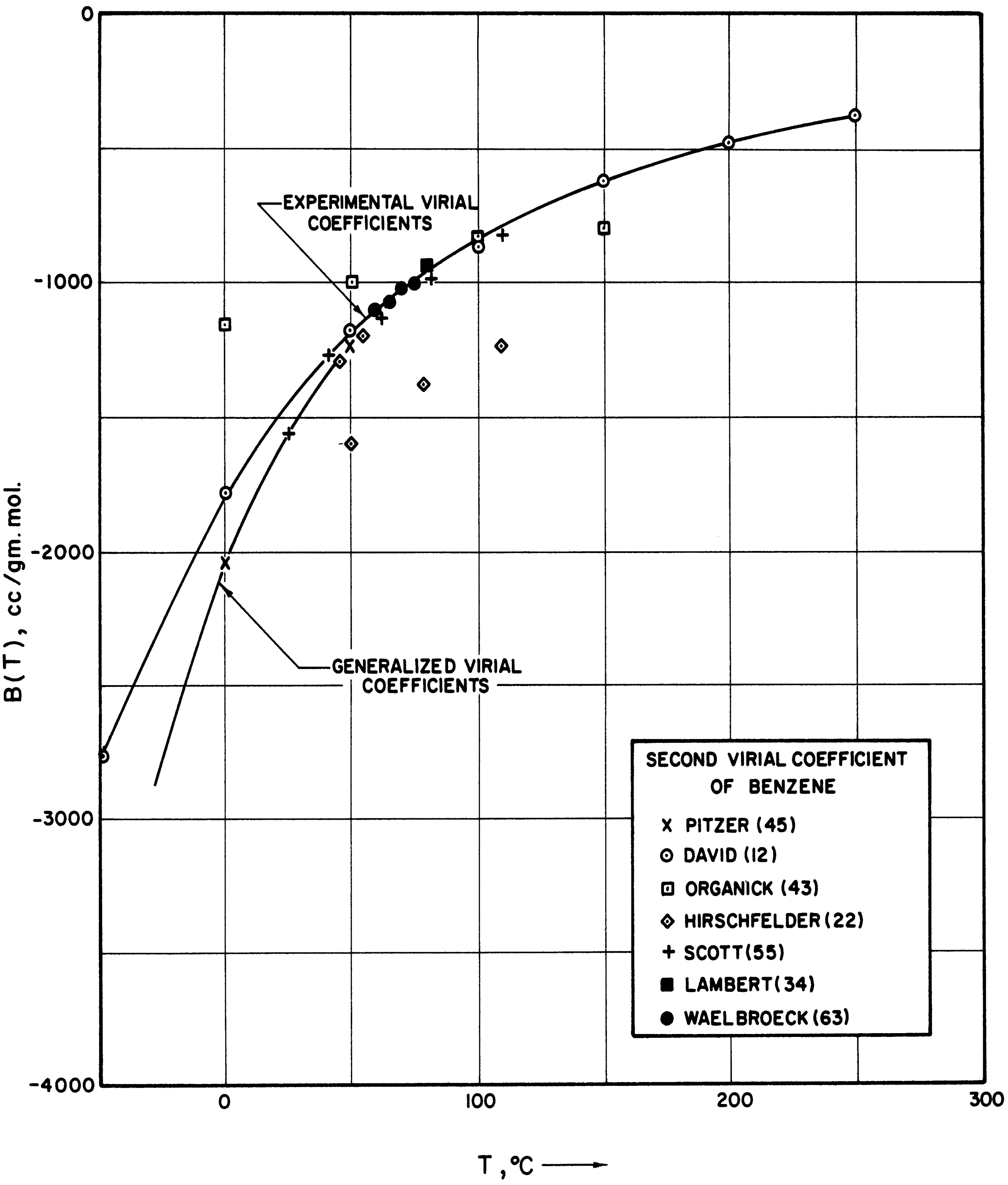


Figure 4. Second Virial Coefficient of Benzene.

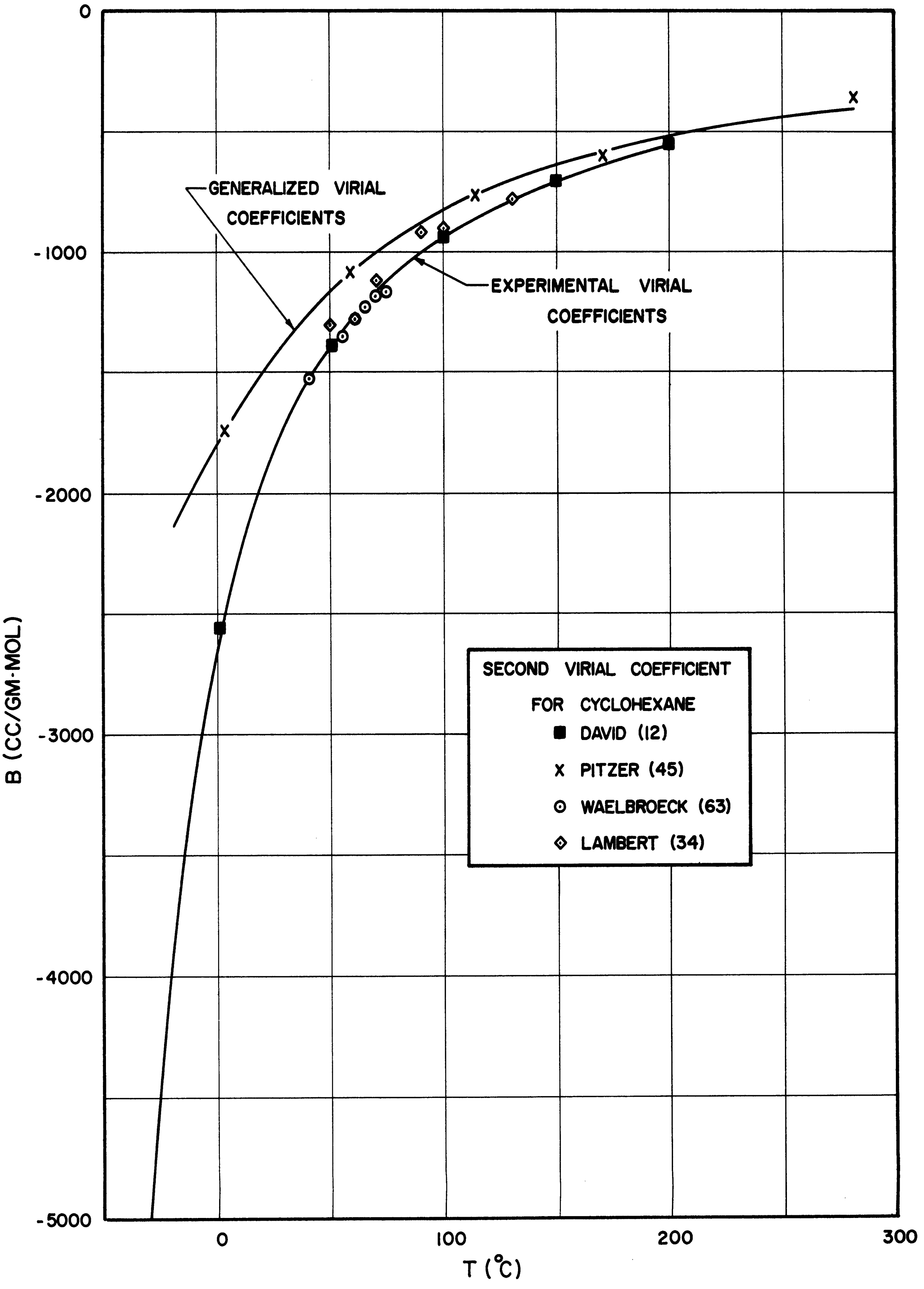


Figure 5. Second Virial Coefficient for Cyclohexane.

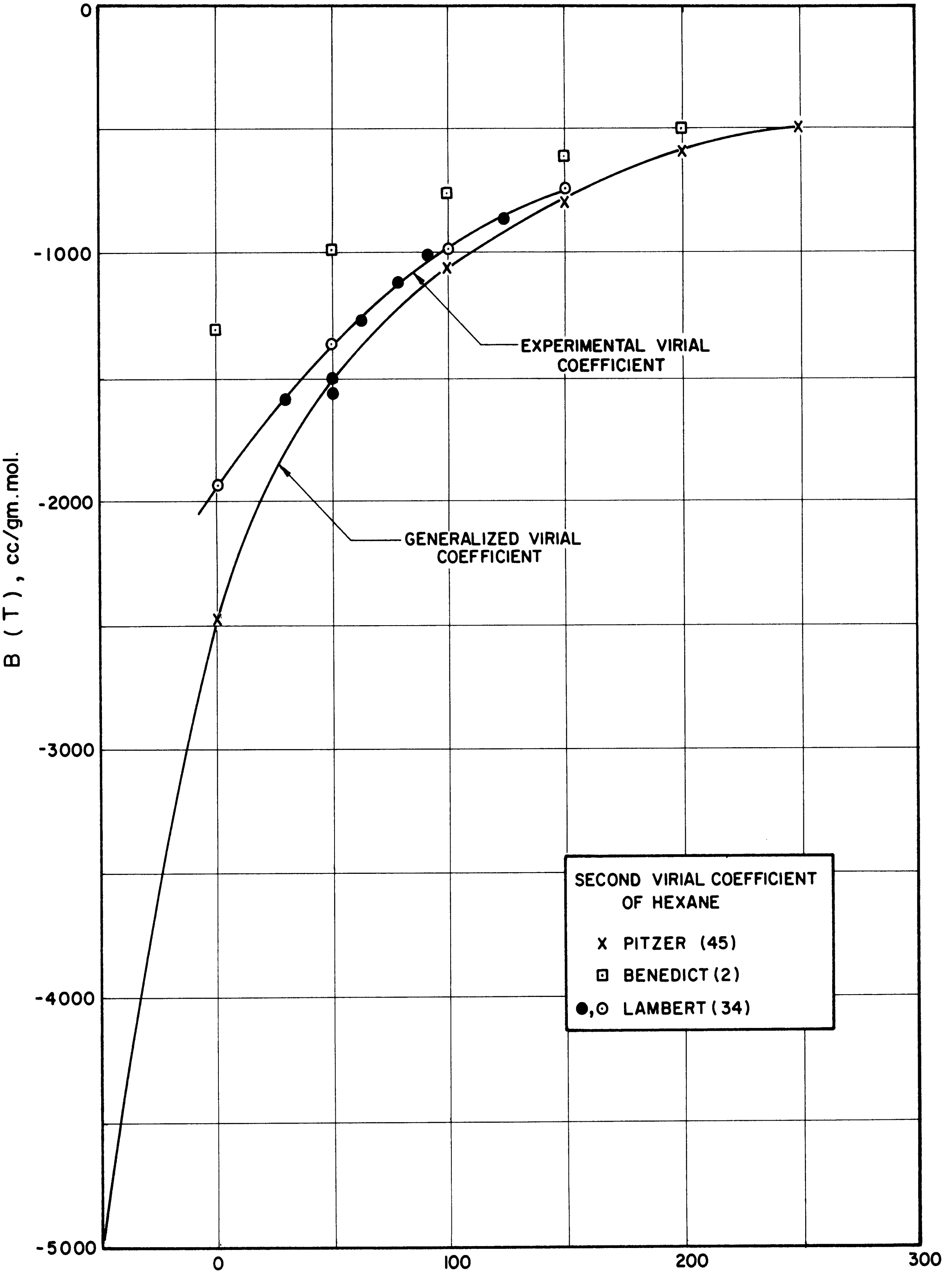


Figure 6. Second Virial Coefficient.

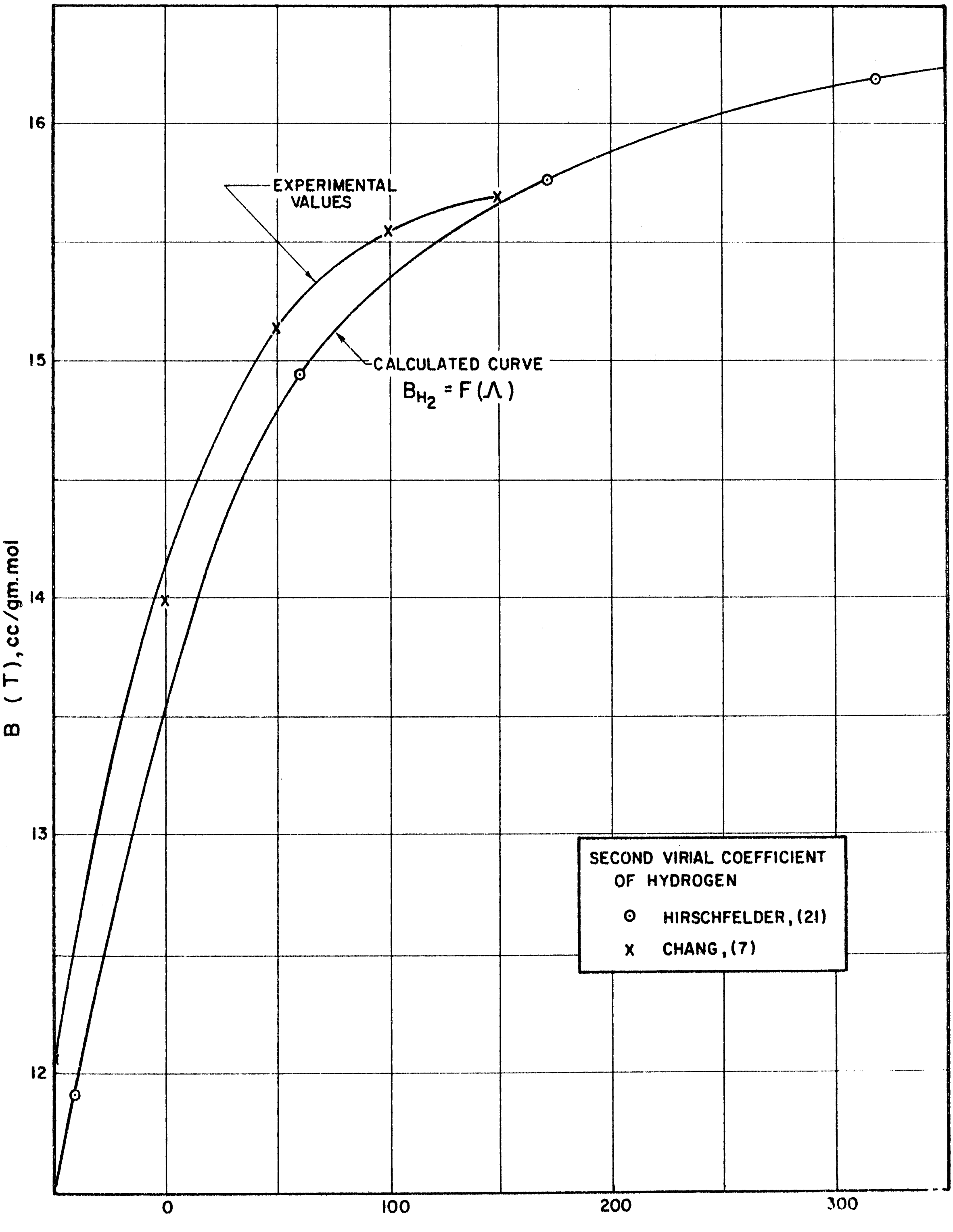


Figure 7. Second Virial Coefficient of Hydrogen.

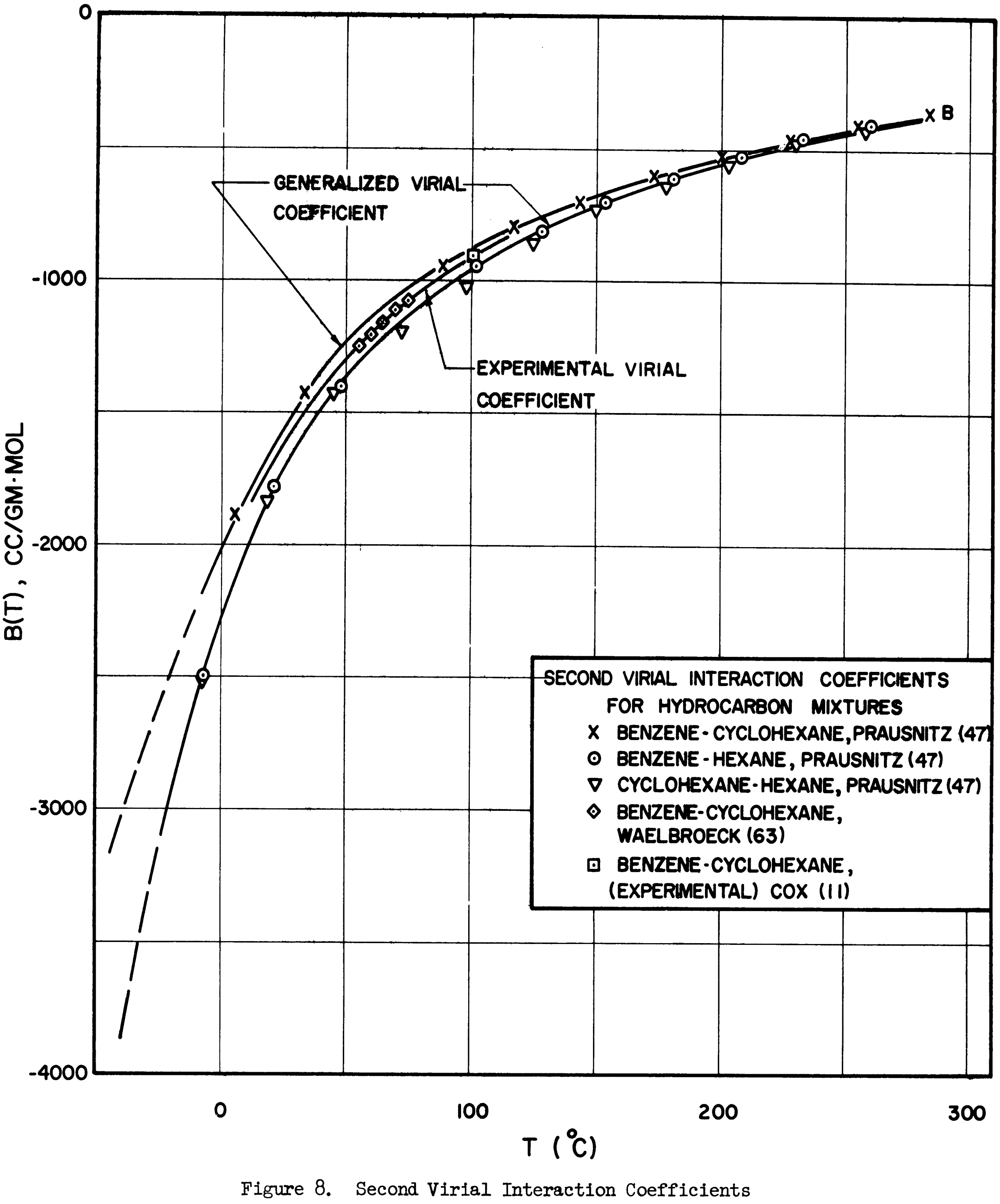


Figure 8. Second Virial Interaction Coefficients for Hydrocarbon Mixtures.

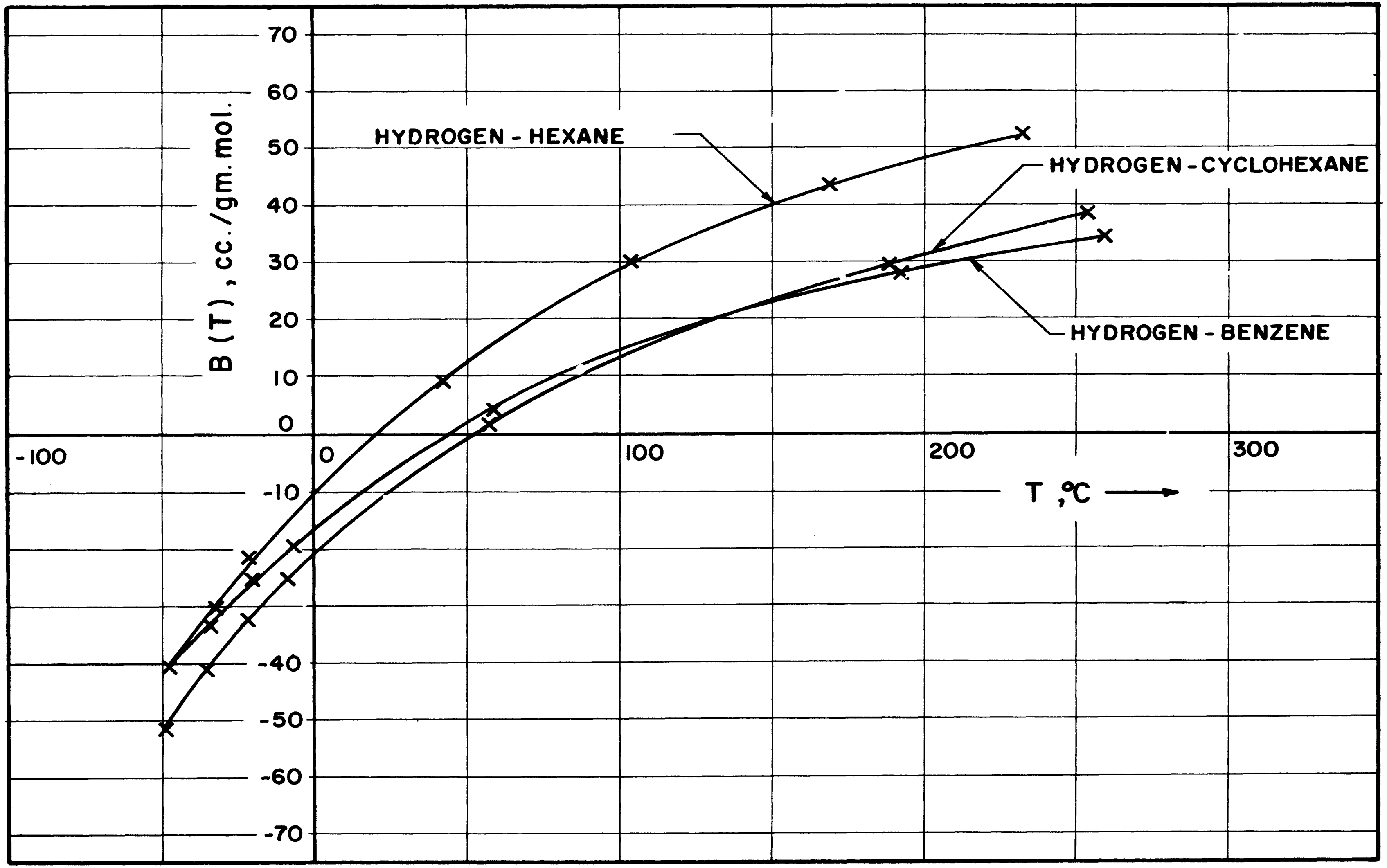


Figure 9. Generalized Second Virial Interaction Coefficients for Hydrogen Systems. Reference: Prausnitz (47)

TABLE V

INTERACTION VIRIAL COEFFICIENTS FOR HYDROGEN-HYDROCARBONS

Run Set	Temp.	$B_{H_2-B_z}$ (cm^3/gm-mole)		$B_{H_2-C_x}$ (cm^3/gm-mole)		$B_{H_2-H_x}$ (cm^3/gm-mole)	
		(1)	(2)	(1)	(2)	(1)	(2)
20	100° F.	-4.0	-140.6	-7.0		7.0	-51.1
30					- 97.2		-52.1
40			-116.6		-150.8		
50			- 80.0		-171.1		-35.4
20	200° F.	13.0	2.5	12.0		27.0	76.0
30					14.9		39.1
40			59.2		- 6.7		
50			46.1		- 8.1		66.3

NOTE: 1. Predicted by method of Prausnitz.(47)
2. Calculated by method of least squares from experimental data.

Liquid Activity Coefficient

Attention has recently been directed to solubility theory as a means of predicting the liquid activity coefficients. Chao, Edmister, and Prausnitz have recommended that the Hildebrand-Scott regular solution theory correlation for multi-component mixtures:

$$RT \ln \gamma_i = \underline{V}_i^L (\delta_i - \delta_M)^2$$

be used.(49) Here:

$$\gamma_i = \frac{\bar{f}_i^L}{x_i f_i^o}$$

$\underline{V}_i^L$ ≡ Molar liquid volume of component i

δ_i ≡ Solubility parameter of component i = $(\Delta E_{V_i}/\underline{V}_i^L)^{1/2}$

where $\Delta \underline{E}_{V_i}$ ≡ Isothermal molar change in energy of component i in going from liquid to the ideal gas state

and δ_M ≡ Solubility parameter of the mixture = $\sum x_i \underline{V}_i^L \delta_i / \sum x_i \underline{V}_i^L$

An equation of this form was first developed by Van Laar for a liquid that obeyed the van der Waal Equation of State.(59,60) Hildebrand has shown that this equation can be applied to a broader class of mixtures, called "regular solutions."(20) A regular solution, as defined by Hildebrand, is a solution in which the entropy of mixing is given by the equation:

$$\Delta S_{mix} = -R(n_1 \ln x_1 + n_2 \ln x_2 + \cdots + n_N \ln x_N)$$

All the nonideality of the mixture is attributable to its enthalpy. Although no real solution can be expected to be a regular solution, the Hildebrand theory has been surprisingly successful.

Flory(16,17) and Huggins(25) independently considered the properties of mixtures of two kinds of molecules sufficiently similar to mix in all proportions without any heat of mixing, but differing widely in size. Such a solution is called an "athermal solution," and the entropy of mixing, based on a lattice type model, is given by:

$$\Delta S_{mix} = - R\left(n_1 \ln \frac{n_1 \underline{V}_1^L}{n_1 \underline{V}_1^L + n_2 \underline{V}_2^L} + n_2 \ln \frac{n_2 \underline{V}_2^L}{n_1 \underline{V}_1^L + n_2 \underline{V}_2^L}\right)$$

Extending this to multi-component mixtures:

$$\Delta S_{mix} = - R\left(n_1 \ln \frac{n_1 \underline{V}_1^L}{\sum_i n_i \underline{V}_i^L} + n_2 \ln \frac{n_2 \underline{V}_2^L}{\sum_i n_i \underline{V}_i^L} + \cdots\right)$$

so that

$$\overline{\Delta S}_1 = \frac{\partial(\Delta S_{mix})}{\partial n_1} = -\ R\left(\ln\frac{x_1\underline{V}_1^L}{\underline{V}_M^L} + 1.0 - \frac{\underline{V}_1^L}{\underline{V}_M^L}\ \right)$$

where

$$\underline{V}_M^L = \sum_i x_i\underline{V}_i^L$$

If this expression defines the change in the partial molal entropy of a component, and if the change in its partial molal enthalpy in the multi-component mixture is given by the relationship developed by Hildebrand for a regular solution:

$$\Delta\overline{H}_1 = \underline{V}_1^L\ (\delta_1 - \delta_M)^2$$

the partial molal change in the Gibbs Free Energy is given by the equation:

$$\overline{\Delta G}_1 = RT\ \ln\frac{\overline{f}_1}{f_1^o}$$

$$= \underline{V}_1^L\ (\delta_1 - \delta_M)^2 + RT\ \ln\frac{x_1\underline{V}_1^L}{\underline{V}_M^L} + RT\left(1.0 - \frac{\underline{V}_1^L}{\underline{V}_M^L}\ \right)$$

or

$$\ln\gamma_1 = \ln\frac{\underline{V}_1^L}{\underline{V}_M^L} + \frac{\underline{V}_1^L(\delta_1-\delta_M)^2}{RT} + 1.0 - \frac{\underline{V}_1^L}{\underline{V}_M^L}$$

If

$$\underline{V}_1^L = \underline{V}_2^L = \underline{V}_3^L = \cdots = \underline{V}_N^L$$

this equation reduces to Hildebrand's equation for mixtures. This volumetric correction has not previously been applied to multi-component mixtures in the form presented here.

Prausnitz has pointed out that the assumptions used by Hildebrand in developing the theory of regular solutions do not necessarily apply to a gaseous solute in a liquid solution.(47)

The definitions of a solubility parameter and liquid molar volume, as given, cannot be readily applied to a component at a temperature above its critical temperature. Chao, Edmister and Prausnitz(49) do suggest the use of effective solubility parameters and effective molar volumes for gaseous solutes, however. These factors have been back-calculated from vapor-liquid equilibrium data. The results of this work have been applied directly to the correlation of data obtained in the present investigation.

Fugacity Coefficient of the Pure Liquid Component

At low pressures, the fugacity coefficient of the pure liquid component, ν_i, is equal to the ratio of the component vapor pressure, P_i^o, to the total pressure. At higher pressures, ν_i is given by:

$$\ln \nu_i = \ln \frac{P_i^o}{P} + \ln \left(\frac{f_i}{P}\right)_{P^o} + \frac{\underline{V}_i^L(P-P_i^o)}{RT}$$

where $\left(\frac{f_i}{P}\right)_{P^o}$ is a function of reduced vapor pressure and temperature. At the conditions encountered in this work, $\left(\frac{f_i}{P}\right)_{P^o}$ was essentially unity.

Generalized fugacity coefficients have been presented with the critical compressibility factor as a third parameter.(38) Pitzer(46) has correlated this coefficient analytically using the acentric factor as a third parameter. For components that do not exist as liquids at the system temperature and pressure, Chao(8) has proposed effective fugacity coefficients, which were determined from experimental data. He proposes that the relationship:

$$\log \nu = \log \nu^{(o)} + \omega' \log \nu^{(1)}$$

be used to represent both actual and effective fugacity coefficients, where ω' is a pseudo-acentric factor calculated to give the best fit for the largest amount of experimental vapor-liquid equilibrium data. It varies from Pitzer's acentric factor. The factor $\nu^{(o)}$ is the pure liquid fugacity coefficient of a "simple fluid" and is given by the equation:

$$\log \nu^{(o)} = A_0 + A_1/T_r + A_2T_r + A_3T_r^2 + A_4T_r^3 + (A_5 + A_6T_r + A_7T_r^2)P_r + (A_8 + A_9T_r)P_r^2 - \log P_r$$

while the factor $\nu^{(1)}$ is given by:

$$\log \nu^{(1)} = -4.23893 + 8.65808T_r - 1.22060/T_r - 3.15224T_r^3 - 0.025\,(P_r - 0.6)$$

and may be considered to be a correction term. Tables VI and VII give values of constants recommended by Chao for use in this correlation, as well as Pitzer's acentric factor, ω.

Phase Rule Considerations

If an estimate of the vapor-liquid equilibrium phase compositions can be made, the correlations that have been presented thus far can be used to provide improved estimates of vapor-liquid equilibrium composition ratios. However, for multi-component systems, the Gibbs Phase Rule indicates that additional information must be provided before these ratios can in turn be used to provide improved estimates of equilibrium compositions.

The Gibbs Phase Rule may be deduced from elementary algebraic considerations. Any set of N independent variables is said to be

TABLE VI

COEFFICIENTS IN PURE LIQUID FUGACITY COEFFICIENT EQUATIONS

	Simple Fluid	Hydrogen
A_0	5.75748	1.96718
A_1	-3.01761	1.02972
A_2	-4.98500	-0.054009
A_3	2.02299	0.0005288
A_4	0	0
A_5	0.08427	0.008585
A_6	0.26667	0
A_7	-0.31138	0
A_8	-0.02655	0
A_9	0.02883	0

TABLE VII

PHYSICAL CONSTANTS

Component	T_C(°R)	P_C(psia)	V(cc/gm-mole)	$\delta(\frac{cal}{cc})^{1/2}$	ω'	ω
Benzene	1012.7	714.0	89.4	9.158	.2130	0.215
Cyclohexane	997.7	561.0	108.7	8.196	.2032	0.158
Hexane	914.2	440.0	131.6	7.266	.2972	0.300
Hydrogen	60.2	190.8	31.0	3.250	.0000	0.000

completely defined by N independent relationships between these variables. If the number of independent relationships between the variables is greater than the number of independent variables, statistical methods can be used to determine the best values of the independent variables that will satisfy all the relationships. If, however, the number of relationships is less than the number of variables, the number of independent variables can only be reduced by the number of relationships.

This fundamental idea underlies the Gibbs Phase Rule. For a two phase, N-component, noninteracting system consisting of vapor and liquid at equilibrium, the variables in the liquid phase are:

$$x_1, x_2, x_3, \ldots x_N, P, T$$

while the variables in the vapor phase are:

$$y_1, y_2, y_3, \ldots y_N, P, T$$

In this case, there are 2N + 2 independent variables, as the pressure and temperature in both phases are equal.

The relationships between these variables include:

$$\sum_i x_i = 1.0$$

$$\sum_i y_i = 1.0$$

and

$$\bar{G}_i^L = \bar{G}_i^V$$

so that there is a total of N + 2 relationships.

The number of independent variables can be reduced by the number of relationships, so that there remain:

$$(2N + 2) - (N + 2) = N$$

independent variables that must be specified before the system is defined. For binary mixtures, the specification of pressure and temperature completely defines the system. Multi-component systems require that N - 2 additional variables be specified.

If this problem is considered in relation to a physical application, material balance equations may be added. Along with a specified operating pressure and temperature, this will provide sufficient additional information so that the system will be completely defined.

The variables in the feed stream to an equilibrium stage are compositions:

$$x_{F_1}, x_{F_2}, x_{F_3}, \ldots x_{F_N}$$

the flow rate, pressure and temperature of the stream. The variables in the product streams are also compositions, pressure and temperature, so that the total number of independent variables is 3N + 7. In this case, the relationships between these variables include:

$$\Sigma x_i = 1.0$$

$$\Sigma y_i = 1.0$$

$$\Sigma x_{F_i} = 1.0$$

$$\bar{G}_i^L = \bar{G}_i^V$$

$$F = L + D$$

$$Fx_{F_i} = Lx_i + Dy_i$$

so that there are 2N + 3 relationships between the variables.

Generally, the composition, flow rate, pressure and temperature of the feed stream are specified. In this case, there would be 2N + 4 independent variables and 2N + 2 relationships between the variables. The number of independent variables remaining to be specified is 2: the pressure and temperature of the equilibrium stage.

The energy balance can be used to determine the operating temperature of the equilibrium stage. Alternatively, if the operating temperature is specified, the energy balance determines the amount of heat that must be supplied or removed from the equilibrium stage in order to maintain this temperature.

This type of analysis can be applied to the many types of equilibrium stage separation equipment found in a chemical or petroleum process plant.

Outline of Correlation Procedure

The concepts presented in this section have been combined to predict the experimental vapor-liquid equilibrium compositions measured in this work. The experimental compositions were used to calculate a complete material balance around the equilibrium cell. The hydrogen-free composition of the liquid phase and the calculated feed were assumed to be equal. This information was then used as a basis for predicting vapor-liquid equilibrium ratios by means of the two equations of state method.

For a specific example, consider the prediction of equilibrium compositions in a four component system. The feed composition to the cell has been estimated and the pressure and temperature of the run are specified. By a material balance, we have:

$$F = L + D$$

$$Fx_{F_i} = Lx_i + Dy_i$$

Per mole of feed, we find:

$$\frac{x_{F_2}-x_2}{y_2-x_2} = \frac{x_{F_3}-x_3}{y_3-x_3} = \frac{x_{F_4}-x_4}{y_4-x_4}$$

Solving for x_2 and x_3 in terms of x_4:

$$x_2 = \frac{x_4 x_{F_2}(K_4-1)}{x_{F_4}(K_2-1) + x_4(K_4-K_2)}$$

$$x_3 = \frac{x_4 x_{F_3}(K_4-1)}{x_{F_4}(K_3-1) + x_4(K_4-K_3)}$$

where

$$K_i \equiv y_i/x_i$$

The quantity x_1 can be found from the relationship:

$$x_1 = 1.0 - x_2 - x_3 - x_4$$

and the final equation relating these variables is found from the relationship:

$$y_1 + y_2 + y_3 + y_4 = 1.0$$

so that

$$x_4(K_4-1)\left(\frac{x_{F_1}(K_1-K_3)}{x_{F_4}(K_1-1) + x_4(K_4-K_1)} + \frac{x_{F_2}(K_2-K_3)}{x_{F_4}(K_2-1) + x_4(K_4-K_2)}\right)$$
$$+ K_3(1-x_4) + K_4x_4 = 1.0$$

This last equation has been solved for x_4 on a 704 IBM computer using Newton's method of approximation. The vapor-liquid equilibrium ratios, K_i, were found from the two equations of state method:

$$K_i = \gamma_i \nu_i / \varphi_i$$

where the liquid activity coefficient, γ_i, was given either by:

$$\gamma_i = \exp\left(\frac{\underline{V}_i^L (\delta_i - \delta_M)^2}{RT} \right)$$

from Hildebrand's regular solution theory, or by:

$$\gamma_i = \frac{\underline{V}_i^L}{\underline{V}_M^L} \exp\left(\frac{\underline{V}_i^L (\delta_i - \delta_M)^2}{RT} + 1.0 - \frac{\underline{V}_i^L}{\underline{V}_M^L} \right)$$

from the present modification of this theory. Further, the vapor phase fugacity coefficient, φ_i, was given either by:

$$\varphi_i = \exp\{[B_i - A_i^2 + (A_i - A_M)^2]P\}$$

from the Redlich-Kwong Equation for moderate pressures, or by:

$$\varphi_i = \frac{RT}{P\underline{V}_M^V} \exp\left[\frac{2}{\underline{V}_M^V} \sum_j y_j B_{ij} \right]$$

from the Virial Equation of State. The pure component liquid fugacity coefficients were found either from Chao's correlation, or from vapor pressure and liquid volume data on the pure hydrocarbons.

A first estimate was made of all unknown compositions and these estimates were used to calculate activity and fugacity coefficients, from which K-values were calculated. The improved K-values were then used to re-estimate x_4.

When the integrated form of the Virial Equation of State was used, the equation of state was first solved for the largest root of V at constant pressure and temperature. In general, the number of positive real roots of an equation of degree N is either equal to the number of its variations of sign or is less than that number by a positive even integer. The largest positive real root of the Virial Equation of State has been assumed to be the dew point volume, while the smallest root has been assumed to be the bubble point volume.

The Virial Equation of State, terminated at the second virial, is a quadratic equation in volume, and so may be solved directly for the dew point volume.

Having solved for x_4, the values of x_1, x_2 and x_3 were found. The vapor compositions were estimated from the relationship:

$$y_i = K_i x_i$$

The new values of compositions were then used to make new estimates of the activity and fugacity coefficients. This process was repeated until two successively calculated compositions agreed as closely as was desired. This method of calculation can be used for an N-component mixture. While it is tedious if computed by hand, it is easily programmed for a digital computer.

Two different sets of parameters for these equations have been used to predict the measured vapor-liquid equilibrium composition ratios. In one set, the empirical solubility parameters, liquid volumes and pure liquid component fugacity coefficients recommended by Chao were used(8). Virial coefficients were predicted by the methods of Pitzer and Curl(45) and of Prausnitz.(47) These results are reported as being calculated from generalized data in Tables VIII, IX, X and XI.

TABLE VIII

VAPOR-LIQUID EQUILIBRIUM COMPOSITION RATIOS FOR BENZENE USING VIRIAL EQUATION OF STATE

		Volumetric Entropy				Ideal Entropy			
Run	Observed K-Value	Calculated K-Value(1)	% Dev(2)	Calculated K-Value(4)	% Dev(2)	Calculated K-Value(1)	% Dev(2)	Calculated K-Value(4)	% Dev(2)
100°F. 18	0.019	0.011	- 42.1	.012	- 36.9	0.011	- 42.1	0.013	- 31.6
22	0.013	0.007	- 46.2	.009	- 30.8	0.007	- 46.2	0.009	- 30.8
21	0.015	0.007	- 53.4	.008	- 46.7	0.007	- 53.4	0.008	- 46.7
25	0.008	0.005	- 37.5	.006	- 25.0	0.005	- 37.5	0.006	- 25.0
40	0.014	0.007	- 50.0	.009	- 35.7	0.007	- 50.0	0.009	- 35.7
44	0.009	0.007	- 22.2	.008	- 11.1	0.007	- 22.2	0.008	- 11.1
41	0.007	0.005	- 28.6	.006	- 14.3	0.005	- 28.6	0.006	- 14.3
45	0.005	0.004	- 20.0	.005	0.0	0.004	- 20.0	0.005	0.0
50	0.010	0.008	- 20.0	.010	0.0	0.008	- 20.0	0.010	0.0
51	0.008	0.005	- 37.5	.006	- 25.0	0.005	- 37.5	0.006	- 25.0
Abs.sum of Deviations			357.5		225.5		357.5		220.2
Abs.avg.% Deviation			35.8(3)		22.6(3)		35.8(3)		22.0(3)
200°F. 19	0.067	0.072	+ 7.4	.070	+ 4.5	0.074	+ 10.5	0.072	+ 7.4
20	0.050	0.045	- 10.0	.046	- 8.0	0.046	- 8.0	0.047	- 6.0
23	0.056	0.051	- 8.9	.052	- 7.1	0.051	- 8.9	0.052	- 7.1
24	0.030	0.031	+ 3.3	.033	+ 10.0	0.031	+ 3.3	0.033	+ 10.0
43	0.042	0.050	+ 19.0	.051	+ 21.4	0.050	+ 19.0	0.051	+ 21.4
47	0.041	0.046	+ 12.2	.047	+ 14.6	0.046	+ 12.2	0.047	+ 14.6
42	0.029	0.030	+ 3.5	.033	+ 13.8	0.031	+ 6.9	0.033	+ 13.8
46	0.023	0.027	+ 17.4	.030	+ 30.5	0.028	+ 21.7	0.030	+ 30.5
52	0.026	0.034	+ 30.8	.036	+ 38.5	0.034	+ 30.8	0.036	+ 38.5
53	0.056	0.058	+ 3.6	.058	+ 3.6	0.059	+ 5.4	0.058	+ 3.6
Abs.sum of Deviations			116.1		152.0		126.7		152.9
Abs.avg. % Deviation			11.6(3)		15.2(3)		12.7(3)		15.3(3)

NOTES:

(1) Calculation based on specific data

(2) Percent deviation = $((K_{calc} - K_{obs})/K_{obs}) \times 100$

(3) Absolute average percent deviation = $(\Sigma|\%\ \text{dev.}|)$/number of samples

(4) Calculation based on generalized data

TABLE IX

VAPOR-LIQUID EQUILIBRIUM COMPOSITION RATIOS FOR CYCLOHEXANE USING VIRIAL EQUATION OF STATE

			Volumetric Entropy				Ideal Entropy			
	Run	Observed K-Value	Calculated K-Value$^{(1)}$	% Dev$^{(2)}$	Calculated K-Value$^{(4)}$	% Dev$^{(2)}$	Calculated K-Value$^{(1)}$	% Dev$^{(2)}$	Calculated K-Value$^{(4)}$	% Dev$^{(2)}$
100°F.	30	.016	.008	- 50.0	.010	- 37.5	.008	- 50.0	.010	- 37.5
	32	.011	.006	- 45.4	.007	- 36.4	.006	- 45.4	.007	- 36.4
	34	.009	.008	- 11.1	.009	0.0	.008	- 11.1	.009	0.0
	35	.005	.005	0.0	.006	+ 10.0	.005	0.0	.006	+ 10.0
	40	.015	.007	- 53.4	.009	- 40.0	.007	- 53.4	.009	- 40.0
	44	.015	.008	- 46.7	.009	- 40.0	.008	- 46.7	.009	- 40.0
	41	.007	.004	- 42.8	.006	- 14.3	.005	- 28.6	.006	- 14.3
	45	.007	.005	- 28.6	.006	- 14.3	.005	- 28.6	.007	0.0
	50	.012	.008	- 33.3	.009	- 25.0	.008	- 33.3	.009	- 25.0
	51	.012	.005	- 58.4	.006	- 50.0	.005	- 58.4	.006	- 50.0
	Abs.sum of Deviations			369.7		267.5		355.5		253.2
	Abs.avg. % Deviation			37.0$^{(3)}$		26.8$^{(3)}$		35.6$^{(3)}$		25.3$^{(3)}$
200°F.	31	.063	.058	- 7.9	.055	- 12.7	.059	- 6.4	.055	- 12.7
	33	.038	.036	- 5.2	.037	- 2.6	.036	- 5.2	.037	- 2.6
	36	.029	.030	+ 3.5	.032	+ 10.0	.030	+ 3.5	.032	+ 10.0
	37	.042	.049	+ 16.7	.048	+ 14.3	.049	+ 16.7	.048	+ 14.3
	43	.042	.047	+ 11.9	.047	+ 11.9	.047	+ 11.9	.047	+ 11.9
	47	.045	.047	+ 4.5	.049	+ 8.9	.048	+ 6.7	.050	+ 11.1
	42	.027	.028	+ 3.7	.031	+ 14.8	.028	+ 3.7	.031	+ 14.8
	46	.045	.028	- 37.8	.032	- 28.8	.029	- 35.6	.033	- 26.6
	52	.025	.029	+ 16.0	.032	+ 28.0	.030	+ 20.0	.032	+ 28.0
	53	.060	.051	- 15.0	.051	- 15.0	.052	- 10.0	.051	- 15.0
	Abs.sum of Deviations			132.2		147.0		119.7		147.0
	Abs.avg. % Deviation			13.2$^{(3)}$		14.7$^{(3)}$		12.0$^{(3)}$		14.7$^{(3)}$

NOTES:

(1) Calculation based on specific data
(2) Percent deviation = $((K_{calc} - K_{obs})/K_{obs}) \times 100$
(3) Absolute average percent deviation = $(\Sigma|\%\ \mathrm{dev}|)$/number of samples
(4) Calculation based on generalized data

TABLE X

VAPOR-LIQUID EQUILIBRIUM COMPOSITION RATIOS FOR HEXANE USING VIRIAL EQUATION OF STATE

		Volumetric Entropy				Ideal Entropy			
Run	Observed K-Value	Calculated K-Value(1)	% Dev(2)	Calculated K-Value(4)	% Dev(2)	Calculated K-Value(1)	% Dev(2)	Calculated K-Value(4)	% Dev(2)
100°F. 18	.015	.011	- 26.6	.013	- 13.3	.011	- 26.6	.013	- 13.3
22	.014	.014	0.0	.017	+ 21.4	.015	+ 7.1	.018	+ 28.6
21	.011	.007	- 36.4	.009	- 18.2	.007	- 36.4	.009	- 18.2
25	.010	.008	- 20.0	.011	+ 10.0	.009	- 10.0	.012	+ 20.0
30	.017	.011	- 35.3	.013	- 23.6	.011	- 35.3	.013	- 23.6
32	.008	.007	- 12.5	.009	+ 12.5	.007	- 12.5	.009	+ 12.5
34	.011	.012	+ 18.2	.014	+ 27.3	.012	+ 18.2	.014	+ 27.3
35	.006	.007	+ 16.7	.009	+ 50.0	.007	+ 16.7	.009	+ 50.0
50	.013	.013	0.0	.015	+ 15.4	.013	0.0	.016	+ 23.1
51	.013	.007	- 46.1	.010	- 23.1	.008	- 38.4	.010	- 23.1
Abs.sum of Deviations			211.8		214.8		201.2		239.7
Abs.avg. % Deviation			21.2(3)		21.5(3)		20.1(3)		24.0(3)
200°F. 19	.062	.071	+ 14.5	.072	+ 16.1	.073	+ 17.8	.074	+ 19.4
20	.042	.042	0.0	.047	+ 11.9	.043	+ 2.4	.048	+ 14.3
23	.067	.085	+ 26.9	.088	+ 30.4	.091	+ 35.8	.094	+ 40.3
24	.034	.048	+ 41.3	.055	+ 61.8	.052	+ 53.0	.061	+ 79.5
31	.062	.070	+ 12.9	.071	+ 14.5	.071	+ 14.5	.072	+ 11.6
33	.038	.041	+ 7.9	.045	+ 18.4	.042	+ 10.5	.047	+ 23.7
36	.048	.042	- 12.5	.046	- 4.2	.044	- 8.3	.048	0.0
37	.070	.072	+ 2.9	.071	+ 1.4	.074	+ 5.7	.074	+ 5.7
52	.033	.043	+ 30.3	.049	+ 48.5	.046	+ 39.4	.052	+ 57.6
53	.073	.080	+ 9.6	.081	+ 11.0	.083	+ 13.7	.085	+ 16.4
Abs.sum of Deviations			158.8		218.2		201.1		268.5
Abs.avg. % Deviation			15.9(3)		21.8(3)		20.1(3)		26.9(3)

NOTES:

(1) Calculation based on specific data
(2) Percent deviation = $((K_{calc} - K_{obs})/K_{obs}) \times 100$
(3) Absolute average percent deviation = $(\Sigma|\%\ dev|)$/number of samples
(4) Calculation based on generalized data

TABLE XI

VAPOR-LIQUID EQUILIBRIUM COMPOSITION RATIOS FOR HYDROGEN USING VIRIAL EQUATION OF STATE

		Volumetric Entropy				Ideal Entropy			
Run	Observed K-Value	Calculated K-Value(1)	% Dev(2)	Calculated K-Value(4)	% Dev(2)	Calculated K-Value(1)	% Dev(2)	Calculated K-Value(4)	% Dev(2)
100°F. 18	25.256	24.612	- 2.5	20.005	- 20.8	41.977	+ 66.3	36.805	+ 45.8
22	37.962	48.981	+ 29.0	37.314	- 1.7	72.737	+ 91.6	59.573	+ 57.0
21	13.736	13.078	- 4.8	10.709	- 22.1	22.103	+ 60.9	19.418	+ 41.3
25	18.717	26.312	+ 40.5	20.110	+ 7.4	39.055	+ 108.3	32.022	+ 71.2
30	27.333	22.072	- 19.3	18.062	- 34.0	38.568	+ 41.2	34.060	+ 24.7
32	16.000	12.379	- 22.6	10.205	- 36.2	21.412	+ 33.8	18.942	+ 18.4
34	45.045	32.878	- 27.1	25.857	- 42.7	53.184	+ 18.1	45.115	+ 0.2
35	21.609	17.169	- 20.6	13.584	- 37.1	27.648	+ 28.0	23.493	+ 8.7
40	46.952	43.392	- 7.6	33.160	- 29.4	66.188	+ 41.0	54.472	+ 16.0
44	52.105	64.667	+ 24.1	47.823	- 8.2	92.070	+ 76.8	73.097	+ 40.4
41	22.568	23.012	+ 2.0	17.657	- 21.8	35.057	+ 55.4	28.886	+ 28.0
45	34.276	35.610	+ 4.1	26.391	- 23.0	50.735	+ 48.0	40.304	+ 17.7
50	36.630	39.659	+ 8.6	30.931	- 15.6	61.860	+ 69.0	51.963	+ 41.9
51	17.069	20.543	+ 20.8	16.101	- 5.7	31.967	+ 87.4	26.891	+ 57.6
Abs.sum of Deviations			232.7		305.7		825.8		468.9
Abs.avg.% Deviation			16.6(3)		21.8(3)		59.0(3)		33.6(3)
200°F. 19	20.435	19.497	- 4.6	14.402	- 29.5	31.874	+ 51.0	26.284	+ 28.6
20	11.707	10.612	- 9.3	7.946	- 32.2	17.165	+ 46.7	14.198	+ 21.3
23	26.971	37.086	+ 37.4	24.818	- 8.0	52.807	+ 95.9	39.480	+ 46.4
24	14.697	20.169	+ 37.2	13.592	- 7.5	28.697	+ 95.3	21.501	+ 46.3
31	20.457	17.806	- 12.9	13.143	- 35.6	29.745	+ 45.3	24.564	+ 20.0
33	11.768	9.611	- 18.4	7.206	- 38.8	15.843	+ 34.7	13.128	+ 11.6
36	13.472	14.519	+ 7.8	9.720	- 27.8	22.142	+ 65.4	16.625	+ 23.4
37	23.293	26.415	+ 13.4	17.471	- 25.0	40.456	+ 73.6	30.285	+ 30.0
43	27.429	35.161	+ 28.2	22.137	- 19.3	50.846	+ 85.5	36.206	+ 32.0
47	40.000	48.104	+ 20.2	30.189	- 24.5	65.533	+ 63.7	46.033	+ 15.0
42	14.758	19.264	+ 30.6	12.234	- 17.1	27.826	+ 88.5	19.859	+ 34.6
46	21.667	26.009	+ 20.0	16.405	- 24.3	35.458	+ 63.6	24.946	+ 15.1
52	12.025	15.652	+ 30.5	10.821	- 9.8	23.265	+ 93.5	17.894	+ 48.9
53	26.111	30.673	+ 17.9	20.987	- 19.4	45.747	+ 75.2	35.088	+ 34.4
Abs.sum of Deviations			287.7		319.3		977.9		407.6
Abs.avg. % Deviation			20.6(3)		22.8(3)		69.9(3)		29.1(3)

NOTES:

(1) Calculation based on specific data
(2) Percent deviation = $((K_{calc} - K_{obs})/K_{obs}) \times 100$
(3) Absolute average percent deviation = $(\Sigma|\%\ dev|)$/number of samples
(4) Calculation based on generalized data

In the second set, the solubility parameters of the hydrocarbons were calculated from the heat of vaporization data and density data. Chao's solubility parameter for hydrogen, reported at 25° C, was corrected for use at 100° and 200° F. Experimental density data was used for hydrocarbon liquid volumes,(15) and the Gamson-Watson Expansion Factor method was used to predict the liquid molal volume of hydrogen.(49) The pure hydrocarbon liquid fugacity coefficients were predicted from vapor pressure data. Experimental virial coefficients were used wherever available. These results are reported as being calculated from specific data in Tables VIII, IX, X and XI.

For both sets of parameters, liquid activity coefficients were predicted using both the ideal liquid entropy relationship and the entropy predicted by the volumetric correlation.

The results of using the second set of parameters with the volumetric entropy function are presented in Table XVII, taken directly from the IBM computer and placed in the Appendix. These tables include the calculated interaction virial coefficients for hydrogen-hydrocarbon mixtures, and the vapor-liquid equilibrium composition calculations using these experimental interaction coefficients. Coefficients for the Redlich-Kwong Equation were estimated from the physical properties of the pure components.

CONCLUSIONS

Examination of the data obtained in this work reveals that specification of the temperature and pressure of a hydrogen-hydrocarbon mixture does not completely define the vapor-liquid equilibrium composition ratios of the components studied. These ratios also depend upon the relative amounts and the physical properties of the other components in the mixture.

The interaction of all variables is difficult to present in a concise graphical correlation. However, the experimental vapor-liquid equilibrium composition ratios have been correlated analytically by means of the two equations of state method:

$$K_i = \gamma_i \nu_i / \varphi_i$$

The fugacity and activity coefficients in this correlation have been predicted independently of the experimental data obtained in this research. This correlation predicts the benzene-cyclohexane azeotrope at the elevated pressures. The over-all consistency of the experimental and predicted results indicates that this method of predicting K-values has general applicability.

The fugacity coefficients of components in the vapor phase have been estimated by means of integrated equations of state. The Virial Equation of State, terminated after the second virial, as well as the Redlich-Kwong Equation of State, integrated for moderate pressures,(50) has been used. Results from the two equations of state were consistent.

Interaction virial coefficients for hydrogen-hydrocarbons were back-calculated from the data for comparison with values predicted by a method proposed by Prausnitz.(47) The accuracy of the calculated hydrogen-hydrocarbon interaction virial coefficients depended upon the accuracy to which all the other parameters used in predicting K-values were known. As experimental data did not exist for all the parameters required, the accuracy of the calculated hydrogen-hydrocarbon interaction virial coefficients may be insufficient to provide a definite check on Prausnitz's correlation for molecules of widely differing size.

Chao and Seader(8) have used the Hildebrand Solubility Theory to predict activity coefficients in the liquid phase. Using the empirical solubility parameters and pure liquid component fugacity coefficients calculated by Chao from existing vapor-liquid equilibrium data, and generalized P-V-T data of Pitzer and Curl,(45) the average absolute deviation of predicted hydrogen equilibrium values from the measured values was 31.4%. This deviation increased to 64.5% when hydrocarbon solubility parameters based on physical properties of the pure liquid hydrocarbons were used. Available experimental P-V-T data was used in this latter case to evaluate vapor phase fugacity coefficients.

The Hildebrand Solubility Theory used by Chao is based on the assumption that, despite differences in molecular size, thermal agitation is sufficient to provide complete randomization of the molecules in the liquid phase.(20) This implies ideal entropy of mixing. As the difference in the molecular size of hydrogen and the hydrocarbons studied in this work was appreciable, the Flory-Huggins type volumetric correction to the entropy of mixing was applied.(16,17,25)

Hildebrand has used this correction for binary mixtures, but it has not previously been applied to multi-component mixtures in the form presented here.

This change in the liquid activity coefficient correlation reduced the absolute average deviation of the hydrogen equilibrium values based on Chao's empirical solubility parameters and pure liquid component fugacity coefficients from 31.4 to 22.3%. When the proposed correlation was used with the solubility parameters calculated from pure liquid hydrocarbon physical properties, it reduced the deviation from 64.5 to 18.6%.

As the molecular size of the hydrocarbons was approximately equal, this new correlation did not improve the predictions of the hydrocarbon vapor-liquid equilibrium ratios. These ratios had an average absolute deviation of 15.4% at 200°F. and an average absolute deviation of 27.3% at 100°F.

At the relatively low hydrogen liquid and hydrocarbon vapor concentrations encountered in this work, these results indicate that compositions have been predicted to within approximately 0.005 mole fraction of the measured composition.

Prediction of vapor-liquid equilibrium compositions may be improved further in the future. Work is needed to clarify and improve the prediction of mixture coefficients in equations of state, as well as the prediction of equilibrium compositions of mixtures containing polar components. The concept of ideal mixing of volumes in the liquid phase should also be re-examined. Finally, as physical chemists improve statistical methods of treating liquids, their results should be incorporated into generalized correlations for engineering use.

APPENDICES

SOLUBILITY PARAMETER ESTIMATION

The solubility parameter, δ, used in this work, can be estimated in at least four different ways. For components that exist as liquids under the conditions being studied, the solubility parameter can be estimated from the properties of the component.

For example, an interpolation of data on heats of vaporization of benzene, reported by Rossini,(53), indicates that at 100°F.:

$$\Delta H_V = 7.918 \text{ kcal/mole}$$

and from density data reported in the N.G.A.A. Data Book (1957):(15)

$$\rho_{Bz}(100°\text{F.}) = 0.859 \text{ gms/c.c.}$$

By definition, it follows that:

$$\delta_{Bz}(100°\text{F.}) = \left(\frac{\Delta \underline{E}_V}{\underline{V}_L}\right)^{1/2}$$

$$= \left(\frac{\Delta \underline{H}_V - RT}{\underline{V}_L}\right)^{1/2}$$

$$= \left(\frac{7918 - 1.9872 \times 310.9}{78/0.859}\right)^{1/2}$$

$$= 8.97$$

Table XII includes solubility parameters of the hydrocarbon mixtures which were calculated in this manner.

A second method of calculating solubility parameters consists of considering the solubility parameter to be a correlating function for liquid activity coefficients, similar to Van Laar's or Margules' constants. By comparing Van Laar's equations, as used by White for isobaric equilibria:(66)

$$\ln \gamma_1 = \frac{A/T}{[1 + Ax_1/Bx_2]^2}$$

and

$$\ln \gamma_2 = \frac{B/T}{[1 + Bx_2/Ax_1]^2}$$

with Hildebrand's equation for liquid activity coefficients of binary mixtures:(20)

$$RT \ln \gamma_1 = \underline{V}_1^L(\delta_1-\delta_2)^2\left(\frac{x_2\underline{V}_2^L}{x_1\underline{V}_1^L + x_2\underline{V}_2^L}\right)^2$$

$$RT \ln \gamma_2 = \underline{V}_2^L(\delta_2-\delta_1)^2\left(\frac{x_1\underline{V}_1^L}{x_1\underline{V}_1^L + x_2\underline{V}_2^L}\right)^2$$

Edmister(14) has shown that:

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

$$B = \underline{V}_2^L/R\ (\delta_1-\delta_2)^2$$

Solubility parameters of substances that do not exist as liquids at the temperature of interest can be estimated from their Van Laar coefficients or calculated directly from vapor-liquid equilibrium data. Chao has calculated a number of solubility parameters from data on vapor-liquid equilibrium. The values he reports for the components of interest are also in Table XII.

Hildebrand and Scott report that the variation of solubility parameter with temperature is given approximately by the relationship:

$$\frac{d\ln\delta}{dT} = -1.25\alpha$$

where α denotes the coefficient of thermal expansion. Over a moderate range of temperature, α may be taken as constant. For hydrogen at one atmosphere, α is 0.00366 from 0 to 100°C.(44) Using this value of α to evaluate the variation of solubility parameter with temperature gives the result:

$$\ln \delta_{H_2}[(\text{cal/ml})^{1/2}] = 1.17865 - 0.004575(T(°C) - 25)$$

for hydrogen. The value of the hydrogen solubility parameter, reported by Chao at 25° C., was extrapolated by means of this equation to 100° and 200°F. and is tabulated as a calculated solubility parameter in Table XII.

Still another method of obtaining solubility parameters is used by Hildebrand. From the thermal equation of state:

$$\left(\frac{\partial E}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V - P$$

Hildebrand measures the slopes of a component's vapor-pressure curve at a series of pressures and temperatures in order to evaluate the right side of this equation. Then:

$$\delta = \left(\frac{\partial E}{\partial V}\right)_T^{1/2}$$

Values reported by Hildebrand are tabulated in Table XII.

Finally, Van Laar(59,60) has shown that for a van der Waal fluid:

$$\delta = \frac{\sqrt{a}}{\underline{V}^L}$$

where "a" is the van der Waal "a". Values of $\frac{\sqrt{a}}{\underline{V}^L}$ are also in Table XII.

TABLE XII

SOLUBILITY PARAMETERS

Compound	Calculated 100°F.	 200°F.	Reported by Chao(8) at 25°C.	 Hildebrand(20) at 25°C.	$\frac{\sqrt{a}}{V^L}$ *
Benzene	8.97	8.13	9.158	9.0	7.87
Cyclohexane	8.03	7.35	8.196	7.8	7.37
Hexane	7.09	6.31	7.266	7.2	6.22
Hydrogen	3.06	2.38	3.25	-	2.18

*NOTE: $a = \frac{27}{64}\frac{R^2T_c^2}{P_c}$

THERMOCOUPLE CALIBRATION

The thermocouples used in this work were calibrated against standardized thermometers in a temperature control bath. The thermometers had been calibrated by the U.S. Bureau of Standards.

Readings were taken at two elevated temperatures and at the ice point. This permitted evaluation of the constants in the equation:

$$E = a + bT + cT^2$$

By alternately reading the thermometer and the standardized portable potentiometer, a good estimate could be made of the actual temperature of the thermocouple at the instant the potentiometer was read.

For the thermocouple used to indicate the equilibrium temperature, the constants in the temperature-EMF relationship were:

$$a = -6.9005 \times 10^{-1}$$

$$b = 2.13531 \times 10^{-2}$$

$$c = 6.59597 \times 10^{-6}$$

for T in degrees Fahrenheit.

At 100°F., this thermocouple gave the reading:

$$E = 1.511 \text{ millivolts}$$

while at 200°F., it gave the reading:

$$E = 3.844 \text{ millivolts}$$

Experimental calibration data obtained for the thermocouples used in this work is presented in Table XIII.

TABLE XIII

THERMOCOUPLE CALIBRATION DATA

	T.C. No. 0		T.C. No.2		T.C. No.3[4]		T.C. No. 4		T.C. No.5		T.C. No.6		T.C. No.10	
Reading	Temp. (°C)	Milli Volts	Temp. (°C)	Milli Volts	Temp. (°C)	Milli Volts	Temp. (°C)	Milli Volts	Temp. (°C)	Milli Volts	Temp. (°C)	Milli Volts	Temp. (°C)	Milli Volts
0[1]	0	0	0	0	0	0	0	0	0	0	0	0	0	0
1[2]	64.48		62.80		65.33		64.17		63.82		64.80		65.10	
		2.614		2.539		2.651		2.591		2.577		2.615		2.638
2	64.42		62.76		65.29		64.10		63.75		64.76		65.02	
3[3]	103.7		103.6		103.6		103.6		103.7		103.7		103.7	
		4.283		4.281		4.290		4.278		4.278		4.277		4.276
4	103.7		103.6		103.6		103.6		103.7		103.7		103.7	

NOTES:

(1) Both junctions immersed in ice water
(2) Calibrated with Princo thermometer 253197
(3) Calibrated with Princo thermometer 503944
(4) Thermocouple used to indicate temperature of bath

CHANDLER GAUGE TESTER CALIBRATION

The absolute accuracy of the Chandler Gauge Tester, No. D3-13, has been determined in the pressure range of interest by comparing the calibration of a 1500 psi pressure gauge, No. C2-473, obtained by using the Chandler tester, with a calibration obtained using American Gauge Tester, No. 1315.

These results, shown in Table XIV, indicate that the gauge tester used in this work is accurate to within ± 3 psi in the pressure range studied.

TABLE XIV

GAUGE TESTER EVALUATION

American Gauge Tester No. 1315	Pressure Gauge	Difference	Chandler Gauge Tester No. D3-13	Pressure Gauge	Difference
525	535	-10			
			600	613	-13
			700	709	- 9
775	783	- 8			
			800	809	- 9
			1000	1009	- 9
1025	1033	- 8			
			1100	1110	-10
			1200	1211	-11
1275	1285	-10			
			1300	1311	-11
			1400	1411	-11
1475	1484	- 9			
			1500	1510	-10

EQUILIBRIUM DATA SOURCES FOR BINARY SYSTEMS

Experimental vapor-liquid equilibrium data sources for the binary systems of components studied in this work are listed in Tables XV and XVI.

TABLE XV

EQUILIBRIUM DATA SOURCES FOR HYDROGEN-HYDROCARBON SYSTEMS

Hydrocarbon	Ref.	Author	Press.Range psi	Temp.Range °F.	Phases Studied
Benzene	9	Connolly	116-3050	320-500	Vapor,Liquid
	26	Ipatieff	380-4420	77-212	Liquid
	31	Krichevskii	15-3500	77	Liquid
Cyclohexane	18	Frolich	0-1550	77	Liquid
	32	Krichevskii	720-10,000	68-140	Vapor,Liquid
Hexane	18	Frolich	0-1620	77	Liquid
	41	Nichols	0-10,000	40-460	Vapor,Liquid

TABLE XVI

EQUILIBRIUM DATA SOURCES FOR HYDROCARBON-HYDROCARBON SYSTEMS (Data at one atmosphere)

System	Ref.	Author
Benzene-Cyclohexane	19	Harrison
	33	Kumarkrishna
	51	Richards
	54	Scatchard
	57	Thornton
	65	Weck
Benzene-Hexane	33	Kumarkrishna
	40	Myers
	58	Tongberg

CALCULATION RESULTS

The calculations shown in Table XVII were based on the two equations of state method of calculating K-values. This method is discussed in detail in the sub-section entitled "Outline of Correlation Procedure". Generalized data was used only where experimental data did not exist. Further, the entropy of the liquid solution has been assumed to be a function of component volumes.

The "Initial Value" column contains the values of composition that were obtained experimentally, and the results of the first calculation of activity and fugacity coefficients. The K-values reported in this column are not the ratio of y_i to x_i, but rather are ratios of activity and fugacity coefficients.

The "Virial Equation Values" columns are the summary of the results of this calculation using the Virial Equation of State to calculate the vapor phase fugacity coefficients. All data was supplied to the computer in the program for the results reported in the column, "Unadjusted". The data in the "Adjusted" virial column are the results of using hydrogen-hydrocarbon interaction virial coefficients that were calculated from the data.

In this calculation, the vapor phase activity coefficient was calculated from the relationship:

$$\varphi_i = \gamma_i \nu_i / K_i$$

where K_i is the experimentally determined equilibrium composition ratio. This step required the assumption that γ_i and ν_i were known exactly.

Then values of all variables, except those that were to be solved for, were substituted into the integrated virial equation:

$$\ln \varphi_i = \frac{2}{\underline{V}_M^V} \sum_j y_j B_{ij}(T) - \ln \frac{P\underline{V}_M^V}{RT}$$

These calculations were run in groups of four, and the desired interaction virials were solved for by a method of least squares.

The data presented in the "Redlich-Kwong Values" column is based on the use of the Redlich-Kwong equation, integrated for moderate pressures, to estimate vapor-phase fugacity coefficients.

TABLE XVII

TABULATED CALCULATION RESULTS

```
RUN NUMBER            18
TEMPERATURE       100.00    DEGREES FAHRENHEIT
PRESSURE            567.    PSIA
                                                              VIRIAL EQUATION   VALUES    REDLICH-KWONG
                                              INITIAL VALUE    ADJUSTED        UNADJUSTED       VALUES
 VOLUME OF LIQUID (CC PER GM MOLE)                 121.042        120.975         120.899        120.890
 VOLUME OF VAPOR (CC PER GM MOLE)                  675.430        661.582         675.695
 BENZENE
  Y                                                  0.004          0.002           0.002          0.002
  X                                                  0.210          0.210           0.210          0.210
  K VALUE                                            0.017          0.010           0.011          0.010
  ACTIVITY COEFFICIENT,LIQUID PHASE                  1.423          1.424           1.425          1.425
  FUGACITY,PURE                                      0.007          0.007           0.007          0.007
  FUGACITY COEFFICIENT,VAPOR PHASE                   0.904          0.988           0.922          0.928
 CYCLOHEXANE
  Y                                                  0.             0.              0.             0.
  X                                                  0.             0.              0.             0.
  K VALUE                                            0.             0.008           0.008          0.008
  ACTIVITY COEFFICIENT,LIQUID PHASE                  1.084          1.084           1.085          1.085
  FUGACITY,PURE                                      0.007          0.007           0.007          0.007
  FUGACITY COEFFICIENT,VAPOR PHASE                   0.895          0.979           0.913          0.937
 HEXANE
  Y                                                  0.011          0.008           0.008          0.008
  X                                                  0.751          0.750           0.750          0.750
  K VALUE                                            0.015          0.010           0.011          0.011
  ACTIVITY COEFFICIENT,LIQUID PHASE                  1.009          1.008           1.008          1.008
  FUGACITY,PURE                                      0.010          0.010           0.010          0.010
  FUGACITY COEFFICIENT,VAPOR PHASE                   0.932          1.021           0.951          0.960
 HYDROGEN
  Y                                                  0.985          0.990           0.989          0.990
  X                                                  0.039          0.039           0.040          0.040
  K VALUE                                           25.518         25.179          24.612         24.591
  ACTIVITY COEFFICIENT,LIQUID PHASE                  1.686          1.686           1.686          1.686
  FUGACITY,PURE                                     14.929         14.929          14.929         14.929
  FUGACITY COEFFICIENT,VAPOR PHASE                   1.023          1.000           1.023          1.024
 INTERACTION VIRIAL COEFFICIENTS
  B(HYDROGEN-BENZENE)                                            -140.588          -4.000
  B(HYDROGEN-CYCLOHEXANE)                                           0.             -7.000
  B(HYDROGEN-HEXANE)                                              -51.052           7.000
```

```
RUN NUMBER            22
TEMPERATURE       100.00    DEGREES FAHRENHEIT
PRESSURE            580.    PSIA
                                                              VIRIAL EQUATION   VALUES    REDLICH-KWONG
                                              INITIAL VALUE    ADJUSTED        UNADJUSTED       VALUES
 VOLUME OF LIQUID (CC PER GM MOLE)                  98.540         98.950          98.920         98.919
 VOLUME OF VAPOR (CC PER GM MOLE)                  660.599        646.661         660.880
 BENZENE
  Y                                                  0.010          0.005           0.006          0.006
  X                                                  0.763          0.768           0.767          0.767
  K VALUE                                            0.013          0.007           0.007          0.007
  ACTIVITY COEFFICIENT,LIQUID PHASE                  1.050          1.048           1.048          1.048
  FUGACITY,PURE                                      0.006          0.006           0.006          0.006
  FUGACITY COEFFICIENT,VAPOR PHASE                   0.915          0.988           0.931          0.933
 CYCLOHEXANE
  Y                                                  0.             0.              0.             0.
  X                                                  0.             0.              0.             0.
  K VALUE                                            0.             0.007           0.007          0.007
  ACTIVITY COEFFICIENT,LIQUID PHASE                  1.015          1.017           1.017          1.017
  FUGACITY,PURE                                      0.007          0.007           0.007          0.007
  FUGACITY COEFFICIENT,VAPOR PHASE                   0.903          0.979           0.920          0.943
 HEXANE
  Y                                                  0.003          0.003           0.003          0.003
  X                                                  0.211          0.213           0.213          0.213
  K VALUE                                            0.015          0.013           0.014          0.014
  ACTIVITY COEFFICIENT,LIQUID PHASE                  1.358          1.369           1.368          1.368
  FUGACITY,PURE                                      0.010          0.010           0.010          0.010
  FUGACITY COEFFICIENT,VAPOR PHASE                   0.939          1.022           0.959          0.967
 HYDROGEN
  Y                                                  0.987          0.992           0.991          0.991
  X                                                  0.026          0.020           0.020          0.020
  K VALUE                                           37.962         50.135          48.981         48.935
  ACTIVITY COEFFICIENT,LIQUID PHASE                  3.415          3.431           3.429          3.429
  FUGACITY,PURE                                     14.614         14.614          14.614         14.614
  FUGACITY COEFFICIENT,VAPOR PHASE                   1.023          1.000           1.023          1.024
 INTERACTION VIRIAL COEFFICIENTS
  B(HYDROGEN-BENZENE)                                            -140.588          -4.000
  B(HYDROGEN-CYCLOHEXANE)                                           0.             -7.000
  B(HYDROGEN-HEXANE)                                              -51.052           7.000
```

```
RUN NUMBER              21
TEMPERATURE         100.00    DEGREES FAHRENHEIT
PRESSURE             1100.    PSIA
                                                          VIRIAL EQUATION  VALUES    REDLICH-KWONG
                                          INITIAL VALUE   ADJUSTED     UNADJUSTED        VALUES
 VOLUME OF LIQUID (CC PER GM MOLE)           118.027       117.990       117.702        117.687
 VOLUME OF VAPOR (CC PER GM MOLE)            354.881       341.020       355.093
 BENZENE
  Y                                            0.003         0.001         0.001          0.001
  X                                            0.203         0.203         0.202          0.202
  K VALUE                                      0.013         0.006         0.007          0.007
  ACTIVITY COEFFICIENT,LIQUID PHASE            1.463         1.464         1.468          1.468
  FUGACITY,PURE                                0.004         0.004         0.004          0.004
  FUGACITY COEFFICIENT,VAPOR PHASE             0.855         0.977         0.889          0.887
 CYCLOHEXANE
  Y                                            0.            0.            0.             0.
  X                                            0.            0.            0.             0.
  K VALUE                                      0.            0.005         0.005          0.005
  ACTIVITY COEFFICIENT,LIQUID PHASE            1.098         1.099         1.100          1.100
  FUGACITY,PURE                                0.004         0.004         0.004          0.004
  FUGACITY COEFFICIENT,VAPOR PHASE             0.839         0.960         0.874          0.906
 HEXANE
  Y                                            0.008         0.004         0.005          0.005
  X                                            0.724         0.724         0.722          0.722
  K VALUE                                      0.012         0.006         0.007          0.007
  ACTIVITY COEFFICIENT,LIQUID PHASE            1.001         1.001         1.000          1.000
  FUGACITY,PURE                                0.006         0.006         0.006          0.006
  FUGACITY COEFFICIENT,VAPOR PHASE             0.906         1.042         0.944          0.950
 HYDROGEN
  Y                                            0.989         0.994         0.994          0.994
  X                                            0.072         0.073         0.076          0.076
  K VALUE                                     13.660        13.660        13.078         13.048
  ACTIVITY COEFFICIENT,LIQUID PHASE            1.680         1.679         1.679          1.679
  FUGACITY,PURE                                8.132         8.132         8.132          8.132
  FUGACITY COEFFICIENT,VAPOR PHASE             1.044         1.000         1.044          1.046
 INTERACTION VIRIAL COEFFICIENTS
  B(HYDROGEN-BENZENE)                                     -140.588        -4.000
  B(HYDROGEN-CYCLOHEXANE)                                    0.           -7.000
  B(HYDROGEN-HEXANE)                                       -51.052         7.000
```

```
RUN NUMBER              25
TEMPERATURE         100.00    DEGREES FAHRENHEIT
PRESSURE             1102.    PSIA
                                                          VIRIAL EQUATION  VALUES    REDLICH-KWONG
                                          INITIAL VALUE   ADJUSTED     UNADJUSTED        VALUES
 VOLUME OF LIQUID (CC PER GM MOLE)            96.789        97.889        97.783         97.777
 VOLUME OF VAPOR (CC PER GM MOLE)            354.336       340.347       354.466
 BENZENE
  Y                                            0.006         0.003         0.003          0.003
  X                                            0.741         0.755         0.753          0.753
  K VALUE                                      0.008         0.004         0.005          0.005
  ACTIVITY COEFFICIENT,LIQUID PHASE            1.062         1.054         1.055          1.055
  FUGACITY,PURE                                0.004         0.004         0.004          0.004
  FUGACITY COEFFICIENT,VAPOR PHASE             0.881         0.977         0.900          0.893
 CYCLOHEXANE
  Y                                            0.            0.            0.             0.
  X                                            0.            0.            0.             0.
  K VALUE                                      0.            0.004         0.005          0.004
  ACTIVITY COEFFICIENT,LIQUID PHASE            1.006         1.011         1.011          1.011
  FUGACITY,PURE                                0.004         0.004         0.004          0.004
  FUGACITY COEFFICIENT,VAPOR PHASE             0.862         0.960         0.883          0.913
 HEXANE
  Y                                            0.002         0.002         0.002          0.002
  X                                            0.205         0.209         0.209          0.209
  K VALUE                                      0.010         0.008         0.008          0.008
  ACTIVITY COEFFICIENT,LIQUID PHASE            1.310         1.339         1.336          1.336
  FUGACITY,PURE                                0.006         0.006         0.006          0.006
  FUGACITY COEFFICIENT,VAPOR PHASE             0.930         1.042         0.954          0.958
 HYDROGEN
  Y                                            0.992         0.995         0.995          0.995
  X                                            0.053         0.036         0.038          0.038
  K VALUE                                     18.725        27.501        26.312         26.251
  ACTIVITY COEFFICIENT,LIQUID PHASE            3.343         3.387         3.383          3.383
  FUGACITY,PURE                                8.119         8.119         8.119          8.119
  FUGACITY COEFFICIENT,VAPOR PHASE             1.044         1.000         1.044          1.046
 INTERACTION VIRIAL COEFFICIENTS
  B(HYDROGEN-BENZENE)                                     -140.588        -4.000
  B(HYDROGEN-CYCLOHEXANE)                                    0.           -7.000
  B(HYDROGEN-HEXANE)                                       -51.052         7.000
```

```
RUN NUMBER            30
TEMPERATURE        100.00    DEGREES FAHRENHEIT
PRESSURE            577.     PSIA
                                                            VIRIAL EQUATION  VALUES    REDLICH-KWONG
                                           . INITIAL VALUE  ADJUSTED      UNADJUSTED      VALUES
 VOLUME OF LIQUID (CC PER GM MOLE)             125.782      125.081       124.988        124.984
 VOLUME OF VAPOR (CC PER GM MOLE)              663.886      650.113       664.255
 BENZENE
  Y                                            0.           0.            0.             0.
  X                                            0.           0.            0.             0.
  K VALUE                                      0.           0.010         0.011          0.011
  ACTIVITY COEFFICIENT,LIQUID PHASE            1.506        1.515         1.517          1.517
  FUGACITY,PURE                                0.007        0.007         0.007          0.007
  FUGACITY COEFFICIENT,VAPOR PHASE             0.897        0.988         0.922          0.928
 CYCLOHEXANE
  Y                                            0.003        0.002         0.002          0.002
  X                                            0.193        0.191         0.191          0.191
  K VALUE                                      0.017        0.008         0.008          0.008
  ACTIVITY COEFFICIENT,LIQUID PHASE            1.119        1.123         1.123          1.124
  FUGACITY,PURE                                0.007        0.007         0.007          0.007
  FUGACITY COEFFICIENT,VAPOR PHASE             0.888        0.979         0.914          0.937
 HEXANE
  Y                                            0.013        0.008         0.008          0.008
  X                                            0.771        0.765         0.764          0.764
  K VALUE                                      0.017        0.010         0.011          0.011
  ACTIVITY COEFFICIENT,LIQUID PHASE            1.001        1.000         1.000          1.000
  FUGACITY,PURE                                0.010        0.010         0.010          0.010
  FUGACITY COEFFICIENT,VAPOR PHASE             0.927        1.021         0.953          0.961
 HYDROGEN
  Y                                            0.984        0.991         0.990          0.990
  X                                            0.036        0.044         0.045          0.045
  K VALUE                                     27.033       22.588        22.072         22.052
  ACTIVITY COEFFICIENT,LIQUID PHASE            1.538        1.538         1.538          1.538
  FUGACITY,PURE                               14.685       14.685        14.685         14.685
  FUGACITY COEFFICIENT,VAPOR PHASE             1.024        1.000         1.023          1.024
 INTERACTION VIRIAL COEFFICIENTS
  B(HYDROGEN-BENZENE)                                       0.           -4.000
  B(HYDROGEN-CYCLOHEXANE)                                 -97.207        -7.000
  B(HYDROGEN-HEXANE)                                      -52.143         7.000
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RUN NUMBER            32
TEMPERATURE        100.00    DEGREES FAHRENHEIT
PRESSURE           1060.     PSIA
                                                            VIRIAL EQUATION  VALUES    REDLICH-KWONG
                                             INITIAL VALUE  ADJUSTED      UNADJUSTED      VALUES
 VOLUME OF LIQUID (CC PER GM MOLE)             123.377      121.969       121.666        121.649
 VOLUME OF VAPOR (CC PER GM MOLE)              367.904      353.886       367.984
 BENZENE
  Y                                            0.           0.            0.             0.
  X                                            0.           0.            0.             0.
  K VALUE                                      0.           0.007         0.007          0.008
  ACTIVITY COEFFICIENT,LIQUID PHASE            1.539        1.559         1.564          1.564
  FUGACITY,PURE                                0.004        0.004         0.004          0.004
  FUGACITY COEFFICIENT,VAPOR PHASE             0.879        0.978         0.893          0.891
 CYCLOHEXANE
  Y                                            0.002        0.001         0.001          0.001
  X                                            0.188        0.185         0.184          0.184
  K VALUE                                      0.009        0.005         0.006          0.005
  ACTIVITY COEFFICIENT,LIQUID PHASE            1.132        1.140         1.142          1.142
  FUGACITY,PURE                                0.004        0.004         0.004          0.004
  FUGACITY COEFFICIENT,VAPOR PHASE             0.864        0.961         0.878          0.909
 HEXANE
  Y                                            0.006        0.005         0.005          0.005
  X                                            0.750        0.738         0.736          0.736
  K VALUE                                      0.009        0.006         0.007          0.007
  ACTIVITY COEFFICIENT,LIQUID PHASE            0.998        0.996         0.996          0.996
  FUGACITY,PURE                                0.007        0.007         0.007          0.007
  FUGACITY COEFFICIENT,VAPOR PHASE             0.933        1.040         0.948          0.952
 HYDROGEN
  Y                                            0.992        0.994         0.994          0.994
  X                                            0.062        0.077         0.080          0.080
  K VALUE                                     16.000       12.907        12.379         12.353
  ACTIVITY COEFFICIENT,LIQUID PHASE            1.537        1.536         1.535          1.535
  FUGACITY,PURE                                8.404        8.404         8.404          8.404
  FUGACITY COEFFICIENT,VAPOR PHASE             1.042        1.000         1.042          1.045
 INTERACTION VIRIAL COEFFICIENTS
  B(HYDROGEN-BENZENE)                                       0.           -4.000
  B(HYDROGEN-CYCLOHEXANE)                                 -97.207        -7.000
  B(HYDROGEN-HEXANE)                                      -52.143         7.000
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RUN NUMBER              34
TEMPERATURE         100.00   DEGREES FAHRENHEIT
PRESSURE             563.    PSIA
                                                            VIRIAL EQUATION  VALUES    REDLICH-KWONG
                                            INITIAL VALUE   ADJUSTED     UNADJUSTED       VALUES
 VOLUME OF LIQUID (CC PER GM MOLE)             112.852       112.263       112.211        112.208
 VOLUME OF VAPOR (CC PER GM MOLE)              680.331       666.138       680.389
 BENZENE
  Y                                              0.            0.            0.             0.
  X                                              0.            0.            0.             0.
  K VALUE                                        0.            0.008         0.009          0.009
  ACTIVITY COEFFICIENT,LIQUID PHASE              1.197         1.202         1.203          1.203
  FUGACITY,PURE                                  0.007         0.007         0.007          0.007
  FUGACITY COEFFICIENT,VAPOR PHASE               0.930         0.988         0.934          0.936
 CYCLOHEXANE
  Y                                              0.007         0.006         0.006          0.006
  X                                              0.803         0.797         0.796          0.796
  K VALUE                                        0.008         0.007         0.008          0.007
  ACTIVITY COEFFICIENT,LIQUID PHASE              1.009         1.010         1.010          1.010
  FUGACITY,PURE                                  0.007         0.007         0.007          0.007
  FUGACITY COEFFICIENT,VAPOR PHASE               0.919         0.979         0.923          0.945
 HEXANE
  Y                                              0.002         0.002         0.002          0.002
  X                                              0.175         0.174         0.174          0.174
  K VALUE                                        0.013         0.011         0.012          0.012
  ACTIVITY COEFFICIENT,LIQUID PHASE              1.098         1.094         1.093          1.093
  FUGACITY,PURE                                  0.010         0.010         0.010          0.010
  FUGACITY COEFFICIENT,VAPOR PHASE               0.959         1.021         0.963          0.968
 HYDROGEN
  Y                                              0.991         0.992         0.992          0.992
  X                                              0.022         0.030         0.030          0.030
  K VALUE                                       44.842        33.624        32.878         32.848
  ACTIVITY COEFFICIENT,LIQUID PHASE              2.243         2.237         2.237          2.237
  FUGACITY,PURE                                 15.029        15.029        15.029         15.029
  FUGACITY COEFFICIENT,VAPOR PHASE               1.023         1.000         1.023          1.023
 INTERACTION VIRIAL COEFFICIENTS
  B(HYDROGEN-BENZENE)                                          0.           -4.000
  B(HYDROGEN-CYCLOHEXANE)                                    -97.207        -7.000
  B(HYDROGEN-HEXANE)                                         -52.143         7.000
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RUN NUMBER              35
TEMPERATURE         100.00   DEGREES FAHRENHEIT
PRESSURE            1106.    PSIA
                                                            VIRIAL EQUATION  VALUES    REDLICH-KWONG
                                            INITIAL VALUE   ADJUSTED     UNADJUSTED       VALUES
 VOLUME OF LIQUID (CC PER GM MOLE)             110.918       110.202       110.005        109.994
 VOLUME OF VAPOR (CC PER GM MOLE)              353.159       339.087       353.220
 BENZENE
  Y                                              0.            0.            0.             0.
  X                                              0.            0.            0.             0.
  K VALUE                                        0.            0.005         0.005          0.006
  ACTIVITY COEFFICIENT,LIQUID.PHASE              1.216         1.224         1.226          1.226
  FUGACITY,PURE                                  0.004         0.004         0.004          0.004
  FUGACITY COEFFICIENT,VAPOR PHASE               0.892         0.977         0.901          0.894
 CYCLOHEXANE
  Y                                              0.004         0.003         0.004          0.004
  X                                              0.783         0.775         0.773          0.773
  K VALUE                                        0.006         0.004         0.005          0.005
  ACTIVITY COEFFICIENT,LIQUID PHASE              1.013         1.014         1.015          1.015
  FUGACITY,PURE                                  0.004         0.004         0.004          0.004
  FUGACITY COEFFICIENT,VAPOR PHASE               0.873         0.960         0.883          0.914
 HEXANE
  Y                                              0.001         0.001         0.001          0.001
  X                                              0.171         0.169         0.169          0.169
  K VALUE                                        0.009         0.006         0.007          0.007
  ACTIVITY COEFFICIENT,LIQUID PHASE              1.082         1.077         1.075          1.075
  FUGACITY,PURE                                  0.006         0.006         0.006          0.006
  FUGACITY COEFFICIENT,VAPOR PHASE               0.947         1.042         0.957          0.959
 HYDROGEN
  Y                                              0.994         0.996         0.995          0.995
  X                                              0.046         0.055         0.058          0.058
  K VALUE                                       21.376        17.940        17.169         17.130
  ACTIVITY COEFFICIENT,LIQUID PHASE              2.224         2.217         2.215          2.215
  FUGACITY,PURE                                  8.093         8.093         8.093          8.093
  FUGACITY COEFFICIENT,VAPOR PHASE               1.044         1.000         1.044          1.046
 INTERACTION VIRIAL COEFFICIENTS
  B(HYDROGEN-BENZENE)                                          0.           -4.000
  B(HYDROGEN-CYCLOHEXANE)                                    -97.207        -7.000
  B(HYDROGEN-HEXANE)                                         -52.143         7.000
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RUN NUMBER              40
TEMPERATURE         100.00    DEGREES FAHRENHEIT
PRESSURE              582.    PSIA
                                                             VIRIAL EQUATION  VALUES     REDLICH-KWONG
                                           INITIAL VALUE    ADJUSTED     UNADJUSTED         VALUES
 VOLUME OF LIQUID (CC PER GM MOLE)            103.087        103.019        102.984         102.981
 VOLUME OF VAPOR (CC PER GM MOLE)             658.161        644.361        658.653
 BENZENE
  Y                                             0.004          0.002          0.002           0.002
  X                                             0.293          0.292          0.292           0.292
  K VALUE                                       0.014          0.007          0.007           0.007
  ACTIVITY COEFFICIENT,LIQUID PHASE             1.074          1.075          1.075           1.075
  FUGACITY,PURE                                 0.006          0.006          0.006           0.006
  FUGACITY COEFFICIENT,VAPOR PHASE              0.909          0.988          0.937           0.937
 CYCLOHEXANE
  Y                                             0.010          0.005          0.005           0.005
  X                                             0.686          0.685          0.685           0.685
  K VALUE                                       0.014          0.007          0.007           0.007
  ACTIVITY COEFFICIENT,LIQUID PHASE             1.005          1.005          1.005           1.005
  FUGACITY,PURE                                 0.007          0.007          0.007           0.007
  FUGACITY COEFFICIENT,VAPOR PHASE              0.896          0.979          0.925           0.947
 HEXANE
  Y                                             0.             0.             0.              0.
  X                                             0.             0.             0.              0.
  K VALUE                                       0.             0.012          0.013           0.013
  ACTIVITY COEFFICIENT,LIQUID PHASE             1.281          1.279          1.278           1.278
  FUGACITY,PURE                                 0.010          0.010          0.010           0.010
  FUGACITY COEFFICIENT,VAPOR PHASE              0.935          1.022          0.966           0.971
 HYDROGEN
  Y                                             0.986          0.993          0.993           0.993
  X                                             0.021          0.022          0.023           0.023
  K VALUE                                      46.075         44.410         43.392          43.351
  ACTIVITY COEFFICIENT,LIQUID PHASE             3.051          3.049          3.048           3.048
  FUGACITY,PURE                                14.567         14.567         14.567          14.567
  FUGACITY COEFFICIENT,VAPOR PHASE              1.024          1.000          1.023           1.024
 INTERACTION VIRIAL COEFFICIENTS
  B(HYDROGEN-BENZENE)                                       -116.621         -4.000
  B(HYDROGEN-CYCLOHEXANE)                                   -150.809         -7.000
  B(HYDROGEN-HEXANE)                                           0.             7.000
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RUN NUMBER              44
TEMPERATURE         100.00    DEGREES FAHRENHEIT
PRESSURE              588.    PSIA
                                                             VIRIAL EQUATION  VALUES     REDLICH-KWONG
                                           INITIAL VALUE    ADJUSTED     UNADJUSTED         VALUES
 VOLUME OF LIQUID (CC PER GM MOLE)             92.495         92.731         92.710          92.710
 VOLUME OF VAPOR (CC PER GM MOLE)             651.923        637.809        652.119
 BENZENE
  Y                                             0.008          0.005          0.006           0.006
  X                                             0.845          0.848          0.848           0.848
  K VALUE                                       0.009          0.006          0.007           0.007
  ACTIVITY COEFFICIENT,LIQUID PHASE             1.005          1.005          1.005           1.005
  FUGACITY,PURE                                 0.006          0.006          0.006           0.006
  FUGACITY COEFFICIENT,VAPOR PHASE              0.926          0.988          0.938           0.938
 CYCLOHEXANE
  Y                                             0.002          0.001          0.001           0.001
  X                                             0.136          0.137          0.137           0.137
  K VALUE                                       0.015          0.007          0.008           0.007
  ACTIVITY COEFFICIENT,LIQUID PHASE             1.086          1.089          1.089           1.089
  FUGACITY,PURE                                 0.006          0.006          0.006           0.006
  FUGACITY COEFFICIENT,VAPOR PHASE              0.914          0.979          0.927           0.948
 HEXANE
  Y                                             0.             0.             0.              0.
  X                                             0.             0.             0.              0.
  K VALUE                                       0.             0.016          0.017           0.017
  ACTIVITY COEFFICIENT,LIQUID PHASE             1.711          1.725          1.723           1.723
  FUGACITY,PURE                                 0.010          0.010          0.010           0.010
  FUGACITY COEFFICIENT,VAPOR PHASE              0.952          1.022          0.967           0.973
 HYDROGEN
  Y                                             0.990          0.994          0.993           0.993
  X                                             0.019          0.015          0.015           0.015
  K VALUE                                      52.100         66.203         64.667          64.604
  ACTIVITY COEFFICIENT,LIQUID PHASE             4.570          4.589          4.588           4.587
  FUGACITY,PURE                                14.427         14.427         14.427          14.427
  FUGACITY COEFFICIENT,VAPOR PHASE              1.024          1.000          1.023           1.024
 INTERACTION VIRIAL COEFFICIENTS
  B(HYDROGEN-BENZENE)                                       -116.621         -4.000
  B(HYDROGEN-CYCLOHEXANE)                                   -150.809         -7.000
  B(HYDROGEN-HEXANE)                                           0.             7.000
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RUN NUMBER              41
TEMPERATURE         100.00    DEGREES FAHRENHEIT
PRESSURE             1122.    PSIA
                                                              VIRIAL EQUATION  VALUES       REDLICH-KWONG
                                               INITIAL VALUE  ADJUSTED        UNADJUSTED        VALUES
 VOLUME OF LIQUID (CC PER GM MOLE)                101.522       101.709         101.574        101.567
 VOLUME OF VAPOR (CC PER GM MOLE)                 348.228       334.234         348.376
 BENZENE
  Y                                                 0.002         0.001           0.001          0.001
  X                                                 0.286         0.287           0.286          0.286
  K VALUE                                           0.007         0.004           0.005          0.005
  ACTIVITY COEFFICIENT,LIQUID PHASE                 1.086         1.085           1.086          1.086
  FUGACITY,PURE                                     0.004         0.004           0.004          0.004
  FUGACITY COEFFICIENT,VAPOR PHASE                  0.885         0.977           0.904          0.895
 CYCLOHEXANE
  Y                                                 0.005         0.003           0.003          0.003
  X                                                 0.670         0.672           0.671          0.671
  K VALUE                                           0.007         0.004           0.004          0.004
  ACTIVITY COEFFICIENT,LIQUID PHASE                 1.001         1.002           1.001          1.001
  FUGACITY,PURE                                     0.004         0.004           0.004          0.004
  FUGACITY COEFFICIENT,VAPOR PHASE                  0.865         0.959           0.885          0.916
 HEXANE
  Y                                                 0.            0.              0.             0.
  X                                                 0.            0.              0.             0.
  K VALUE                                           0.            0.007           0.008          0.008
  ACTIVITY COEFFICIENT,LIQUID PHASE                 1.249         1.253           1.250          1.250
  FUGACITY,PURE                                     0.006         0.006           0.006          0.006
  FUGACITY COEFFICIENT,VAPOR PHASE                  0.938         1.043           0.960          0.961
 HYDROGEN
  Y                                                 0.993         0.996           0.996          0.996
  X                                                 0.044         0.041           0.043          0.043
  K VALUE                                          22.566        24.066          23.012         22.958
  ACTIVITY COEFFICIENT,LIQUID PHASE                 3.007         3.012           3.008          3.008
  FUGACITY,PURE                                     7.991         7.991           7.991          7.991
  FUGACITY COEFFICIENT,VAPOR PHASE                  1.045         1.000           1.045          1.047
 INTERACTION VIRIAL COEFFICIENTS
  B(HYDROGEN-BENZENE)                                          -116.621          -4.000
  B(HYDROGEN-CYCLOHEXANE)                                      -150.809          -7.000
  B(HYDROGEN-HEXANE)                                              0.              7.000
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RUN NUMBER              45
TEMPERATURE         100.00    DEGREES FAHRENHEIT
PRESSURE             1088.    PSIA
                                                              VIRIAL EQUATION  VALUES       REDLICH-KWONG
                                               INITIAL VALUE  ADJUSTED        UNADJUSTED        VALUES
 VOLUME OF LIQUID (CC PER GM MOLE)                 91.916        92.057          91.986         91.982
 VOLUME OF VAPOR (CC PER GM MOLE)                 358.774       344.694         358.860
 BENZENE
  Y                                                 0.005         0.003           0.004          0.004
  X                                                 0.836         0.838           0.837          0.837
  K VALUE                                           0.006         0.004           0.004          0.004
  ACTIVITY COEFFICIENT,LIQUID PHASE                 1.007         1.007           1.007          1.007
  FUGACITY,PURE                                     0.004         0.004           0.004          0.004
  FUGACITY COEFFICIENT,VAPOR PHASE                  0.897         0.977           0.909          0.900
 CYCLOHEXANE
  Y                                                 0.001         0.001           0.001          0.001
  X                                                 0.135         0.135           0.135          0.135
  K VALUE                                           0.007         0.004           0.005          0.005
  ACTIVITY COEFFICIENT,LIQUID PHASE                 1.078         1.080           1.079          1.079
  FUGACITY,PURE                                     0.004         0.004           0.004          0.004
  FUGACITY COEFFICIENT,VAPOR PHASE                  0.878         0.960           0.891          0.920
 HEXANE
  Y                                                 0.            0.              0.             0.
  X                                                 0.            0.000           0.000          0.000
  K VALUE                                           0.            0.010           0.010          0.010
  ACTIVITY COEFFICIENT,LIQUID PHASE                 1.679         1.686           1.682          1.682
  FUGACITY,PURE                                     0.006         0.006           0.006          0.006
  FUGACITY COEFFICIENT,VAPOR PHASE                  0.947         1.041           0.962          0.964
 HYDROGEN
  Y                                                 0.994         0.996           0.996          0.996
  X                                                 0.029         0.027           0.028          0.028
  K VALUE                                          34.394        37.196          35.610         35.529
  ACTIVITY COEFFICIENT,LIQUID PHASE                 4.521         4.530           4.524          4.524
  FUGACITY,PURE                                     8.212         8.212           8.212          8.212
  FUGACITY COEFFICIENT,VAPOR PHASE                  1.043         1.000           1.043          1.046
 INTERACTION VIRIAL COEFFICIENTS
  B(HYDROGEN-BENZENE)                                          -116.621          -4.000
  B(HYDROGEN-CYCLOHEXANE)                                      -150.809          -7.000
  B(HYDROGEN-HEXANE)                                              0.              7.000
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RUN NUMBER              50
TEMPERATURE         100.00    DEGREES FAHRENHEIT
PRESSURE              544.    PSIA
                                                       VIRIAL EQUATION  VALUES       REDLICH-KWONG
                                         INITIAL VALUE  ADJUSTED       UNADJUSTED       VALUES
 VOLUME OF LIQUID (CC PER GM MOLE)          106.348     106.538         106.499         106.498
 VOLUME OF VAPOR (CC PER GM MOLE)           703.547     689.464         703.651
 BENZENE
  Y                                           0.005       0.004           0.004           0.004
  X                                           0.487       0.488           0.488           0.488
  K VALUE                                     0.010       0.008           0.008           0.008
  ACTIVITY COEFFICIENT,LIQUID PHASE           1.135       1.133           1.134           1.134
  FUGACITY,PURE                               0.007       0.007           0.007           0.007
  FUGACITY COEFFICIENT,VAPOR PHASE            0.925       0.989           0.931           0.935
 CYCLOHEXANE
  Y                                           0.002       0.001           0.001           0.001
  X                                           0.168       0.168           0.168           0.168
  K VALUE                                     0.012       0.007           0.008           0.007
  ACTIVITY COEFFICIENT,LIQUID PHASE           0.999       0.999           0.999           0.999
  FUGACITY,PURE                               0.007       0.007           0.007           0.007
  FUGACITY COEFFICIENT,VAPOR PHASE            0.915       0.980           0.921           0.944
 HEXANE
  Y                                           0.004       0.004           0.004           0.004
  X                                           0.318       0.319           0.319           0.319
  K VALUE                                     0.013       0.012           0.013           0.013
  ACTIVITY COEFFICIENT,LIQUID PHASE           1.163       1.165           1.165           1.165
  FUGACITY,PURE                               0.011       0.011           0.011           0.011
  FUGACITY COEFFICIENT,VAPOR PHASE            0.951       1.020           0.958           0.966
 HYDROGEN
  Y                                           0.989       0.991           0.990           0.991
  X                                           0.027       0.024           0.025           0.025
  K VALUE                                    36.630      40.535          39.659          39.625
  ACTIVITY COEFFICIENT,LIQUID PHASE           2.608       2.611           2.611           2.611
  FUGACITY,PURE                              15.523      15.523          15.523          15.523
  FUGACITY COEFFICIENT,VAPOR PHASE            1.022       1.000           1.022           1.023
 INTERACTION VIRIAL COEFFICIENTS
  B(HYDROGEN-BENZENE)                                   -80.047          -4.000
  B(HYDROGEN-CYCLOHEXANE)                              -171.164          -7.000
  B(HYDROGEN-HEXANE)                                    -35.368           7.000
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RUN NUMBER              51
TEMPERATURE         100.00    DEGREES FAHRENHEIT
PRESSURE             1074.    PSIA
                                                       VIRIAL EQUATION  VALUES       REDLICH-KWONG
                                         INITIAL VALUE  ADJUSTED       UNADJUSTED       VALUES
 VOLUME OF LIQUID (CC PER GM MOLE)          104.097     104.964         104.814         104.806
 VOLUME OF VAPOR (CC PER GM MOLE)           363.119     349.224         363.341
 BENZENE
  Y                                           0.004       0.002           0.002           0.002
  X                                           0.471       0.477           0.476           0.476
  K VALUE                                     0.008       0.005           0.005           0.005
  ACTIVITY COEFFICIENT,LIQUID PHASE           1.156       1.148           1.150           1.150
  FUGACITY,PURE                               0.004       0.004           0.004           0.004
  FUGACITY COEFFICIENT,VAPOR PHASE            0.867       0.977           0.898           0.894
 CYCLOHEXANE
  Y                                           0.002       0.001           0.001           0.001
  X                                           0.163       0.165           0.165           0.165
  K VALUE                                     0.012       0.004           0.005           0.004
  ACTIVITY COEFFICIENT,LIQUID PHASE           0.999       0.999           0.999           0.999
  FUGACITY,PURE                               0.004       0.004           0.004           0.004
  FUGACITY COEFFICIENT,VAPOR PHASE            0.849       0.961           0.882           0.912
 HEXANE
  Y                                           0.004       0.002           0.002           0.002
  X                                           0.308       0.312           0.311           0.311
  K VALUE                                     0.013       0.007           0.007           0.007
  ACTIVITY COEFFICIENT,LIQUID PHASE           1.133       1.144           1.142           1.142
  FUGACITY,PURE                               0.006       0.006           0.006           0.006
  FUGACITY COEFFICIENT,VAPOR PHASE            0.916       1.041           0.951           0.956
 HYDROGEN
  Y                                           0.990       0.995           0.994           0.994
  X                                           0.058       0.046           0.048           0.049
  K VALUE                                    17.071      21.444          20.543          20.498
  ACTIVITY COEFFICIENT,LIQUID PHASE           2.567       2.581           2.579           2.579
  FUGACITY,PURE                               8.307       8.307           8.307           8.307
  FUGACITY COEFFICIENT,VAPOR PHASE            1.043       1.000           1.043           1.045
 INTERACTION VIRIAL COEFFICIENTS
  B(HYDROGEN-BENZENE)                                   -80.047          -4.000
  B(HYDROGEN-CYCLOHEXANE)                              -171.164          -7.000
  B(HYDROGEN-HEXANE)                                    -35.368           7.000
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RUN NUMBER           19
TEMPERATURE      200.00   DEGREES FAHRENHEIT
PRESSURE           558.   PSIA
                                                             VIRIAL EQUATION  VALUES    REDLICH-KWONG
                                             INITIAL VALUE   ADJUSTED      UNADJUSTED      VALUES
 VOLUME OF LIQUID (CC PER GM MOLE)              131.058       130.942       130.868       130.866
 VOLUME OF VAPOR (CC PER GM MOLE)               805.230       794.805       804.345
 BENZENE
  Y                                               0.014         0.013         0.015         0.015
  X                                               0.209         0.209         0.209         0.209
  K VALUE                                         0.068         0.060         0.072         0.070
  ACTIVITY COEFFICIENT,LIQUID PHASE               1.350         1.352         1.352         1.353
  FUGACITY,PURE                                   0.046         0.046         0.046         0.046
  FUGACITY COEFFICIENT,VAPOR PHASE                0.877         1.028         0.861         0.882
 CYCLOHEXANE
  Y                                               0.            0.            0.            0.
  X                                               0.            0.            0.            0.
  K VALUE                                         0.            0.048         0.057         0.056
  ACTIVITY COEFFICIENT,LIQUID PHASE               1.104         1.105         1.105         1.105
  FUGACITY,PURE                                   0.044         0.044         0.044         0.044
  FUGACITY COEFFICIENT,VAPOR PHASE                0.873         1.026         0.856         0.882
 HEXANE
  Y                                               0.046         0.044         0.053         0.052
  X                                               0.745         0.744         0.744         0.744
  K VALUE                                         0.061         0.059         0.071         0.070
  ACTIVITY COEFFICIENT,LIQUID PHASE               1.004         1.004         1.004         1.004
  FUGACITY,PURE                                   0.063         0.063         0.063         0.063
  FUGACITY COEFFICIENT,VAPOR PHASE                0.901         1.063         0.883         0.899
 HYDROGEN
  Y                                               0.940         0.943         0.932         0.933
  X                                               0.046         0.047         0.048         0.048
  K VALUE                                        20.524        20.077        19.497        19.514
  ACTIVITY COEFFICIENT,LIQUID PHASE               1.620         1.620         1.620         1.620
  FUGACITY,PURE                                  12.355        12.355        12.355        12.355
  FUGACITY COEFFICIENT,VAPOR PHASE                1.025         0.997         1.026         1.025
 INTERACTION VIRIAL COEFFICIENTS
  B(HYDROGEN-BENZENE)                                           2.481        13.000
  B(HYDROGEN-CYCLOHEXANE)                                       0.           12.000
  B(HYDROGEN-HEXANE)                                           75.954        27.000
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RUN NUMBER           20
TEMPERATURE      200.00   DEGREES FAHRENHEIT
PRESSURE          1057.   PSIA
                                                             VIRIAL EQUATION  VALUES    REDLICH-KWONG
                                             INITIAL VALUE   ADJUSTED      UNADJUSTED      VALUES
 VOLUME OF LIQUID (CC PER GM MOLE)              127.582       127.126       126.818       126.812
 VOLUME OF VAPOR (CC PER GM MOLE)               432.683       419.672       432.787
 BENZENE
  Y                                               0.010         0.007         0.009         0.009
  X                                               0.201         0.200         0.199         0.199
  K VALUE                                         0.050         0.037         0.045         0.045
  ACTIVITY COEFFICIENT,LIQUID PHASE               1.390         1.395         1.399         1.399
  FUGACITY,PURE                                   0.028         0.028         0.028         0.028
  FUGACITY COEFFICIENT,VAPOR PHASE                0.855         1.058         0.861         0.869
 CYCLOHEXANE
  Y                                               0.            0.            0.            0.
  X                                               0.            0.            0.            0.
  K VALUE                                         0.            0.029         0.036         0.035
  ACTIVITY COEFFICIENT,LIQUID PHASE               1.122         1.125         1.126         1.126
  FUGACITY,PURE                                   0.027         0.027         0.027         0.027
  FUGACITY COEFFICIENT,VAPOR PHASE                0.849         1.053         0.854         0.879
 HEXANE
  Y                                               0.030         0.024         0.030         0.030
  X                                               0.717         0.713         0.710         0.710
  K VALUE                                         0.042         0.034         0.042         0.042
  ACTIVITY COEFFICIENT,LIQUID PHASE               0.997         0.996         0.995         0.995
  FUGACITY,PURE                                   0.038         0.038         0.038         0.038
  FUGACITY COEFFICIENT,VAPOR PHASE                0.903         1.129         0.909         0.912
 HYDROGEN
  Y                                               0.960         0.969         0.961         0.962
  X                                               0.082         0.087         0.091         0.091
  K VALUE                                        11.636        11.102        10.612        10.608
  ACTIVITY COEFFICIENT,LIQUID PHASE               1.612         1.611         1.610         1.610
  FUGACITY,PURE                                   6.869         6.869         6.869         6.869
  FUGACITY COEFFICIENT,VAPOR PHASE                1.042         0.997         1.042         1.042
 INTERACTION VIRIAL COEFFICIENTS
  B(HYDROGEN-BENZENE)                                           2.481        13.000
  B(HYDROGEN-CYCLOHEXANE)                                       0.           12.000
  B(HYDROGEN-HEXANE)                                           75.954        27.000
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RUN NUMBER              23
TEMPERATURE         200.00    DEGREES FAHRENHEIT
PRESSURE              570.    PSIA
                                                           VIRIAL EQUATION  VALUES     REDLICH-KWONG
                                         INITIAL VALUE    ADJUSTED      UNADJUSTED       VALUES
 VOLUME OF LIQUID (CC PER GM MOLE)           105.752       106.416       106.381        106.381
 VOLUME OF VAPOR (CC PER GM MOLE)            788.400       777.189       788.391
 BENZENE
  Y                                            0.042         0.034         0.039          0.038
  X                                            0.756         0.764         0.763          0.763
  K VALUE                                      0.056         0.044         0.051          0.050
  ACTIVITY COEFFICIENT,LIQUID PHASE            1.047         1.043         1.043          1.043
  FUGACITY,PURE                                0.043         0.044         0.043          0.043
  FUGACITY COEFFICIENT,VAPOR PHASE             0.890         1.030         0.888          0.902
 CYCLOHEXANE
  Y                                            0.            0.            0.             0.
  X                                            0.            0.            0.             0.
  K VALUE                                      0.            0.041         0.048          0.047
  ACTIVITY COEFFICIENT,LIQUID PHASE            1.000         1.002         1.002          1.002
  FUGACITY,PURE                                0.042         0.042         0.042          0.042
  FUGACITY COEFFICIENT,VAPOR PHASE             0.882         1.028         0.880          0.905
 HEXANE
  Y                                            0.014         0.015         0.018          0.018
  X                                            0.209         0.212         0.211          0.211
  K VALUE                                      0.067         0.072         0.085          0.083
  ACTIVITY COEFFICIENT,LIQUID PHASE            1.270         1.285         1.285          1.285
  FUGACITY,PURE                                0.060         0.060         0.060          0.060
  FUGACITY COEFFICIENT,VAPOR PHASE             0.909         1.066         0.908          0.923
 HYDROGEN
  Y                                            0.944         0.951         0.943          0.944
  X                                            0.025         0.025         0.025          0.025
  K VALUE                                     27.121        38.093        37.086         37.107
  ACTIVITY COEFFICIENT,LIQUID PHASE            3.115         3.139         3.138          3.138
  FUGACITY,PURE                               12.110        12.110        12.110         12.110
  FUGACITY COEFFICIENT,VAPOR PHASE             1.025         0.998         1.025          1.024
 INTERACTION VIRIAL COEFFICIENTS
  B(HYDROGEN-BENZENE)                                        2.481        13.000
  B(HYDROGEN-CYCLOHEXANE)                                    0.           12.000
  B(HYDROGEN-HEXANE)                                        75.954        27.000
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RUN NUMBER              24
TEMPERATURE         200.00    DEGREES FAHRENHEIT
PRESSURE             1067.    PSIA
                                                           VIRIAL EQUATION  VALUES     REDLICH-KWONG
                                         INITIAL VALUE    ADJUSTED      UNADJUSTED       VALUES
 VOLUME OF LIQUID (CC PER GM MOLE)           103.666       104.997       104.863        104.860
 VOLUME OF VAPOR (CC PER GM MOLE)            428.970       415.238       428.843
 BENZENE
  Y                                            0.022         0.019         0.023          0.023
  X                                            0.732         0.747         0.746          0.746
  K VALUE                                      0.031         0.026         0.031          0.031
  ACTIVITY COEFFICIENT,LIQUID PHASE            1.060         1.051         1.052          1.052
  FUGACITY,PURE                                0.026         0.026         0.026          0.026
  FUGACITY COEFFICIENT,VAPOR PHASE             0.901         1.060         0.889          0.891
 CYCLOHEXANE
  Y                                            0.            0.            0.             0.
  X                                            0.            0.            0.             0.
  K VALUE                                      0.            0.024         0.029          0.028
  ACTIVITY COEFFICIENT,LIQUID PHASE            0.995         0.998         0.998          0.998
  FUGACITY,PURE                                0.025         0.025         0.025          0.025
  FUGACITY COEFFICIENT,VAPOR PHASE             0.890         1.055         0.879          0.904
 HEXANE
  Y                                            0.007         0.008         0.010          0.010
  X                                            0.203         0.207         0.206          0.206
  K VALUE                                      0.037         0.040         0.048          0.048
  ACTIVITY COEFFICIENT,LIQUID PHASE            1.222         1.252         1.249          1.249
  FUGACITY,PURE                                0.036         0.036         0.036          0.036
  FUGACITY COEFFICIENT,VAPOR PHASE             0.948         1.132         0.935          0.938
 HYDROGEN
  Y                                            0.970         0.972         0.967          0.967
  X                                            0.066         0.046         0.048          0.048
  K VALUE                                     14.764        21.073        20.169         20.157
  ACTIVITY COEFFICIENT,LIQUID PHASE            3.039         3.087         3.083          3.083
  FUGACITY,PURE                                6.811         6.811         6.811          6.811
  FUGACITY COEFFICIENT,VAPOR PHASE             1.041         0.998         1.041          1.042
 INTERACTION VIRIAL COEFFICIENTS
  B(HYDROGEN-BENZENE)                                        2.481        13.000
  B(HYDROGEN-CYCLOHEXANE)                                    0.           12.000
  B(HYDROGEN-HEXANE)                                        75.954        27.000
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RUN NUMBER              31
TEMPERATURE         200.00    DEGREES FAHRENHEIT
PRESSURE              568.    PSIA
                                                       VIRIAL EQUATION  VALUES     REDLICH-KWONG
                                        INITIAL VALUE   ADJUSTED      UNADJUSTED       VALUES
 VOLUME OF LIQUID (CC PER GM MOLE)         135.534       134.964       134.871        134.869
 VOLUME OF VAPOR (CC PER GM MOLE)          791.387       780.774       790.918
 BENZENE
  Y                                        0.            0.            0.             0.
  X                                        0.            0.            0.             0.
  K VALUE                                  0.            0.062         0.074          0.072
  ACTIVITY COEFFICIENT,LIQUID PHASE        1.406         1.412         1.413          1.413
  FUGACITY,PURE                            0.045         0.045         0.045          0.045
  FUGACITY COEFFICIENT,VAPOR PHASE         0.875         1.029         0.865          0.884
 CYCLOHEXANE
  Y                                        0.012         0.009         0.011          0.011
  X                                        0.191         0.190         0.189          0.189
  K VALUE                                  0.061         0.049         0.058          0.057
  ACTIVITY COEFFICIENT,LIQUID PHASE        1.134         1.137         1.137          1.137
  FUGACITY,PURE                            0.044         0.044         0.044          0.044
  FUGACITY COEFFICIENT,VAPOR PHASE         0.873         1.026         0.862          0.884
 HEXANE
  Y                                        0.047         0.044         0.053          0.052
  X                                        0.763         0.759         0.758          0.758
  K VALUE                                  0.062         0.058         0.070          0.069
  ACTIVITY COEFFICIENT,LIQUID PHASE        1.000         0.999         0.999          0.999
  FUGACITY,PURE                            0.062         0.062         0.062          0.062
  FUGACITY COEFFICIENT,VAPOR PHASE         0.901         1.064         0.890          0.901
 HYDROGEN
  Y                                        0.941         0.946         0.936          0.937
  X                                        0.046         0.052         0.053          0.053
  K VALUE                                 20.492        18.329        17.806         17.815
  ACTIVITY COEFFICIENT,LIQUID PHASE        1.504         1.504         1.504          1.504
  FUGACITY,PURE                           12.151        12.151        12.151         12.151
  FUGACITY COEFFICIENT,VAPOR PHASE         1.025         0.997         1.026          1.026
 INTERACTION VIRIAL COEFFICIENTS
  B(HYDROGEN-BENZENE)                                    0.           13.000
  B(HYDROGEN-CYCLOHEXANE)                               14.932        12.000
  B(HYDROGEN-HEXANE)                                    39.123        27.000
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RUN NUMBER              33
TEMPERATURE         200.00    DEGREES FAHRENHEIT
PRESSURE             1089.    PSIA
                                                       VIRIAL EQUATION  VALUES     REDLICH-KWONG
                                        INITIAL VALUE   ADJUSTED      UNADJUSTED       VALUES
 VOLUME OF LIQUID (CC PER GM MOLE)         131.892       130.506       130.129        130.122
 VOLUME OF VAPOR (CC PER GM MOLE)          420.695       407.319       420.673
 BENZENE
  Y                                        0.            0.            0.             0.
  X                                        0.            0.            0.             0.
  K VALUE                                  0.            0.038         0.046          0.046
  ACTIVITY COEFFICIENT,LIQUID PHASE        1.448         1.465         1.469          1.470
  FUGACITY,PURE                            0.027         0.027         0.027          0.027
  FUGACITY COEFFICIENT,VAPOR PHASE         0.868         1.060         0.865          0.871
 CYCLOHEXANE
  Y                                        0.007         0.005         0.006          0.006
  X                                        0.183         0.181         0.180          0.180
  K VALUE                                  0.038         0.029         0.036          0.035
  ACTIVITY COEFFICIENT,LIQUID PHASE        1.154         1.163         1.165          1.165
  FUGACITY,PURE                            0.027         0.027         0.027          0.027
  FUGACITY COEFFICIENT,VAPOR PHASE         0.864         1.055         0.861          0.882
 HEXANE
  Y                                        0.028         0.024         0.029          0.029
  X                                        0.734         0.723         0.720          0.720
  K VALUE                                  0.038         0.033         0.041          0.041
  ACTIVITY COEFFICIENT,LIQUID PHASE        0.996         0.994         0.994          0.994
  FUGACITY,PURE                            0.038         0.038         0.038          0.038
  FUGACITY COEFFICIENT,VAPOR PHASE         0.922         1.134         0.919          0.916
 HYDROGEN
  Y                                        0.965         0.971         0.964          0.964
  X                                        0.082         0.097         0.100          0.100
  K VALUE                                 11.697        10.059         9.611          9.604
  ACTIVITY COEFFICIENT,LIQUID PHASE        1.501         1.499         1.498          1.498
  FUGACITY,PURE                            6.689         6.689         6.689          6.689
  FUGACITY COEFFICIENT,VAPOR PHASE         1.043         0.997         1.043          1.043
 INTERACTION VIRIAL COEFFICIENTS
  B(HYDROGEN-BENZENE)                                    0.           13.000
  B(HYDROGEN-CYCLOHEXANE)                               14.932        12.000
  B(HYDROGEN-HEXANE)                                    39.123        27.000
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RUN NUMBER            36
TEMPERATURE       200.00    DEGREES FAHRENHEIT
PRESSURE           1067.    PSIA
                                                      VIRIAL EQUATION  VALUES    REDLICH-KWONG
                                        INITIAL VALUE  ADJUSTED      UNADJUSTED      VALUES
 VOLUME OF LIQUID (CC PER GM MOLE)         115.921      116.564       116.368       116.361
 VOLUME OF VAPOR (CC PER GM MOLE)          428.896      415.079       428.885
 BENZENE
  Y                                         0.           0.            0.            0.
  X                                         0.           0.            0.            0.
  K VALUE                                   0.           0.029         0.035         0.035
  ACTIVITY COEFFICIENT,LIQUID PHASE         1.168        1.162         1.164         1.164
  FUGACITY,PURE                             0.027        0.027         0.027         0.027
  FUGACITY COEFFICIENT,VAPOR PHASE          0.894        1.061         0.895         0.894
 CYCLOHEXANE
  Y                                         0.022        0.019         0.023         0.022
  X                                         0.762        0.768         0.766         0.766
  K VALUE                                   0.029        0.025         0.030         0.029
  ACTIVITY COEFFICIENT,LIQUID PHASE         1.019        1.018         1.018         1.018
  FUGACITY,PURE                             0.026        0.026         0.026         0.026
  FUGACITY COEFFICIENT,VAPOR PHASE          0.890        1.056         0.890         0.908
 HEXANE
  Y                                         0.008        0.006         0.007         0.007
  X                                         0.166        0.168         0.167         0.167
  K VALUE                                   0.046        0.035         0.042         0.042
  ACTIVITY COEFFICIENT,LIQUID PHASE         1.071        1.077         1.075         1.075
  FUGACITY,PURE                             0.037        0.037         0.037         0.037
  FUGACITY COEFFICIENT,VAPOR PHASE          0.948        1.133         0.949         0.942
 HYDROGEN
  Y                                         0.970        0.975         0.970         0.971
  X                                         0.072        0.064         0.067         0.067
  K VALUE                                  13.435       15.156        14.519        14.506
  ACTIVITY COEFFICIENT,LIQUID PHASE         2.213        2.221         2.219         2.219
  FUGACITY,PURE                             6.811        6.811         6.811         6.811
  FUGACITY COEFFICIENT,VAPOR PHASE          1.041        0.998         1.041         1.042
 INTERACTION VIRIAL COEFFICIENTS
  B(HYDROGEN-BENZENE)                                    0.           13.000
  B(HYDROGEN-CYCLOHEXANE)                               14.932        12.000
  B(HYDROGEN-HEXANE)                                    39.123        27.000
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RUN NUMBER            37
TEMPERATURE       200.00    DEGREES FAHRENHEIT
PRESSURE            574.    PSIA
                                                      VIRIAL EQUATION  VALUES    REDLICH-KWONG
                                        INITIAL VALUE  ADJUSTED      UNADJUSTED      VALUES
 VOLUME OF LIQUID (CC PER GM MOLE)         118.443      118.917       118.863       118.865
 VOLUME OF VAPOR (CC PER GM MOLE)          763.889      771.488       783.330
 BENZENE
  Y                                         0.           0.            0.            0.
  X                                         0.           0.            0.            0.
  K VALUE                                   0.           0.049         0.056         0.055
  ACTIVITY COEFFICIENT,LIQUID PHASE         1.146        1.142         1.142         1.142
  FUGACITY,PURE                             0.044        0.044         0.044         0.044
  FUGACITY COEFFICIENT,VAPOR PHASE          0.907        1.031         0.895         0.905
 CYCLOHEXANE
  Y                                         0.033        0.033         0.038         0.038
  X                                         0.787        0.792         0.792         0.792
  K VALUE                                   0.042        0.042         0.049         0.048
  ACTIVITY COEFFICIENT,LIQUID PHASE         1.013        1.012         1.013         1.013
  FUGACITY,PURE                             0.043        0.043         0.043         0.043
  FUGACITY COEFFICIENT,VAPOR PHASE          0.904        1.028         0.892         0.909
 HEXANE
  Y                                         0.012        0.011         0.012         0.012
  X                                         0.172        0.173         0.173         0.173
  K VALUE                                   0.068        0.062         0.072         0.072
  ACTIVITY COEFFICIENT,LIQUID PHASE         1.093        1.098         1.097         1.097
  FUGACITY,PURE                             0.060        0.060         0.060         0.060
  FUGACITY COEFFICIENT,VAPOR PHASE          0.935        1.067         0.921         0.926
 HYDROGEN
  Y                                         0.955        0.956         0.949         0.950
  X                                         0.041        0.035         0.036         0.036
  K VALUE                                  23.236       27.106        26.415        26.416
  ACTIVITY COEFFICIENT,LIQUID PHASE         2.244        2.249         2.249         2.249
  FUGACITY,PURE                            12.031       12.031        12.031        12.031
  FUGACITY COEFFICIENT,VAPOR PHASE          1.023        0.998         1.024         1.024
 INTERACTION VIRIAL COEFFICIENTS
  B(HYDROGEN-BENZENE)                                    0.           13.000
  B(HYDROGEN-CYCLOHEXANE)                               14.932        12.000
  B(HYDROGEN-HEXANE)                                    39.123        27.000
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RUN NUMBER            43
TEMPERATURE         200.00    DEGREES FAHRENHEIT
PRESSURE             579.     PSIA
                                                               VIRIAL EQUATION  VALUES    REDLICH-KWONG
                                              INITIAL VALUE    ADJUSTED      UNADJUSTED      VALUES
 VOLUME OF LIQUID (CC PER GM MOLE)               108.397        108.983        108.943       108.942
 VOLUME OF VAPOR (CC PER GM MOLE)                777.423        764.477        776.888
 BENZENE
  Y                                                0.012          0.013          0.014         0.014
  X                                                0.289          0.291          0.291         0.291
  K VALUE                                          0.041          0.044          0.050         0.049
  ACTIVITY COEFFICIENT,LIQUID PHASE                1.051          1.048          1.048         1.048
  FUGACITY,PURE                                    0.043          0.043          0.043         0.043
  FUGACITY COEFFICIENT,VAPOR PHASE                 0.921          1.032          0.908         0.915
 CYCLOHEXANE
  Y                                                0.028          0.028          0.032         0.031
  X                                                0.676          0.682          0.682         0.682
  K VALUE                                          0.042          0.041          0.047         0.046
  ACTIVITY COEFFICIENT,LIQUID PHASE                1.000          1.002          1.001         1.001
  FUGACITY,PURE                                    0.042          0.042          0.042         0.042
  FUGACITY COEFFICIENT,VAPOR PHASE                 0.916          1.029          0.902         0.920
 HEXANE
  Y                                                0.             0.             0.            0.
  X                                                0.             0.             0.            0.
  K VALUE                                          0.             0.070          0.081         0.080
  ACTIVITY COEFFICIENT,LIQUID PHASE                1.257          1.269          1.269         1.269
  FUGACITY,PURE                                    0.059          0.059          0.059         0.059
  FUGACITY COEFFICIENT,VAPOR PHASE                 0.947          1.069          0.933         0.938
 HYDROGEN
  Y                                                0.960          0.959          0.954         0.955
  X                                                0.035          0.027          0.027         0.027
  K VALUE                                         27.507         36.050         35.161        35.163
  ACTIVITY COEFFICIENT,LIQUID PHASE                2.999          3.017          3.016         3.016
  FUGACITY,PURE                                   11.933         11.933         11.933        11.933
  FUGACITY COEFFICIENT,VAPOR PHASE                 1.023          0.999          1.024         1.024
 INTERACTION VIRIAL COEFFICIENTS
  B(HYDROGEN-BENZENE)                                            59.177         13.000
  B(HYDROGEN-CYCLOHEXANE)                                        -6.674         12.000
  B(HYDROGEN-HEXANE)                                              0.            27.000
```

```
RUN NUMBER            47
TEMPERATURE         200.00    DEGREES FAHRENHEIT
PRESSURE             589.     PSIA
                                                               VIRIAL EQUATION  VALUES    REDLICH-KWONG
                                              INITIAL VALUE    ADJUSTED      UNADJUSTED      VALUES
 VOLUME OF LIQUID (CC PER GM MOLE)                98.820         99.071         99.045        99.044
 VOLUME OF VAPOR (CC PER GM MOLE)                764.570        751.544        764.140
 BENZENE
  Y                                                0.034          0.034          0.039         0.039
  X                                                0.841          0.844          0.844         0.844
  K VALUE                                          0.040          0.041          0.046         0.046
  ACTIVITY COEFFICIENT,LIQUID PHASE                1.004          1.004          1.004         1.004
  FUGACITY,PURE                                    0.042          0.042          0.042         0.042
  FUGACITY COEFFICIENT,VAPOR PHASE                 0.923          1.032          0.912         0.919
 CYCLOHEXANE
  Y                                                0.006          0.006          0.006         0.006
  X                                                0.136          0.136          0.136         0.136
  K VALUE                                          0.046          0.041          0.047         0.046
  ACTIVITY COEFFICIENT,LIQUID PHASE                1.044          1.047          1.046         1.046
  FUGACITY,PURE                                    0.041          0.041          0.041         0.041
  FUGACITY COEFFICIENT,VAPOR PHASE                 0.915          1.030          0.903         0.925
 HEXANE
  Y                                                0.             0.             0.            0.
  X                                                0.             0.             0.            0.
  K VALUE                                          0.             0.085          0.098         0.097
  ACTIVITY COEFFICIENT,LIQUID PHASE                1.571          1.583          1.582         1.582
  FUGACITY,PURE                                    0.058          0.058          0.058         0.058
  FUGACITY COEFFICIENT,VAPOR PHASE                 0.946          1.070          0.933         0.944
 HYDROGEN
  Y                                                0.960          0.960          0.955         0.955
  X                                                0.024          0.019          0.020         0.020
  K VALUE                                         40.678         49.336         48.104        48.110
  ACTIVITY COEFFICIENT,LIQUID PHASE                4.177          4.196          4.194         4.194
  FUGACITY,PURE                                   11.743         11.743         11.743        11.743
  FUGACITY COEFFICIENT,VAPOR PHASE                 1.023          0.999          1.024         1.024
 INTERACTION VIRIAL COEFFICIENTS
  B(HYDROGEN-BENZENE)                                            59.177         13.000
  B(HYDROGEN-CYCLOHEXANE)                                        -6.674         12.000
  B(HYDROGEN-HEXANE)                                              0.            27.000
```

```
RUN NUMBER             42
TEMPERATURE        200.00    DEGREES FAHRENHEIT
PRESSURE           1076.     PSIA
                                                     VIRIAL EQUATION  VALUES    REDLICH-KWONG
                                        INITIAL VALUE   ADJUSTED      UNADJUSTED       VALUES
 VOLUME OF LIQUID (CC PER GM MOLE)           106.228     107.437       107.303        107.298
 VOLUME OF VAPOR (CC PER GM MOLE)            425.492     411.415       425.413
 BENZENE
  Y                                            0.008       0.007         0.009          0.009
  X                                            0.279       0.284         0.284          0.284
  K VALUE                                      0.028       0.026         0.030          0.031
  ACTIVITY COEFFICIENT,LIQUID PHASE            1.065       1.057         1.058          1.058
  FUGACITY,PURE                                0.026       0.026         0.026          0.026
  FUGACITY COEFFICIENT,VAPOR PHASE             0.914       1.062         0.909          0.905
 CYCLOHEXANE
  Y                                            0.018       0.016         0.019          0.018
  X                                            0.655       0.667         0.666          0.666
  K VALUE                                      0.028       0.024         0.028          0.028
  ACTIVITY COEFFICIENT,LIQUID PHASE            0.997       0.999         0.998          0.998
  FUGACITY,PURE                                0.025       0.025         0.025          0.025
  FUGACITY COEFFICIENT,VAPOR PHASE             0.906       1.057         0.901          0.920
 HEXANE
  Y                                            0.          0.            0.             0.
  X                                            0.          0.            0.             0.
  K VALUE                                      0.          0.039         0.046          0.046
  ACTIVITY COEFFICIENT,LIQUID PHASE            1.213       1.237         1.235          1.235
  FUGACITY,PURE                                0.036       0.036         0.036          0.036
  FUGACITY COEFFICIENT,VAPOR PHASE             0.967       1.135         0.961          0.955
 HYDROGEN
  Y                                            0.974       0.977         0.973          0.973
  X                                            0.066       0.049         0.050          0.051
  K VALUE                                     14.805      20.104        19.264         19.247
  ACTIVITY COEFFICIENT,LIQUID PHASE            2.932       2.970         2.965          2.965
  FUGACITY,PURE                                6.761       6.761         6.761          6.761
  FUGACITY COEFFICIENT,VAPOR PHASE             1.041       0.999         1.041          1.042
 INTERACTION VIRIAL COEFFICIENTS
  B(HYDROGEN-BENZENE)                                     59.177        13.000
  B(HYDROGEN-CYCLOHEXANE)                                 -6.674        12.000
  B(HYDROGEN-HEXANE)                                       0.           27.000
```

```
RUN NUMBER             46
TEMPERATURE        200.00    DEGREES FAHRENHEIT
PRESSURE           1108.     PSIA
                                                     VIRIAL EQUATION  VALUES    REDLICH-KWONG
                                        INITIAL VALUE   ADJUSTED      UNADJUSTED       VALUES
 VOLUME OF LIQUID (CC PER GM MOLE)            97.543      98.089        97.996         97.994
 VOLUME OF VAPOR (CC PER GM MOLE)            413.700     399.559       413.635
 BENZENE
  Y                                            0.019       0.020         0.023          0.023
  X                                            0.822       0.830         0.829          0.829
  K VALUE                                      0.023       0.024         0.027          0.028
  ACTIVITY COEFFICIENT,LIQUID PHASE            1.007       1.006         1.006          1.006
  FUGACITY,PURE                                0.025       0.025         0.025          0.025
  FUGACITY COEFFICIENT,VAPOR PHASE             0.919       1.064         0.913          0.908
 CYCLOHEXANE
  Y                                            0.006       0.003         0.004          0.004
  X                                            0.133       0.134         0.134          0.134
  K VALUE                                      0.047       0.024         0.028          0.027
  ACTIVITY COEFFICIENT,LIQUID PHASE            1.032       1.037         1.036          1.036
  FUGACITY,PURE                                0.024       0.024         0.024          0.024
  FUGACITY COEFFICIENT,VAPOR PHASE             0.908       1.059         0.902          0.925
 HEXANE
  Y                                            0.          0.            0.             0.
  X                                            0.          0.            0.             0.
  K VALUE                                      0.          0.046         0.055          0.055
  ACTIVITY COEFFICIENT,LIQUID PHASE            1.511       1.536         1.532          1.532
  FUGACITY,PURE                                0.034       0.034         0.034          0.034
  FUGACITY COEFFICIENT,VAPOR PHASE             0.971       1.140         0.963          0.962
 HYDROGEN
  Y                                            0.975       0.977         0.973          0.973
  X                                            0.045       0.036         0.037          0.037
  K VALUE                                     21.667      27.178        26.009         25.986
  ACTIVITY COEFFICIENT,LIQUID PHASE            4.079       4.120         4.113          4.113
  FUGACITY,PURE                                6.587       6.587         6.587          6.587
  FUGACITY COEFFICIENT,VAPOR PHASE             1.042       0.999         1.042          1.043
 INTERACTION VIRIAL COEFFICIENTS
  B(HYDROGEN-BENZENE)                                     59.177        13.000
  B(HYDROGEN-CYCLOHEXANE)                                 -6.674        12.000
  B(HYDROGEN-HEXANE)                                       0.           27.000
```

```
RUN NUMBER             52
TEMPERATURE        200.00    DEGREES FAHRENHEIT
PRESSURE           1085.     PSIA
                                                          VIRIAL EQUATION  VALUES    REDLICH-KWONG
                                           INITIAL VALUE   ADJUSTED      UNADJUSTED      VALUES
 VOLUME OF LIQUID (CC PER GM MOLE)             110.509      112.152        111.972       111.968
 VOLUME OF VAPOR (CC PER GM MOLE)              422.333      408.435        421.960
 BENZENE
  Y                                              0.012        0.013          0.016         0.016
  X                                              0.460        0.471          0.470         0.470
  K VALUE                                        0.026        0.028          0.034         0.033
  ACTIVITY COEFFICIENT,LIQUID PHASE              1.142        1.128          1.129         1.129
  FUGACITY,PURE                                  0.026        0.026          0.026         0.026
  FUGACITY COEFFICIENT,VAPOR PHASE               0.912        1.061          0.882         0.884
 CYCLOHEXANE
  Y                                              0.004        0.004          0.005         0.005
  X                                              0.159        0.163          0.162         0.162
  K VALUE                                        0.025        0.024          0.029         0.029
  ACTIVITY COEFFICIENT,LIQUID PHASE              1.008        1.006          1.006         1.006
  FUGACITY,PURE                                  0.025        0.026          0.026         0.026
  FUGACITY COEFFICIENT,VAPOR PHASE               0.904        1.056          0.873         0.897
 HEXANE
  Y                                              0.010        0.011          0.013         0.013
  X                                              0.300        0.307          0.306         0.306
  K VALUE                                        0.033        0.035          0.043         0.043
  ACTIVITY COEFFICIENT,LIQUID PHASE              1.088        1.108          1.106         1.106
  FUGACITY,PURE                                  0.036        0.036          0.036         0.036
  FUGACITY COEFFICIENT,VAPOR PHASE               0.965        1.134          0.931         0.932
 HYDROGEN
  Y                                              0.974        0.972          0.966         0.966
  X                                              0.081        0.059          0.062         0.062
  K VALUE                                       12.020       16.371         15.652        15.642
  ACTIVITY COEFFICIENT,LIQUID PHASE              2.405        2.434          2.430         2.430
  FUGACITY,PURE                                  6.711        6.711          6.711         6.711
  FUGACITY COEFFICIENT,VAPOR PHASE               1.041        0.998          1.042         1.043
 INTERACTION VIRIAL COEFFICIENTS
  B(HYDROGEN-BENZENE)                                        46.124         13.000
  B(HYDROGEN-CYCLOHEXANE)                                    -8.115         12.000
  B(HYDROGEN-HEXANE)                                         66.342         27.000
```

```
RUN NUMBER             53
TEMPERATURE        200.00    DEGREES FAHRENHEIT
PRESSURE            541.     PSIA
                                                          VIRIAL EQUATION  VALUES    REDLICH-KWONG
                                           INITIAL VALUE   ADJUSTED      UNADJUSTED      VALUES
 VOLUME OF LIQUID (CC PER GM MOLE)             113.951      114.413        114.363       114.371
 VOLUME OF VAPOR (CC PER GM MOLE)              829.644      819.001        829.470
 BENZENE
  Y                                              0.027        0.024          0.028         0.028
  X                                              0.482        0.485          0.485         0.485
  K VALUE                                        0.056        0.050          0.058         0.057
  ACTIVITY COEFFICIENT,LIQUID PHASE              1.113        1.110          1.110         1.110
  FUGACITY,PURE                                  0.046        0.046          0.046         0.046
  FUGACITY COEFFICIENT,VAPOR PHASE               0.885        1.028          0.881         0.898
 CYCLOHEXANE
  Y                                              0.010        0.007          0.009         0.008
  X                                              0.167        0.168          0.168         0.168
  K VALUE                                        0.060        0.044          0.051         0.050
  ACTIVITY COEFFICIENT,LIQUID PHASE              1.004        1.003          1.004         1.004
  FUGACITY,PURE                                  0.045        0.045          0.045         0.045
  FUGACITY COEFFICIENT,VAPOR PHASE               0.879        1.026          0.875         0.899
 HEXANE
  Y                                              0.023        0.021          0.025         0.025
  X                                              0.315        0.317          0.317         0.317
  K VALUE                                        0.073        0.068          0.080         0.078
  ACTIVITY COEFFICIENT,LIQUID PHASE              1.129        1.134          1.134         1.134
  FUGACITY,PURE                                  0.063        0.063          0.063         0.063
  FUGACITY COEFFICIENT,VAPOR PHASE               0.905        1.062          0.901         0.916
 HYDROGEN
  Y                                              0.940        0.947          0.938         0.939
  X                                              0.036        0.030          0.031         0.031
  K VALUE                                       26.111       31.496         30.673        30.693
  ACTIVITY COEFFICIENT,LIQUID PHASE              2.463        2.470          2.470         2.470
  FUGACITY,PURE                                 12.721       12.721         12.721        12.721
  FUGACITY COEFFICIENT,VAPOR PHASE               1.024        0.998          1.024         1.024
 INTERACTION VIRIAL COEFFICIENTS
  B(HYDROGEN-BENZENE)                                        46.124         13.000
  B(HYDROGEN-CYCLOHEXANE)                                    -8.115         12.000
  B(HYDROGEN-HEXANE)                                         66.342         27.000
```

EXPERIMENTAL DATA

As previously explained, the experimental data presented in Tables III and IV has been smoothed. All experimental data has been compared with data from the literature and has been analysed statistically. The results of this work have been summarized in these tables.

An unexpected amount of difficulty has been encountered in reproducing the analyses of duplicate samples by means of the mass spectrometer. Therefore, this section has been appended to the dissertation in order to provide a more complete picture of the experimental data.

It has been asserted previously that the main source of error in these analyses has been experimentally determined to be in the analysis of the hydrogen in the liquid and in the vapor. Table XVIII shows an example of the consistency of the hydrogen-free hydrocarbon analyses for both vapor and liquid. This data, as well as all the other hydrocarbon data, has been analysed by means of large sample statistical techniques. A Student "t" Test was used to reject sample analyses that deviated from an average value beyond a 99% confidence limit. Table XIX shows the analyses of the hydrogen data for Run 33. Small sample statistics, as well as comparison with literature data results, were used in this case. A sample calculation is given for Run 33 to show how the results of the data analyses have been applied to the experimental data.

As analyses of this type may have been biased by human judgment, a complete set of all the data obtained in this work has been included in Table XX for future reference.

TABLE XVIII

ANALYSES OF CYCLOHEXANE ON HYDROGEN-FREE BASIS

	LIQUID PHASE				VAPOR PHASE		
SAMPLE	X	$\lvert X-\bar{X}\rvert$	$(\lvert X-\bar{X}\rvert)^2$	SAMPLE	Y	$\lvert Y-\bar{Y}\rvert$	$(\lvert Y-\bar{Y}\rvert)^2$
30	202	.002	.000004	30	.210	.010	.000100
30A	.202	.002	.000004	30A	.201	.001	.000001
30B	.205	.005	.000025	31	.208	.008	.000064
30C	.202	.002	.000004	31A	.212	.012	.000144
30D	.208	.008	.000064	31B	.208	.008	.000064
30E	.204	.004	.000016	31D	.203	.003	.000009
31F	.198	.002	.000004	31E	.200	.000	.000000
31G	.198	.002	.000004	31F	.198	.002	.000004
31H	.199	.001	.000001	32	.194	.006	.000036
32	.201	.001	.000001	32A	.198	.002	.000004
32A	.201	.001	.000001	32B	.192	.008	.000064
32B	.200	.000	.000000	32C	.194	.006	.000036
32C	.202	.002	.000004	32D	.194	.006	.000036
32D	.203	.003	.000009	32E	.197	.003	.000009
32E	.204	.004	.000016	33	.199	.001	.000001
33	.196	.004	.000016	33A	.198	.002	.000004
33A	.197	.003	.000009	33B	.200	.000	.000000
33B	.197	.003	.000009	33C	.203	.003	.000009
33C	.197	.003	.000009	33D	.200	.000	.000000
33D	.196	.004	.000016	33E	.197	.003	.000009
33E	.197	.003	.000009				
SUM:	4.209		.000225		4.006		.000493
AVERAGE:	.200				.200		
$\sigma^{(1)} = \sqrt{\frac{(\lvert X-\bar{X}\rvert)^2}{N-1}}$:			.0034				.0051
$P.E.^{(2)} = 0.674\ \sigma/\sqrt{N}$			.0004				.0008

1. Standard deviation
2. Probable error

TABLE XIX

ANALYSIS OF HYDROGEN COMPOSITIONS FOR RUN 33

EXPERIMENTAL DATA

SAMPLE	T(°F)	P(psia)	X_{HX}	X_{CX}	X_{H_2}	Y_{HX}	Y_{CX}	Y_{H_2}
33	200.0	1089	.7358	.1787	.0855	.0430	.0107	.9464
33A			.7335	.1793	.0872	.0308	.0076	.9616
33B		1065	.7394	.1808	.0797	.0516	.0129	.9355
33C			.7389	.1813	.0797	.0318	.0081	.9601
33D		1043	.7383	.1809	.0807	.0283	.0071	.9646
33E			.7274	.1780	.0946	.0208	.0051	.9747

LIQUID

$$\bar{X}_{H_2} = 0.0846$$

$$\text{Range} = 0.0946 - 0.0797 = 0.0149$$

At a 99% Confidence Level,

$$X_{H_2} = 0.0846 \pm (0.628)(.0149)$$

$$= 0.0846 \pm 0.0094$$

Discard Sample 33, which lies outside of this unit.

$$\bar{X}_{H_2} = 0.082$$

The probable error in this analysis is:

$$\text{P.E.} = (0.674)(\text{Range})(.430)/\sqrt{N}$$

$$= (0.674)(.0075)(.430)/\sqrt{5}$$

$$= 0.001$$

VAPOR

$$\bar{Y}_{H_2} = 0.9571$$

$$\text{Range} = .9741 - .9355 = 0.0386$$

At a 99% Confidence Level,

$$\bar{Y}_{H_2} = 0.9571 \pm (0.628)(.0386)$$

$$= 0.9571 \pm .0243$$

Discard Sample 33B, which lies at this limit.

Comparison of vapor-phase hydrogen analyses with other results from other experimental runs and from results in the literature indicates that sample 33 is low.

The rank difference ratio is:

$$\frac{Y_{33C} - Y_{33}}{Y_{33E} - Y_{33}} = 0.49$$

The probability that this point is representative of the true value is approximately 10%.

On the basis of this statistical test and on the basis of comparative data, discard sample 33.

Then $\bar{Y}_{H_2} = 0.965$

The probable error in this analysis is:

$$\text{P.E.} = (0.674)(\text{Range})(.486)/\sqrt{N}$$

$$= (0.674)(.0146)(.486)/2$$

$$= 0.003$$

SAMPLE CALCULATION OF SMOOTHED EXPERIMENTAL RESULTS FOR RUN 33

LIQUID PHASE

$$X_{H_2} = .082$$

$$\frac{X_{CX}}{X_{CX} + X_{HX}} = 0.200$$

$$X_{CX} + X_{HX} = 1.0 - 0.082 = 0.918$$

$$X_{CX} = 0.200\ (X_{CX} + X_{HX}) = 0.200\ (.918) = 0.183$$

$$X_{HX} = 0.918 - 0.183 = 0.734$$

VAPOR PHASE

$$Y_{H_2} = 0.965$$

$$\frac{Y_{CX}}{Y_{CX} + Y_{HX}} = 0.200$$

$$Y_{CX} + Y_{HX} = 1 - 0.965 = 0.035$$

$$Y_{CX} = 0.200\ (Y_{CX} + Y_{HX}) = 0.200\ (.035) = 0.007$$

$$Y_{HX} = 0.035 - 0.007 = 0.028$$

SUMMARY FOR RUN 33

T(°F)	P(psia)	X_{HX}	X_{CX}	X_{H_2}	Y_{HX}	Y_{CX}	Y_{H_2}
200.0	1089	.734	.183	.082	028	.007	.965

TABLE XX

COMPLETE EXPERIMENTAL DATA RESULTS

	LIQUID PHASE MOLE FRACTION				VAPOR PHASE MOLE FRACTION			
SAMPLE	X_{BZ}	X_{CX}	X_{HX}	X_{H_2}	Y_{BZ}	Y_{CX}	Y_{HX}	Y_{H_2}
18	.2312		.7237	.0450	.0036		.0125	.9838
18A	.1923		.7691	.0387	.0015		.0069	.9915
18B	.2212		.7371	.0417	.0032		.0116	.9852
18C	.2057		.7559	.0384	.0017		.0084	.9899
18D	.2148		.7790	.0062	.0058		.0198	.9744
18E	.2004		.7522	.0470	.0022		.0107	.9862
19	.2178		.7275	.0547	.0156		.0506	.9339
19A	.2150		.7441	.0409	.0120		.0373	.9507
19B	.2409		.7087	.0504	.0175		.0592	.9233
19C	.2047		.7490	.0463	.0115		.0359	.9526
19D	.2389		.7195	.0416	.0511		.1414	.8075
19E	.2080		.7535	.0385	.0359		.1232	.8409
20	.2090		.7111	.0800	.0153		.0415	.9431
20A	.2021		.7152	.0827	.0095		.0295	.9609
20B	.2262		.6921	.0816	.0111		.0308	.9581
20C	.2095		.7104	.0801	.0067		.0234	.9699
20D	.2218		.6901	.0881	.0185		.0468	.9347
20E	.2019		.7028	.0953	.0086		.0265	.9649
20F					.0171		.0482	.9518
20G	.2012		.6981	.1007	.0085		.0292	.9623
21	.2382		.6879	.0740	.0075		.0250	.9675
21A	.2019		.7159	.0822	.0030		.0087	.9883
21B	.2302		.7092	.0606	.0050		.0172	.9778
21C	.2102		.7170	.0728				
21D	.2531		.6892	.0577				
21E	.2053		.7097	.0849	.0023		.0071	.9906
21F					.0084		.0226	.9689
22	.8023		.1772	.0204	.0241		.0029	.9692
22A	.7350		.2320	.0329	.0114		.0049	.9838
22B	.8341		.1548	.0111	.0093		.0034	.9873
22C	.7459		.2171	.0370	.0069		.0029	.9902
22D	.7570		.2145	.0285	.0105		.0037	.9858
22E	.8213		.1758	.0029	.0086		.0037	.9877
23	.8195		.1533	.0272	.0611		.0184	.9205
23A	.7424		.2096	.0480	.0361		.0130	.9509
23B	.8093		.1648	.0259	.0291		.0107	.9602
23C	.7474		.2148	.0379	.0325		.0117	.9558
23D	.8140		.1642	.0218	.0512		.0162	.9326
23E	.7487		.2070	.0443	.0428		.0143	.9429
24	.7974		.1466	.0560	.1055		.0165	.8780
24A	.7246		.1993	.0761	.0444		.0141	.9415
24B	.8064		.1740	.0196	.0593		.0185	.9222
24C	.7310		.2040	.0650	.0153		.0089	.9758
24D	.8017		.1546	.0437	.0240		.0088	.9673
24E	.7502		.2028	.0470	.0194		.0073	.9733
25	.7219		.2422	.0359	.0070		.0028	.9902
25A	.7315		.2016	.0669	.0043		.0017	.9941
25B	.8257		.1341	.0403	.0088		.0031	.9881
25C	.7262		.2053	.0686	.0057		.0021	.9922
25D	.8105		.1496	.0399	.0036		.0030	.9933
25E	.7440		.1911	.0649	.0018		.0020	.9962
30		.1930	.7650	.0420		.0064	.0241	.9695
30A		.1931	.7648	.0421		.0066	.0249	.9685
30B		.1984	.7685	.0331		.0047	.0220	.9732
30C		.1943	.7668	.0389		.0029	.0132	.9837
30D		.2015	.7643	.0342		.0077	.0283	.9640
30E		.1963	.7642	.0395		.0039	.0169	.9792
31		.1565	.8051	.0384		.0215	.0817	.8967
31A		.1696	.6826	.1477		.0204	.0759	.9037
31B		.1579	.7956	.0465		.0152	.0578	.9277
31C		.1559	.7778	.0663		.0130	.0478	.9391
31D		.1579	.8012	.0409		.0130	.0510	.9359
31E		.1595	.7917	.0488		.0081	.0324	.9595
31F		.1871	.7608	.0521		.0068	.0276	.9656
31G		.1887	.7643	.0471		.0093	.0304	.9619
31H		.1892	.7646	.0462				
32		.1846	.7385	.0769		.0048	.0200	.9752
32A		.1906	.7581	.0513		.0031	.0125	.9844
32B		.1876	.7519	.0605		.0092	.0388	.9520
32C		.1905	.7500	.0595		.0104	.0432	.9464
32D		.1931	.7578	.0490		.0047	.0196	.9757
32E		.1982	.7713	.0305		.0015	.0061	.9923
33		.1787	.7358	.0855		.0107	.0430	.9464
33A		.1793	.7335	.0872		.0076	.0308	.9616
33B		.1808	.7394	.0797		.0129	.0516	.9355
33C		.1813	.7389	.0797		.0081	.0318	.9601
33D		.1809	.7383	.0807		.0071	.0283	.9646
33E		.1780	.7274	.0946		.0051	.0208	.9741

TABLE XX CONT'D

SAMPLE	LIQUID PHASE MOLE FRACTION X_{BZ}	X_{CX}	X_{HX}	X_{H_2}	VAPOR PHASE MOLE FRACTION Y_{BZ}	Y_{CX}	Y_{HX}	Y_{H_2}
34		.8477	.1349	.0174		.0275	.0288	.9437
34A		.7841	.1805	.0353		.0116	.0143	.9741
34		.8550	.1215	.0235		.0211	.0219	.9570
34A		.8169	.1650	.0241		.0147	.0157	.9696
34B		.8197	.1614	.0188		.0261	.0272	.9467
34C		.8021	.1822	.0157		.0160	.0186	.9654
34D		.8021	.1890	.0088		.0070	.0075	.9855
34E		.8120	.1701	.0178		.0042	.0055	.9903
34						.0282	.0071	.9646
34A						.0116	.0070	.9813
34						.0214	.0037	.9748
34A						.0149	.0037	.9814
34B						.0267	.0074	.9659
34C						.0162	.0061	.9777
34D						.0070	.0028	.9901
34E						.0042	.0021	.9936
35		.7758	.1756	.0459				
35A		.7376	.1866	.0758		.0114	.0118	.9768
35B		.7614	.1778	.0607		.0046	.0051	.9903
35C		.8235	.1535	.0229		.0078	.0142	.9780
35D		.8676	.1039	.0284		.0044	.0049	.9906
35E		.8321	.1233	.0446		.0037	.0037	.9926
35C		.9335	.2242	.0429				
35D		.7921	.1547	.0532				
35E		.7416	.1788	.0796				
35A						.0115	.0023	.9862
35B						.0047	.0013	.9940
35C						.0079	.0005	.9916
35D						.0045	.0015	.9940
35E						.0037	.0009	.9953
36		.7717	.1483	.0800		.0170	.0185	.9645
36A		.7244	.1723	.1034		.0144	.0166	.9690
36B		.7936	.1573	.0492		.0158	.0168	.9674
36C		.7672	.1865	.0463		.0103	.0114	.9783
36D		.7739	.1539	.0722		.0183	.0192	.9624
36E		.7745	.1566	.0688		.0112	.0122	.9767
36						.0173	.0050	.9776
36A						.0145	.0087	.9767
36B						.0160	.0048	.9792
36C						.0103	.0040	.9800
36D						.0186	.0051	.9763
36E						.0113	.0041	.9846
37		.7879	.1925	.0197		.0214	.0214	.9572
37A		.7762	.1844	.0394		.0158	.0163	.9680
37B		.8053	.1532	.0415		.0231	.0240	.9529
37C		.8146	.1648	.0205		.0131	.0131	.9739
37D		.7957	.1582	.0460		.0138	.0144	.9718
37E		.7922	.1681	.0397		.0166	.0180	.9654
40	.2933	.6803		.0264	.0162	.0247		.9591
40A	.2926	.6824		.0249	.0049	.0111		.9839
40B	.2897	.6825		.0278	.0033	.0084		.9883
40C	.2928	.6922		.0149	.0036	.0083		.9880
40D	.2951	.6856		.0193	.0044	.0111		.9845
40E	.2955	.6893		.0152	.0041	.0092		.9867
41	.2796	.6490		.0714	.0071	.0164		.9765
41A	.2757	.6430		.0812	.0011	.0028		.9960
41B	.2791	.6470		.0739	.0028	.0062		.9910
41C	.2586	.6928		.0486	.0023	.0046		.9931
41D	.2745	.6337		.0918	.0031	.0068		.9901
41E	.2881	.6725		.0394	.0017	.0040		.9942
42	.2866	.6482		.0652	.0098	.0220		.9683
42A	.2913	.6606		.0481	.0066	.0152		.9781
42B	.2918	.6608		.0475	.0124	.0278		.9597
42C	.2861	.6449		.0690	.0051	.0118		.9830
42D	.2898	.6623		.0475	.0065	.0158		.9776
42E	.2854	.6513		.0632	.0065	.0148		.9787
43	.2776	.6832		.0392	.0290	.0711		.8998
43A	.2823	.6940		.0237	.0053	.0129		.9819
43B	.2771	.6809		.0421	.0314	.0761		.8926
43C	.2790	.6881		.0329	.0079	.0182		.9739
43D	.2792	.6867		.0340	.0082	.0206		.9711
43E	.2792	.6874		.0334	.0068	.0165		.9767
44	.8229	.1406		.0365	.0425	.0076		.9499
44A	.7500	.1785		.0714	.0194	.0097		.9709
44B	.7965	.1681		.0354	.0084	.0017		.9899
44					.0892	.0125		.8970
44C	.7964	.1713		.0322				
44D	.7967	.1788		.0244	.1689	.0358		.7953
44E	.8238	.1566		.0196				
44	.8456	.1296		.0377	.0501	.0083		.9417
44B	.8417	.1392		.0189	.0200	.0043		.9756
44A	.7712	.1774		.0514				

TABLE XX CONT'D

SAMPLE	LIQUID PHASE MOLE FRACTION X_{BZ}	X_{CX}	X_{HX}	X_{H_2}	VAPOR PHASE MOLE FRACTION Y_{BZ}	Y_{CX}	Y_{HX}	Y_{H_2}
45	.8446	.1338		.0216	.0854	.0149		.8997
45A	.7972	.1664		.0363	.0817	.0154		.9028
45B	.8611	.1335		.0055	.2533	.0404		.7063
45C	.7870	.1559		.0570				
45D	.8684	.1224		.0092	.0091	.0029		.9885
45E	.7873	.1474		.0653	.0047	.0013		.9937
45	.8175	.1264		.0560	.0815	.0131		.9053
45A	.7831	.1650		.0518	.0973	.0165		.8861
45B	.8548	.1287		.0165	.3032	.0448		.6520
46	.7863	.1189		.0947				
46A	.7754	.1323		.0923	.0487	.0081		.9431
46B	.7161	.1355		.1484	.2266	.0368		.7366
46C	.2902	.4814		.2283	.0201	.0034		.9764
46D	.8326	.1224		.0450	.0220	.0041		.9739
46E	.7653	.1306		.1041	.0252	.0048		.9700
47	.8507	.1357		.0136	.0112	.0033		.9856
47A	.8288	.1407		.0305	.0115	.0035		.9850
47B	.8206	.1296		.0499	.0106	.0029		.9865
47C	.8444	.1331		.0267	.0170	.0036		.9794
47D	.8224	.1220		.0556	.0231	.0047		.9721
47E	.7958	.1291		.0751	.0151	.0032		.9817
47E					.0244	.0038		.9718
50	.4955	.1738	.2918	.0389	.0952	.0357	.0876	.7815
50A	.4845	.1679	.3078	.0398	.0310	.0126	.0370	.9194
50B	.5146	.1754	.2792	.0307	.0181	.0075	.0106	.9638
50C	.5039	.1607	.3123	.0231	.0079	.0030	.0060	.9831
50D	.5045	.1655	.3039	.0261	.0277	.0092	.0193	.9437
50E	.4961	.1771	.3072	.0196	.0242	.0089	.0218	.9451
50J	.4822	.1657	.3317	.0241				
50F	.4790	.1632	.3266	.0312				
50G	.4371	.1497	.3696	.0436				
50H	.5031	.1712	.3040	.0217				
50D	.4381	.1634	.2973	.1012	.0266	.0108	.0208	.9419
50E					.0249	.0100	.0224	.9428
50E					.0370	.0139	.0324	.9166
50F					.0049	.0018	.0054	.9879
50G					.0030	.0010	.0035	.9924
50H					.0023	.0054	.0058	.9864
50J					.0047	.0019	.0056	.9878
51	.5301	.1148	.3151	.0400	.0093	.0019	.0056	.9832
51A	.5639	.1137	.2944	.0280	.0163	.0026	.0043	.9769
51B	.5715	.1183	.2800	.0302	.0076	.0019	.0048	.9857
51C	.5457	.1131	.3085	.0327	.0078	.0016	.0039	.9867
51D	.5580	.1214	.2953	.0295	.0060	.0017	.0043	.9881
51	.4139	.1772	.3364	.0724				
51B	.4489	.1785	.3196	.0529				
51C	.4239	.1715	.3561	.0485				
51J					.0016	.0036	.0064	.9884
51J					.0019	.0043	.0071	.9867
51J					.0016	.0031	.0052	.9901
51J					.0012	.0031	.0062	.9893
52	.4932	.1806	.2777	.0485	.0486	.0206	.0374	.8935
52A	.4174	.1651	.3170	.1004	.0365	.0153	.0342	.9140
52B	.4549	.1769	.3026	.0656	.0217	.0092	.0184	.9507
52C	.4224	.1660	.3320	.0796	.0109	.0039	.0109	.9743
52D	.4907	.1678	.2905	.0509	.0116	.0043	.0104	.9736
52E	.4335	.1714	.2964	.0988	.0085	.0035	.0085	.9795
52C	.4363	.1734	.3224	.0678				
52D	.3645	.1496	.3370	.1486				
52E	.3863	.1698	.3405	.1034				
53	.5385	.1678	.2713	.0224	.0494	.0165	.0354	.8987
53A	.5235	.1596	.3122	.0047	.0389	.0128	.0353	.9131
53B	.5478	.1702	.2751	.0070	.0062	.0016	.0016	.9907
53C	.4683	.1519	.3080	.0718	.0111	.0035	.0104	.9750
53D	.5398	.1705	.2557	.0341	.0104	.0031	.0079	.9786
53E	.5342	.1453	.2735	.0470	.0113	.0034	.0090	.9763
53	.4582	.0864	.3806	.0747				
53A	.4731	.1902	.3073	.0296	.0348	.0153	.0344	.9155
53B	.4679	.2032	.2800	.0428	.0044	.0027	.0017	.9911
53C	.4428	.1857	.3000	.0714	.0105	.0047	.0105	.9742
53D	.5015	.2063	.2698	.0222	.0106	.0045	.0090	.9758
53E	.4859	.1771	.2937	.0432	.0117	.0046	.0096	.9741
53E	.5357	.1513	.2842	.0286				
53E	.5231	.1873	.2683	.0212				
53A					.0489	.0209	.0393	.8908
53F	.4874	.1759	.2998	.0368	.0343	.0129	.0324	.9203
53G	.4444	.1628	.3473	.0453	.0265	.0097	.0239	.9398
53H	.4895	.1772	.2954	.0380	.0358	.0140	.0308	.9193
53J	.4333	.1602	.3575	.0490	.0296	.0129	.0276	.9299

The results of repetitive analyses of the same samples have been summarized in Table XXI. It is believed that these results give the most accurate picture of the major definable source of experimental error. The cause of the observable deviations in the data has not been definitely established. However, the wide difference in the molecular weights of the substances analysed in this work is believed to be a contributing factor.

TABLE XXI

REPETITIVE ANALYSES RESULTS

SAMPLE	DATE	MASS SPEC. RUN NO.	LIQUID PHASE MOLE FRACTION				VAPOR PHASE MOLE FRACTION			
			X_{H_2}	X_{BZ}	X_{CX}	X_{HX}	Y_{H_2}	Y_{BZ}	Y_{CX}	Y_{HX}
34V	8/11/60	(6582)					.9437		.0275	.0288
	8/15/60	(6627)					.9570		.0211	.0219
34AV	8/11/60	(6583)					.9741		.0116	.0143
	8/15/60	(6628)					.9696		.0157	.0147
34L	8/11/60	(6584)	.0068		.4932	.5000				
	8/15/60	(6630)	.0109		.4959	.4932				
34AL	8/11/60	(6585)	.0182		.4742	.5076				
	8/15/60	(6631)	.0117		.4851	.5032				
44V	9/30/60	(6858)					.9499	.0425	.0076	
	10/6 /60	(6937)					.8970	.0892	.0125	
	10/11/60	(6954)					.9417	.0501	.0083	
44BV	9/30/60	(6860)					.9899	.0084	.0017	
	10/11/60	(6956)					.9756	.0200	.0043	
44L	9/30/60	(6864)	.0365	.8229	.1406					
	10/11/60	(6960)	.0377	.8456	.1296					
44AL	9/30/60	(6865)	.0714	.7500	.1785					
	10/11/60	(6961)	.0514	.7712	.1774					
44BL	9/30/60	(6866)	.0354	.7965	.1681					
	10/11/60	(6962)	.0189	.8417	.1392					
45V	9/30/60	(6861)					.8997	.0854	.0149	
	10/11/60	(6957)					.9053	.0815	.0131	
45AV	9/30/60	(6862)					.9028	.0817	.0154	
	10/11/60	(6958)					.8861	.0973	.0165	
45BV	9/30/60	(6863)					.7063	.2573	.0404	
	10/11/60	(6959)					.6520	.3032	.0448	
45L	9/30/60	(6867)	.0216	.8446	.1338					
	10/11/60	(6963)	.0560	.8175	.1264					
45AL	9/30/60	(6868)	.0363	.7972	.1664					
	10/11/60	(6964)	.0518	.7831	.1650					
45BL	9/30/60	(6869)	.0055	.8611	.1335					
	10/11/60	(6965)	.0165	.8548	.1287					
50DV	10/13/60	(6982)					.9437	.0277	.0092	.0193
	10/16/60	(7016)					.9419	.0266	.0108	.0208
50EV	10/13/60	(6983)					.9451	.0242	.0089	.0218
	10/16/60	(7017)					.9428	.0249	.0100	.0224
51JV	12/3/60	(7256)					.9884	.0016	.0036	.0064
	12/3/60	(7257)					.9867	.0019	.0043	.0071
	12/3/60	(7247)					.9901	.0016	.0031	.0052
	12/3/60	(7248)					.9893	.0012	.0031	.0062
52DL	10/16/60	(7022)	.0509	.4907	.1678	.2905				
	11/18/60	(7155)	.1486	.3645	.1496	.3370				
53AL	10/25/60	(7059)	.0047	.5235	.1596	.3122				
	11/17/60	(7137)	.0296	.4731	.1902	.3073				
53AV	10/25/60	(7053)					.9131	.0389	.0128	.0353
	11/17/60	(7131)					.9155	.0348	.0153	.0344
	11/17/60	(7144)					.8908	.0489	.0209	.0393
53DL	10/25/60	(7062)	.0341	.5398	.1705	.2557				
	11/17/60	(7140)	.0222	.5015	.2063	.2698				
53DV	10/25/60	(7056)					.9786	.0104	.0031	.0079
	11/17/60	(7134)					.9758	.0106	.0045	.0090
53EL	10/25/60	(7063)	.0470	.5342	.1453	.2735				
	11/17/60	(7141)	.0432	.4859	.1771	.2937				
	11/17/60	(7142)	.0286	.5357	.1513	.2842				
	11/17/60	(7143)	.0212	.5231	.1873	.2683				
53EV	10/25/60	(7057)					.9763	.0113	.0034	.0090
	11/17/60	(7135)					.9741	.0117	.0046	.0096

GRAPHICAL PRESENTATION OF THE DATA

Certain insights into the effect of aromaticity on the K-values of hydrogen and the effect of hydrogen on the K-values of hydrocarbons may be obtained from a graphical presentation of the experimental data obtained in this work.

Figures 10, 11 and 12 show that the effect of solvent composition on hydrogen K-values is not a linear function of composition. The results of calculations based on the two equations of state method are shown to predict the curvature shown in these figures. Relative volatilities of the hydrocarbons from experimental data as well as from the literature are also shown as an indication of the hydrocarbon interactions.

A graphical correlation of these results requires a parameter that indicates the composition of the solvent. One such parameter in common use is the U.O.P. K factor. Elbishlawi and Spencer(71) have shown that the K-values of methane at constant temperature and pressure may be correlated as a function of this parameter. The experimental hydrogen K-values, as well as hydrogen K-values from the literature, have been plotted in this manner in Figures 13 and 14.

This correlation of hydrogen K-values has an average absolute percentage deviation of 10.8 at 200°F., and an average absolute percentage deviation of 17.2 at 100°F. The modified two equation of state method gave an average absolute percentage deviation of 20.6 at 200°F. and 16.6 at 100°F. for hydrogen K-values.

This graphical correlation of hydrogen K-values brings out several points of interest. The K-values of hydrogen increase as the aromaticity of the solvent increases, as the system pressure decreases, and as the system temperature increases. However, the U.O.P. K factor does not completely define the effect of the solvent on hydrogen K-values. Figure 15 shows two different solvents that have a U.O.P. K of 11.0. One is pure cyclohexane, while the other is a mixture of hexane and benzene. Improved accuracy in the prediction of hydrogen K-values will require more specific information about the solvent than the U.O.P. K can provide.

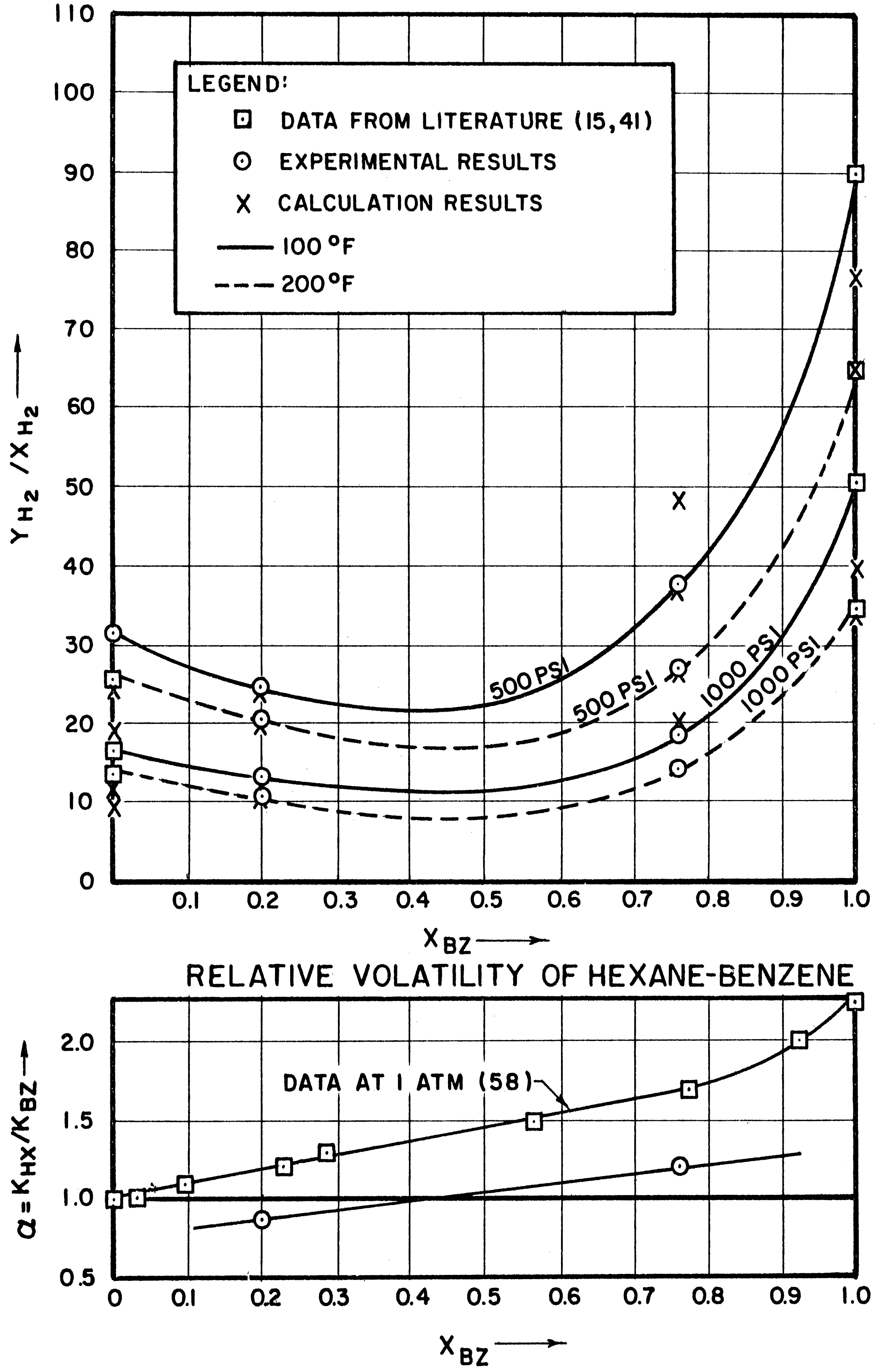
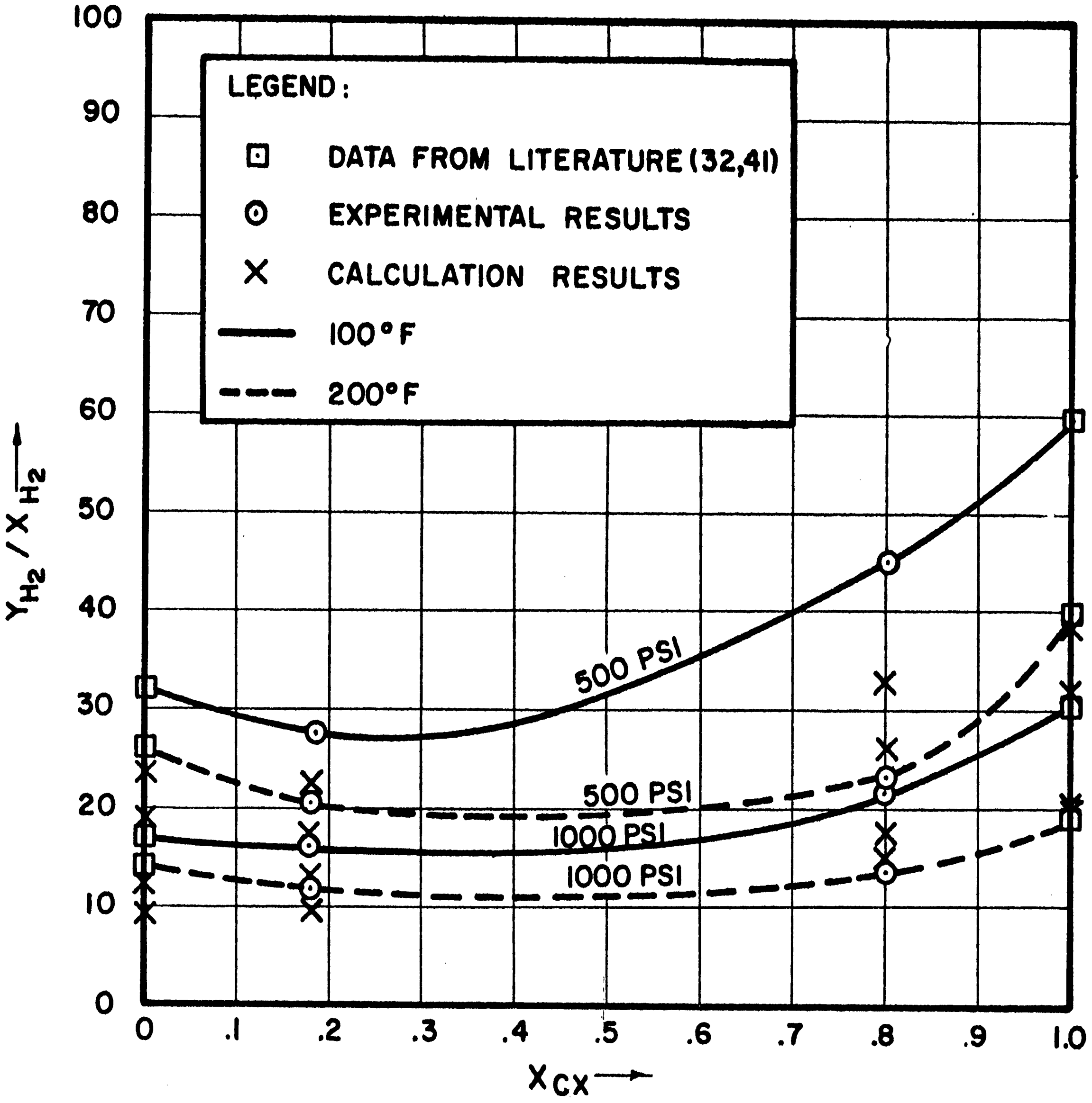


Figure 10. Hydrogen Vapor-Liquid Equilibrium Composition Ratios in Hexane-Benzene.



RELATIVE VOLATILITY OF HEXANE - CYCLOHEXANE

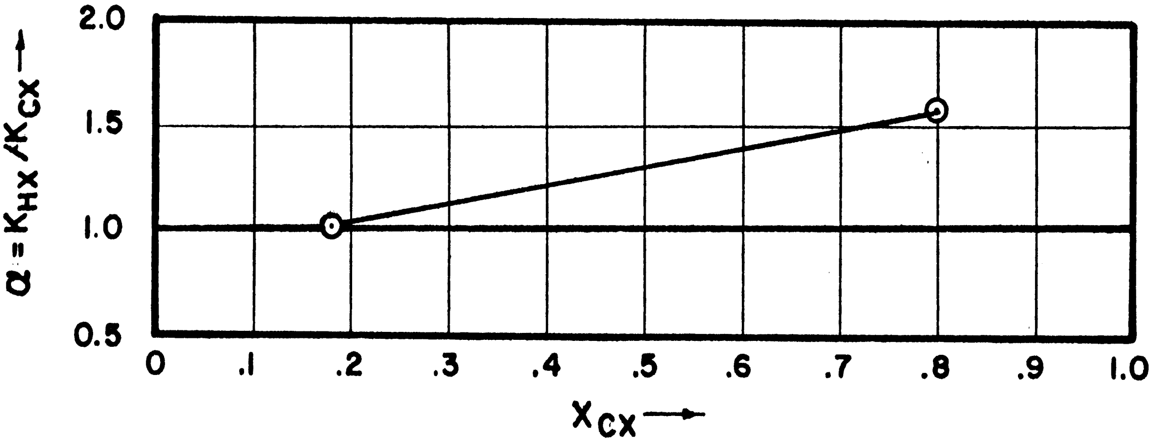
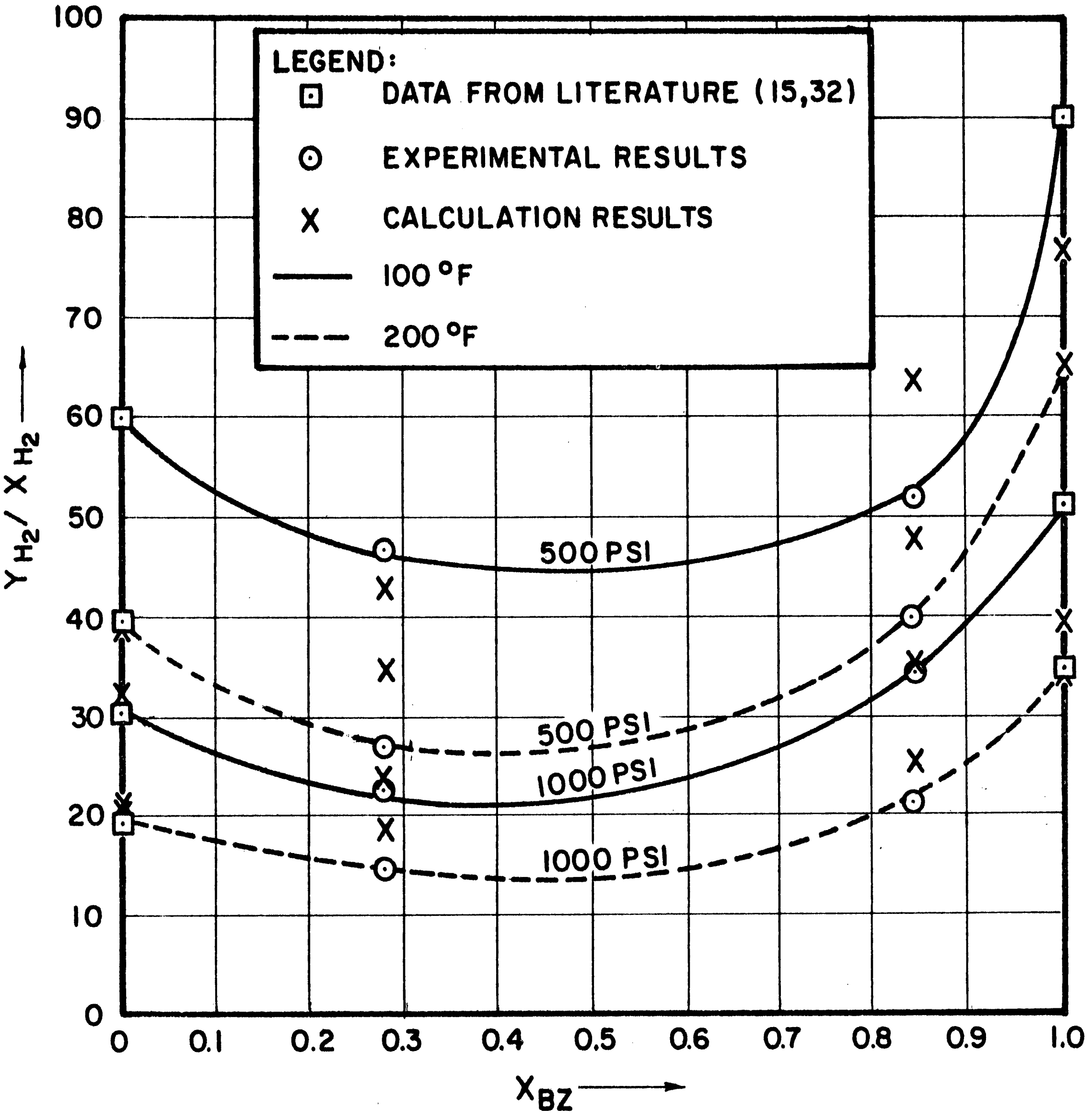


Figure 11. Hydrogen Vapor-Liquid Equilibrium Composition Ratios in Hexane-Cyclohexane.



RELATIVE VOLATILITY OF BENZENE - CYCLOHEXANE

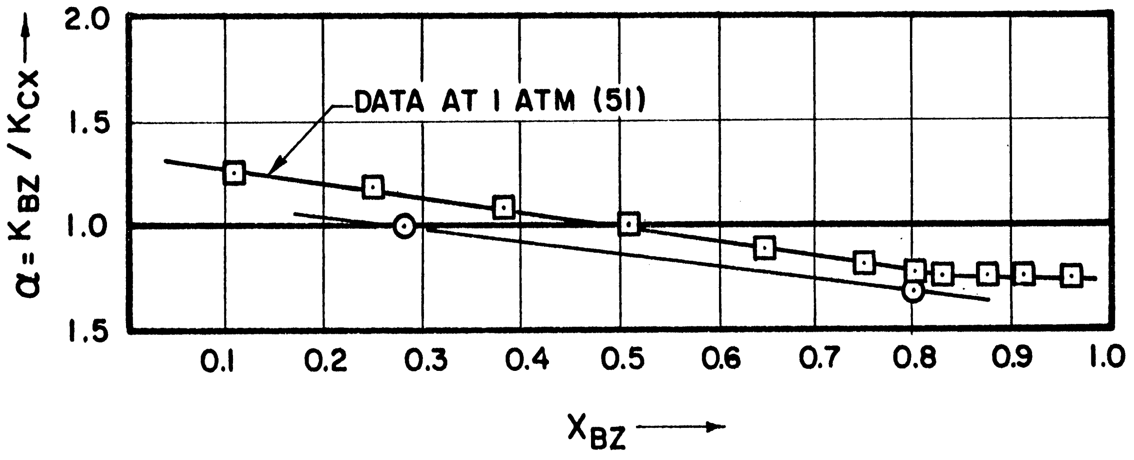


Figure 12. Hydrogen Vapor-Liquid Equilibrium Composition Ratios in Benzene-Cyclohexane.

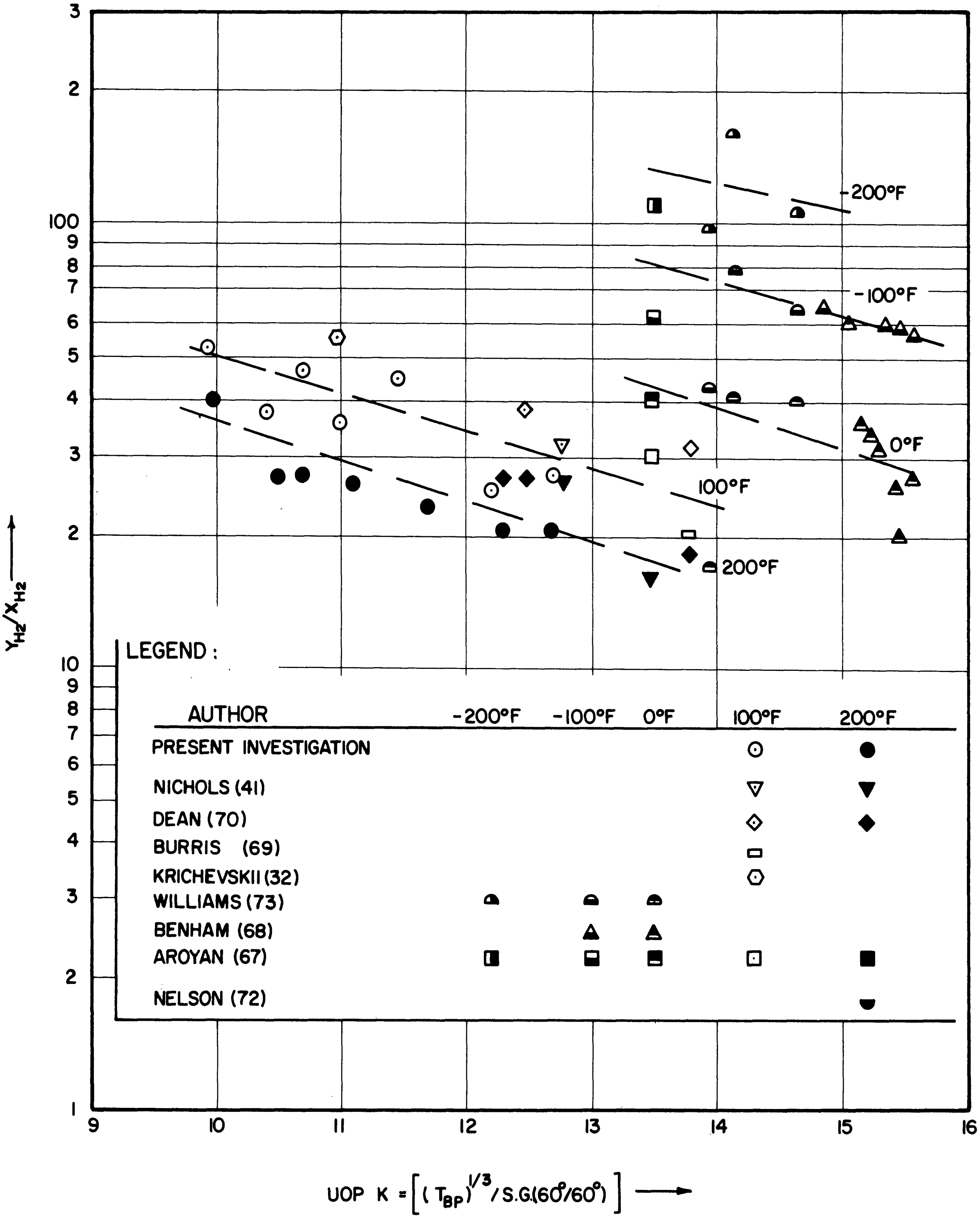


Figure 13. Hydrogen Vapor-Liquid Equilibrium Ratios at 500 Psi as a Function of UOP K Factors of Hydrogen Free Solvent.

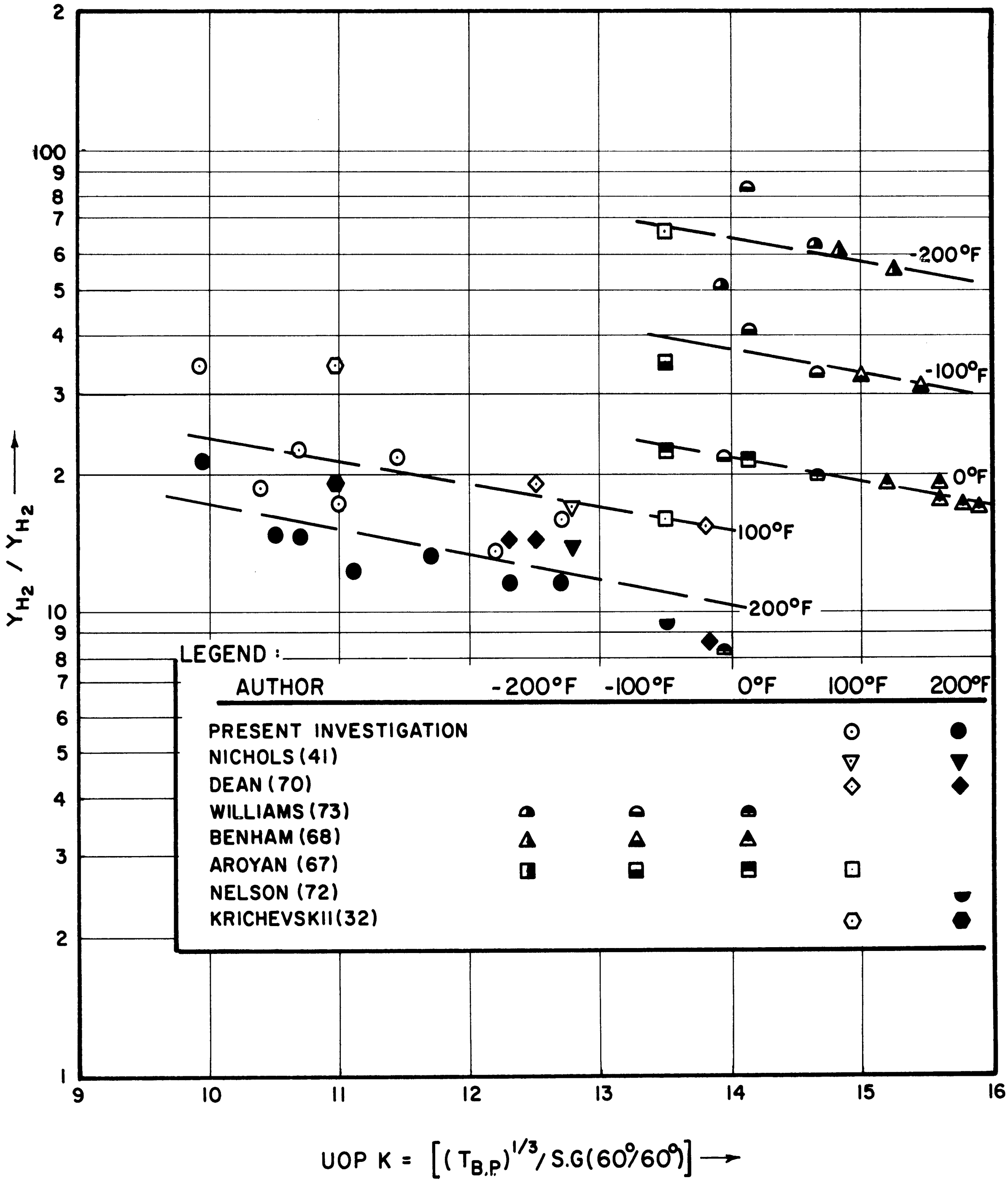


Figure 14. Hydrogen Vapor-Liquid Equilibrium Ratios at 1000 Psi as a Function of UOP K Factors of Hydrogen Free Solvent.

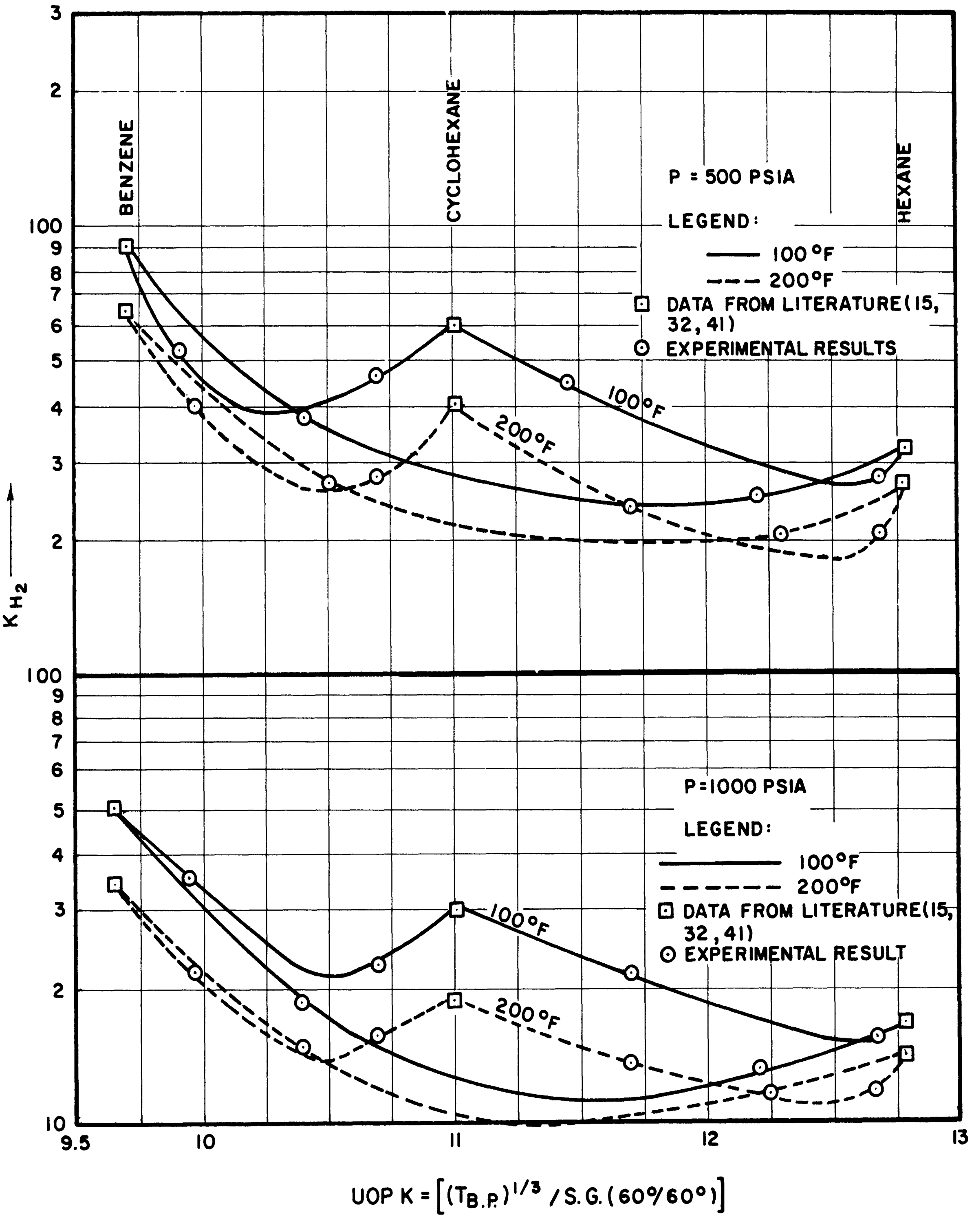


Figure 15. Vapor-Liquid Equilibrium Composition Ratios of Hydrogen as Function of the Solvent's UOP K Factor.

In Figures 16, 17 and 18, the K-values of the hydrocarbons studied in this work are shown on a conventional log-log plot. At a given system temperature and pressure, the K-values of two different hydrocarbons in the presence of hydrogen appear to be proportional to their vapor pressures. That is:

$$\frac{K_i}{K_j} = \frac{P_i^o}{P_j^o}$$

at constant P and T.

Data reported by Nichols(41) for the system hydrogen-hexane has been used to establish the validity of this relationship. All experimental hydrocarbon K-values were predicted to within approximately 25% in this manner.

Another method of correlating hydrocarbon K-values is presented in Figure 19. Several simplifying assumptions are incorporated into this graph. Since the hydrocarbon K-values measured in this work appeared to be proportional to their vapor pressures, Raoult's and Dalton's Laws were assumed to give a first order approximation of these K-values.

$$K_i = Y_i/X_i = P_i^o/P$$

or

$$K_i P = P_i^o$$

The vapor pressure of component "i" may be estimated from the Clausius-Clapeyron Equation:

$$\log \frac{(P_i^o)_1}{(P_i^o)_2} = \frac{\Delta H_V}{2.303R} \left[\frac{1}{T_2} - \frac{1}{T_1}\right]$$

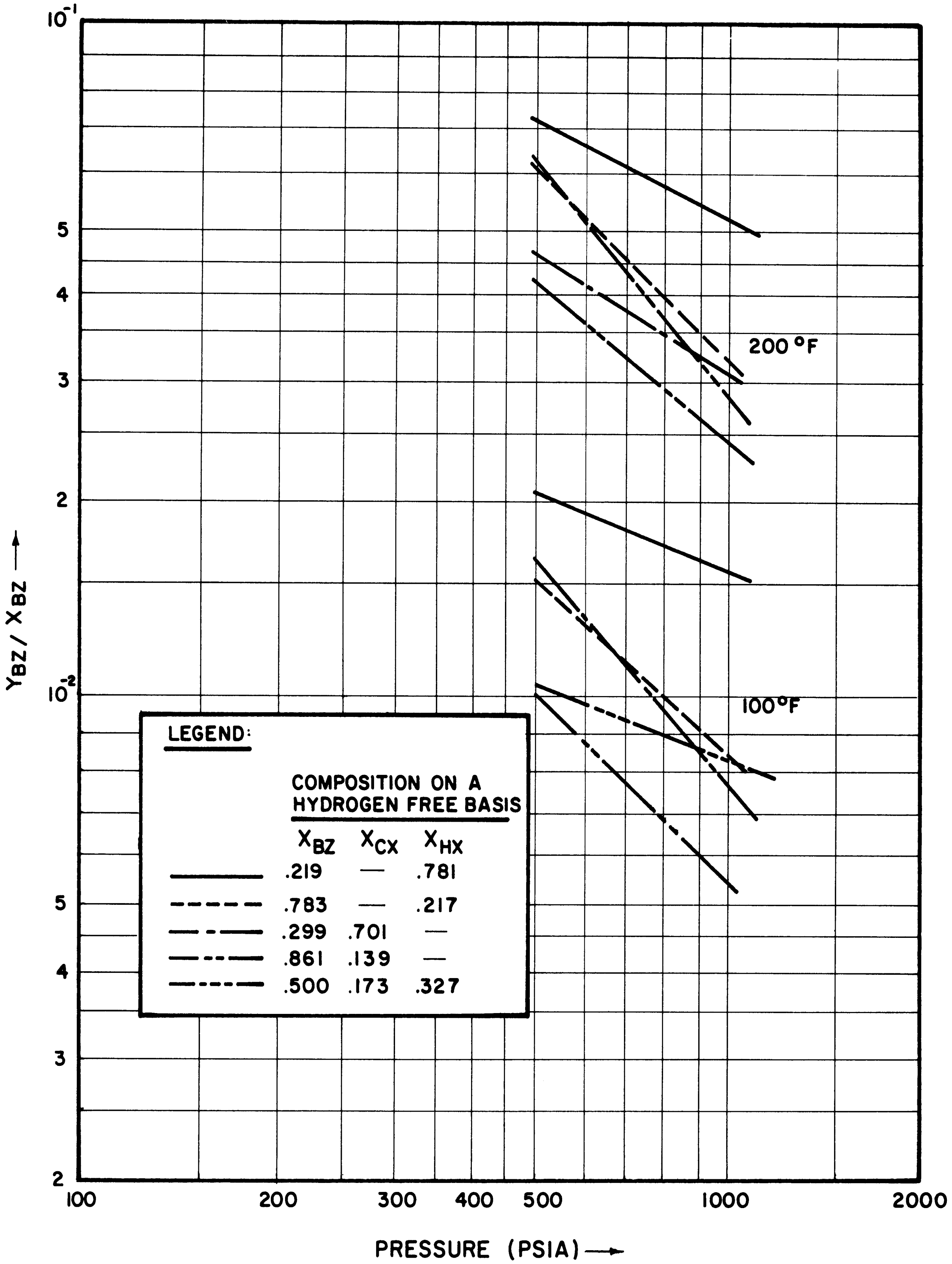
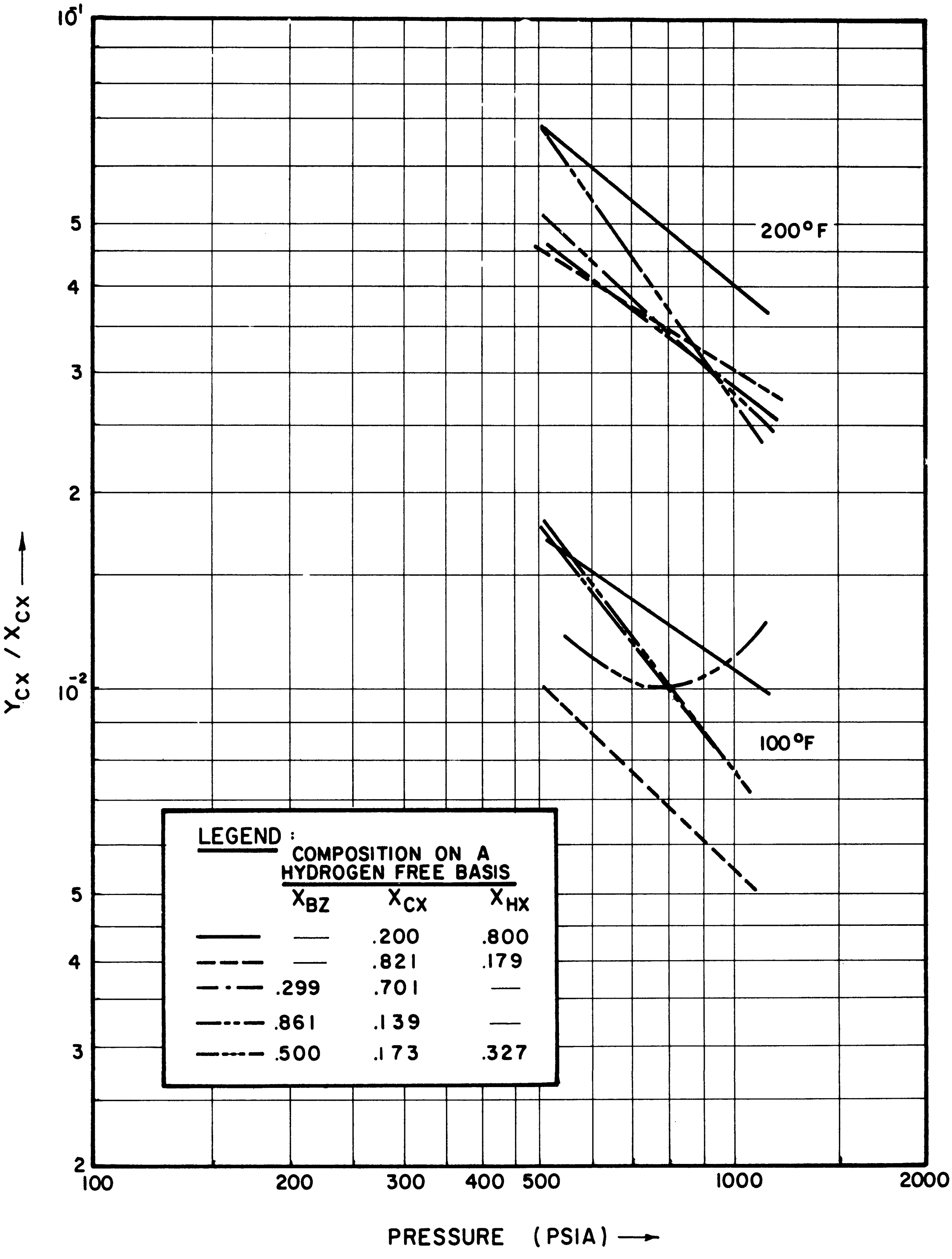


Figure 16. Benzene Vapor-Liquid Equilibrium Composition Ratios.



	X_{BZ}	X_{CX}	X_{HX}
———	—	.200	.800
— — —	—	.821	.179
—·—	.299	.701	—
—··—	.861	.139	—
—···—	.500	.173	.327

Figure 17. Cyclohexane Vapor-Liquid Equilibrium Composition Ratios.

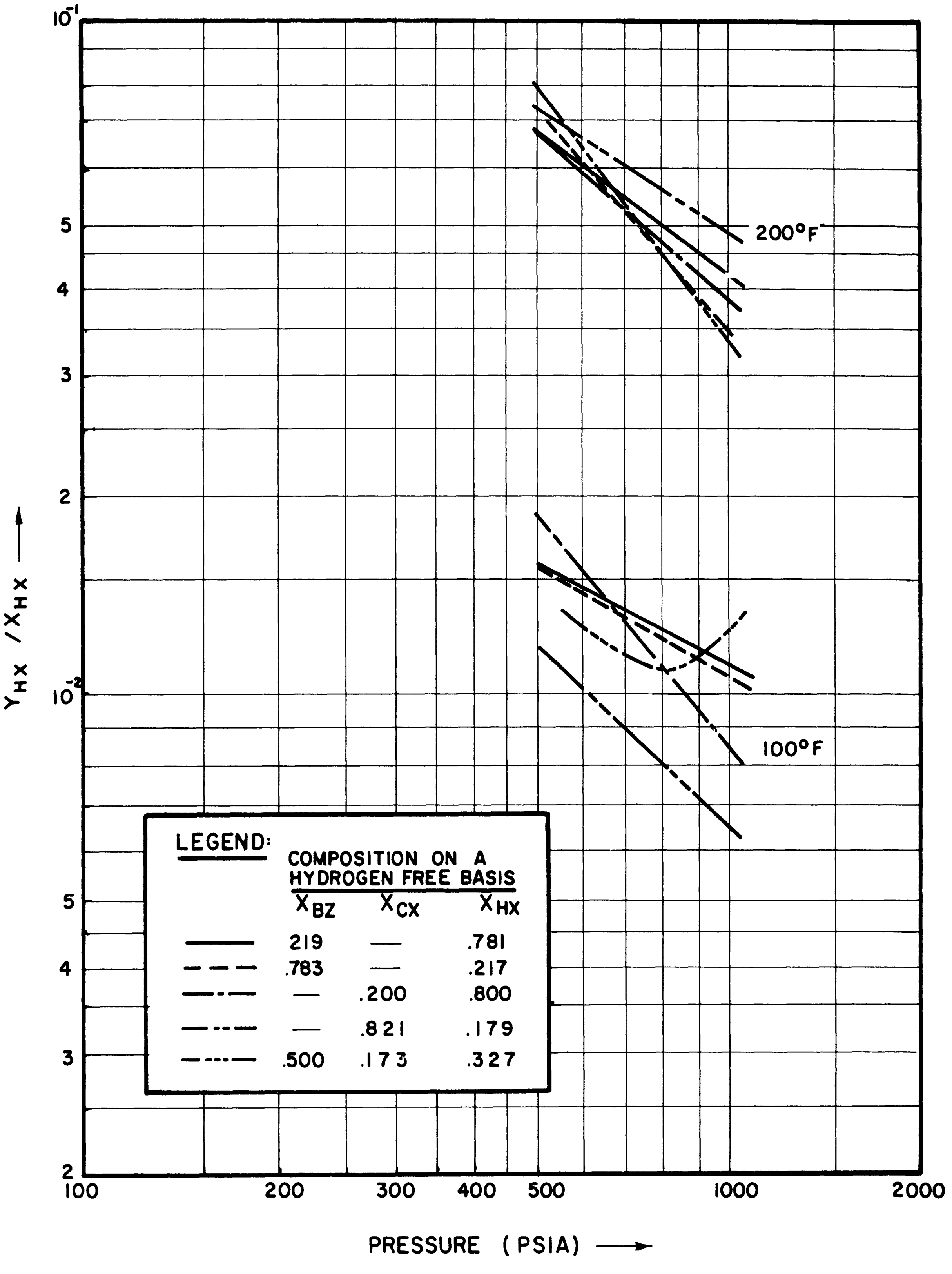


Figure 18. Hexane Vapor-Liquid Equilibrium Composition Ratios.

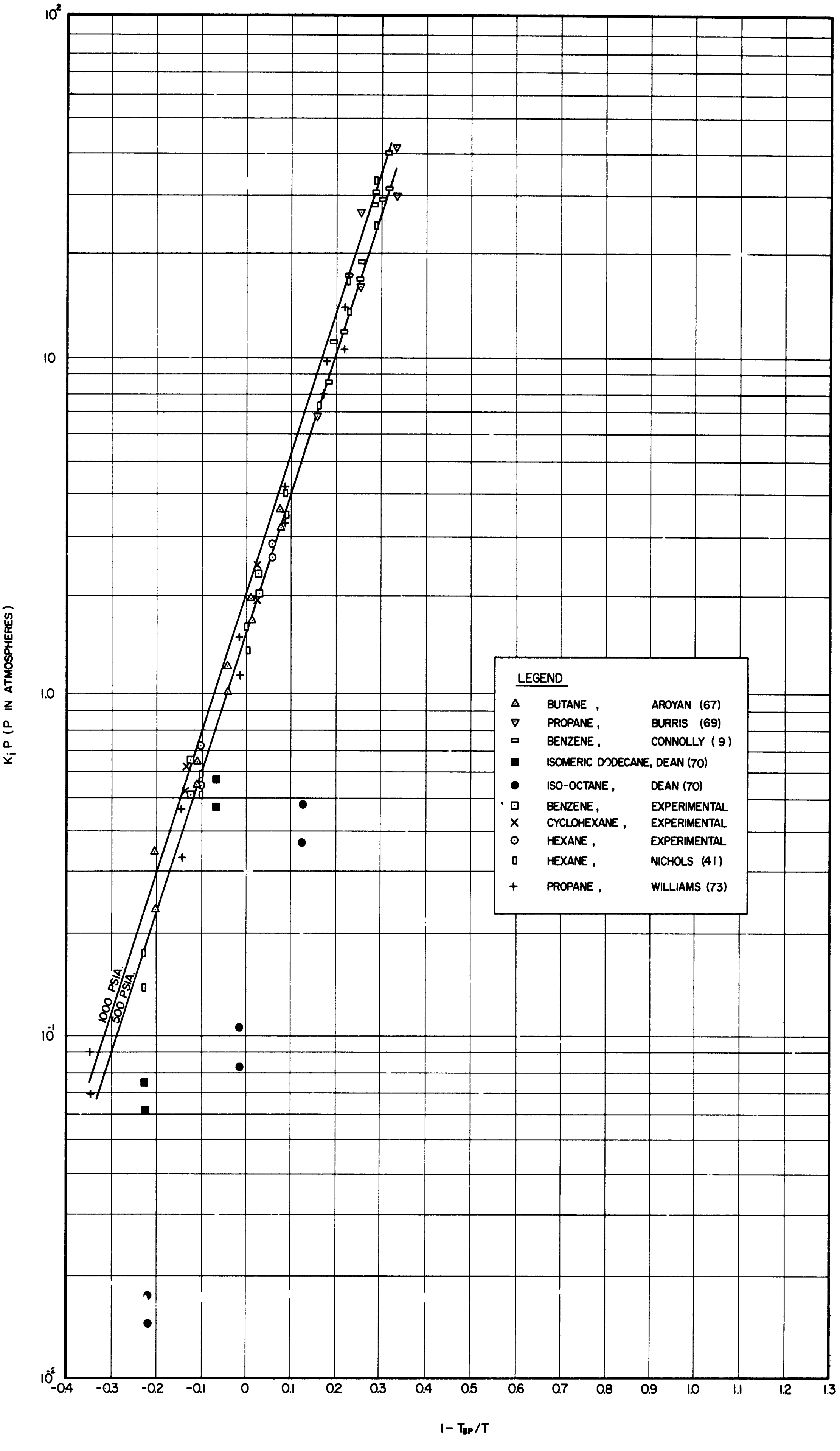


Figure 19. Vapor-Liquid Equilibrium Composition Ratios of Hydrocarbons in Presence of Hydrogen as a Function of the System Pressure and the Ratio of Hydrocarbon Boiling Point Temperature to System Temperature.

If the atmospheric boiling point of the component is chosen as a reference state, the vapor pressure of the component at any other temperature is given by the relationship:

$$\log P_i^o = \frac{\Delta H_V}{2.303R}\left[\frac{1}{T_{B.P.}} - \frac{1}{T}\right]$$

Trouton's empirical ratio indicates that at atmospheric pressure:

$$\frac{\Delta H_V}{T_{B.P.}} = 21$$

so that

$$\log P_i^o = \frac{21}{2.303R}\left(1 - \frac{T_{B.P.}}{T}\right)$$

or

$$\log K_iP = 4.6\left(1 - \frac{T_{B.P.}}{T}\right)$$

This relationship is in a reduced form, and except for data on isomeric dodecane and iso-octane by Dean and Tooke(70), it appears to represent vapor-liquid equilibrium composition ratios of non-polar hydrocarbons in the presence of hydrogen to 1000 psia. The effect of pressure on the hydrocarbon molal heat of vaporization is reflected in the fact that the slope of the lines shown in Figure 19 is 4.2 rather than 4.6.

SAMPLE CALCULATION

In order to further clarify the methods used to predict vapor-liquid equilibrium compositions in this dissertation, the following section has been added.

Estimating Overall Composition

The first step in calculations of this type is to estimate the overall composition of the phases. In industrial practice, the overall composition of the phases is the feed stream composition to an equilibrium stage.

The overall composition of the phases present in the equilibrium cell in this work has been estimated from the experimental equilibrium composition data. By a material balance around the equilibrium cell:

$$F = L + D$$

$$F x_{F_i} = L x_i + D y_i$$

Per mole of feed:

$$D = \frac{x_{F_1} - x_1}{y_1 - x_1} = \frac{x_{F_2} - x_2}{y_2 - x_2} = \frac{x_{F_3} - x_3}{y_3 - x_3} = \frac{x_{F_4} - x_4}{y_4 - x_4}$$

where subscript 1 indicates benzene, subscript 2 indicates cyclohexane, subscript 3 indicates hexane, and subscript 4 indicates hydrogen.

Since hydrogen is present in all runs, x_{F_4} is solved for first:

$$(x_{F_4} - x_4)\left(\frac{y_1 - x_1}{y_4 - x_4}\right) = x_{F_1} - x_1$$

An additional restriction is required to provide a completely defined set of equations for the overall composition. In this work, the assumption was made that the hydrogen free composition of the liquid phase and calculated feed were equal. That is:

$$\frac{x_{F_i}}{1-x_{F_4}} = \frac{x_i}{1-x_4}$$

or for benzene:

$$x_{F_1} = \frac{x_1}{1-x_4} - x_{F_4}\left(\frac{x_1}{1-x_4}\right)$$

Substituting this relationship into the equation for x_{F_4}:

$$x_{F_4}\left(\frac{y_1-x_1}{y_4-x_4}\right) - x_4\left(\frac{y_1-x_1}{y_4-x_4}\right) = \frac{x_1}{1-x_4} - x_{F_4}\left(\frac{x_1}{1-x_4}\right) - x_1$$

Rearranging

$$x_{F_4} = \frac{\frac{x_1}{1-x_4} + x_4\left(\frac{y_1-x_1}{y_4-x_4}\right) - x_1}{\frac{y_1-x_1}{y_4-x_4} + \frac{x_1}{1-x_4}}$$

then

$$x_{F_1} = x_1\left(\frac{1-x_{F_4}}{1-x_4}\right)$$

$$x_{F_2} = x_2\left(\frac{1-x_{F_4}}{1-x_4}\right)$$

and

$$x_{F_3} = x_3\left(\frac{1-x_{F_4}}{1-x_4}\right)$$

Sample Calculation

The ideas and equations presented thus far will be combined to illustrate the calculation presented in Table XVII for Run 18.

The given data is:

Pressure = 567 Psia

Temperature = 100°F.

	x	y
Benzene	0.210	0.004
Cyclohexane	0.000	0.000
Hexane	0.751	0.011
Hydrogen	0.039	0.985

The first step is to calculate the overall phase composition. From the preceding subsection:

$$x_{F_{H_2}} = \frac{\frac{x_{Bz}}{1-x_{H_2}} + x_{H_2}\left(\frac{y_{Bz}-x_{Bz}}{y_{H_2}-x_{H_2}}\right) - x_{Bz}}{\frac{y_{Bz} - x_{Bz}}{y_{H_2} - x_{H_2}} + \frac{x_{bz}}{1-x_{H_2}}}$$

$$x_{F_{H_2}} = 0.039$$

Then

$$x_{F_{Bz}} = x_{Bz}\left(\frac{1-x_{F_{H_2}}}{1-x_{H_2}}\right) = 0.210$$

and

$$x_{F_{Hx}} = x_{Hx}\left(\frac{1-x_{F_{H_2}}}{1-x_{H_2}}\right) = 0.751$$

Vapor-Liquid Equilibrium Composition Ratios

The vapor-liquid equilibrium composition ratios are calculated by means of the two equation of state method.

$$K_i = \gamma_i \nu_i / \varphi_i$$

The vapor phase fugacity coefficient, φ_i, and the liquid phase activity coefficient, γ_i, are functions of composition. Thus, a first estimate of all compositions must be made. For this case, assume:

	x	y
Benzene	0.210	0.002
Hexane	0.750	0.008
Hydrogen	0.040	0.990

Calculations for each of the coefficients shown in the above relationship for the vapor-liquid equilibrium composition ratio follow.

Liquid Phase Activity Coefficient

The Hildebrand Solubility Theory is the basis for the prediction of liquid phase activity coefficients. The equations used are discussed in the main text of this dissertation.

Physical data required for this particular calculation include the liquid phase composition, the liquid molal volume of each component, and the solubility parameter for each component.

Liquid molal volumes have been estimated in two ways. The Watson Expansion factor has been used, where:

$$\underline{V}_i^L = (V_i^o \omega_i^o)(5.7 + 3.0\ T_{r_i})$$

A compilation of $(V_i^o \omega_i^o)$ is given by Edmister(14) and the critical properties of the components studied here are tabulated in Table VII.

At 100°F., the following liquid volumes may be calqulated:

$$\underline{V}_{Bz}^L = 11.64\ (5.7 + 3.0 \times \frac{560}{1012.7}) = 85.7\ \text{cc/gm-mole}$$

$$\underline{V}_{Hx}^L = 16.52\ (5.7 + 3.0 \times \frac{560}{914.2}) = 124.6\ \text{cc/gm-mole}$$

$$\underline{V}_{H_2}^L = 1.05\ \ (5.7 + 3.0 \times \frac{560}{60.2}) = 35.3\ \text{cc/gm-mole}$$

Specific physical data from the Engineering Data Book(15) indicates that for the hydrocarbons at 100° F.:

$$\underline{V}^L_{Bz} = 78/0.860 = 90.6 \text{ cc/gm-mole}$$

$$\underline{V}^L_{Hx} = 86/0.642 = 134 \text{ cc/gm-mole}$$

From Table VII the liquid molal volumes recommended by Chao for all temperatures are found to be:

$$\underline{V}^L_{Bz} = 89.4 \text{ cc/gm-mole}$$

$$\underline{V}^L_{Hx} = 131.6 \text{ cc/gm-mole}$$

$$\underline{V}^L_{H_2} = 31.0 \text{ cc/gm-mole}$$

Solubility parameters needed for this calculation are discussed in a special appendix on page 67.

This information may now be substituted into the volumetric entropy equation:

$$\ln \gamma_i = \ln \frac{\underline{V}^L_i}{\underline{V}^L_M} + \frac{\underline{V}^L_i (\delta_i - \delta_M)^2}{RT} + 1.0 - \frac{\underline{V}^L_i}{\underline{V}^L_M}$$

where

$$\underline{V}^L_M = \sum_i x_i \underline{V}^L_i$$

and

$$\delta_M = \sum_i x_i \underline{V}^L_i \delta_i / \sum_i x_i \underline{V}^L_i$$

By substituting specific data into these equations, the following liquid activity coefficients are found:

$$\gamma_{Bz} = 1.425$$

$$\gamma_{Hx} = 1.008$$

$$\gamma_{H_2} = 1.686$$

Pure Liquid Component Fugacity Coefficient

The pure liquid component fugacity coefficient for hydrogen, ν_{H_2}, has been estimated by Chao's method from the data in Tables VI and VII:

$$\log \nu_{H_2} = 1.96718 + 1.02972/T_r - 0.054009\ T_r + 0.0005288\ T_r^2 + 0.008585\ P_r - \log P_r$$

Here $T_r = 560/60.2$

$P_r = 567/190.8$

and $\nu_{H_2} = 14.929$

The pure liquid component fugacity coefficients for the hydrocarbons has been estimated from a knowledge of the hydrocarbons' vapor pressure and liquid molal volumes:

$$\ln \nu_i = \ln \frac{P_i^o}{P} + \ln \left(\frac{f_i}{P}\right)_{P_i^o} + \frac{V_i^L(P-P_i^o)}{RT}$$

At 100°F., the following vapor pressures are found in the <u>Data Book on Hydrocarbons</u> by Maxwell$^{(39)}$:

$P^o_{Bz} = 0.215$ atmospheres

$P^o_{Hx} = 0.343$ atmospheres

For both hydrocarbons, $(\frac{f_i}{P})_{P^o}$ is essentially unity. Thus:

$\nu_{Bz} = 0.007$

$\nu_{Hx} = 0.010$

Vapor Phase Fugacity Coefficient

The vapor phase fugacity coefficient has been calculated in three different ways. The first method utilizes the Virial Equation of

State. From Figures 4 through 7, the following experimental virial coefficients are found at 100°F.:

$$B_{Bz,Bz}^{(100°F.)} = -1430 \text{ cc/gm-mole}$$

$$B_{Hx,Hx}^{(100°F.)} = -1750 \text{ cc/gm-mole}$$

$$B_{Hz,Hz}^{(100°F.)} = 14.50 \text{ cc/gm-mole}$$

From Figures 8 and 9, the following second virial interaction coefficients are found:

$$B_{Bz,Hx}^{(100°F)} = -1580 \text{ cc/gm-mole}$$

$$B_{Bz,H_2}^{(100°F.)} = -4.0 \text{ cc/gm-mole}$$

$$B_{Hx,H_2}^{(100°F.)} = 7.0 \text{ cc/gm-mole}$$

The virial equation must first be solved for its largest root, the vapor-phase volume:

$$\frac{P\underline{V}_M^V}{RT} = 1 + \frac{B_M(T)}{\underline{V}_M^V}$$

where

$$B_M = y_{Bz}^2 B_{Bz,Bz}^{(T)} + y_{Hx}^2 B_{Hx,Hx}^{(T)} + y_{H_2}^2 B_{H_2,H_2}^{(T)} + 2y_{Bz}y_{Hx}B_{Bz,Hx}^{(T)}$$
$$+ 2y_{Bz}y_{H_2}B_{Bz,H_2}^{(T)} + 2y_{Hx}y_{H_2}B_{Hx,H_2}^{(T)}$$

Upon substitution of values presented earlier, this equation yields the result:

$$\underline{V}_M^V = 675.695 \text{ cc/gm-mole}$$

Then

$$\ln \varphi_i = \frac{2}{V_M^V}\left(y_{Bz}B_{i,Bz}^{(100°F.)} + y_{Hz}B_{i,Hx}^{(100°F.)} + y_{H_2}B_{i,H_2}^{(100°F.)}\right) - \ln \frac{PV_M^V}{RT}$$

Solving this equation gives the result:

$$\varphi_{Bz} = 0.922$$

$$\varphi_{Hx} = 0.951$$

$$\varphi_{H_2} = 1.023$$

The Redlich-Kwong Equation, integrated for moderate pressures, has also been used to predict vapor phase fugacity coefficients.

$$\ln \varphi_i = [B_i - A_i^2 + (A_i - A_M)^2]\, P$$

where

$$A_i^2 = 0.4278\ \frac{T_c^{2.5}}{P_cT^{2.5}}$$

$$B_i = 0.0867\ \frac{T_c}{P_cT}$$

and

$$A_M = \sum_i y_iA_i$$

This equation gives the results

$$\varphi_{Bz} = 0.928$$

$$\varphi_{Hx} = 0.960$$

$$\varphi_{H_2} = 1.024$$

Calculation of K-Values and Improved Estimates of Equilibrium Phase Compositions

The information calculated in the preceding sections may now be used to estimate the K-values for each component.

Using the vapor phase fugacity coefficients based on the Virial Equation of State, the following results are obtained:

$$K_{Bz} = \frac{1.425}{0.922} \times 0.007 = 0.011$$

$$K_{Hx} = \frac{1.008}{0.951} \times 0.010 = 0.011$$

$$K_{H_2} = \frac{1.686}{1.023} \times 14.929 = 24.612$$

These values, plus the overall composition, are used to improve the original estimates made of the equilibrium phase compositions.

From the Outline of Correlation Procedure (see page 54ff):

$$x_{H_2}(K_{H_2}-1)\left(\frac{x_{F_{Bz}}(K_{Bz}-K_{Hx})}{x_{F_{H_2}}(K_{BZ}-1) + x_{H_2}(K_{H_2}-K_{Bz})}\right) + K_{Hx}(1-x_{H_2}) + K_{H_2}x_{H_2} = 1.0$$

Substituting the known values and solving for x_{H_2} gives the result:

$$x_{H_2} = 0.040$$

Then

$$x_{Hx} = \frac{x_{H_2}x_{F_{Hx}}(K_{H_2}-1)}{x_{F_{H_2}}(K_{Hx}-1) + x_{H_2}(K_{H_2}-K_{Hx})}$$

Substituting into this equation gives the result:

$$x_{Hx} = 0.750$$

Finally

$$x_{Bz} = 1.0 - x_{H_2} - x_{Hx}$$

$$= 0.210$$

The vapor phase compositions are found from the relationship:

$$y_i = K_i x_i$$

so that

$$y_{Bz} = 0.002$$

$$y_{Hx} = 0.008$$

$$y_{H_2} = 0.990$$

As these are the initial values assumed, the calculation is complete. This same procedure has been used to re-estimate equilibrium phase compositions in which vapor phase fugacity coefficients were estimated from the Redlich-Kwong Equation of State, integrated for moderate pressures.

Calculation of Interaction Virial Coefficients

This calculation is discussed in the section entitled "Calculation Results" (page 75). The experimentally determined equilibrium phase compositions are assumed to be correct. Then:

$$\varphi_i = \gamma_i \nu_i / K_i$$

Substitution of the experimentally determined compositions into the equations previously discussed gives the results:

$$\varphi_{Bz} = (1.423)(0.007)(0.210)/0.004 = 0.523$$

$$\varphi_{Hx} = (1.009)(0.010)(0.751)/0.011 = 0.690$$

$$\varphi_{H_2} = (1.686)(14.929)(0.039)/0.985 = 0.999$$

The virial equation must be solved for the vapor-phase volume, giving the result:

$$\underline{V}_M^V = 675.430 \text{ cc/gm-mole}$$

for the experimental vapor phase composition.

Assuming that a change in the hydrogen-hydrocarbon second virial interaction coefficients will not affect this last result, the equation for the vapor phase fugacity coefficient may be written:

$$\ln \varphi_i = \frac{2}{\underline{V}_M^V}\left(y_{Bz}B_{i,Bz}(T) + y_{Hx}B_{i,Hx}(T) + y_{H_2}B_{i,H_2}(T)\right) - \ln \frac{P\underline{V}_M^V}{RT}$$

The values of φ_i and $\underline{V}_M^V$, which have just been determined, plus experimentally determined values of vapor phase compositions and all second virial coefficients except the hydrogen-hydrocarbon second virial interaction coefficients, which are the variables in this calculation, are now substituted into the above relationship.

In order to reduce experimental uncertainty, this set of equations from Run 18 has been combined with similar sets of equations utilizing data from Runs 21, 22 and 25. The combined set of equations has been solved by the method of least squares for the hydrogen-hydrocarbon second virial interaction coefficients, giving the results:

$$B_{Bz,H_2}^{(100^\circ F.)} = -140.588 \text{ cc/gm-mole}$$

$$B_{Hx,H_2}^{(100^\circ F.)} = -51.052 \text{ cc/gm-mole}$$

The new estimates of the hydrogen-hydrocarbon second virial interaction coefficients have then been used in a second calculation of equilibrium phase compositions, giving as final results:

	$\underline{x}$	$\underline{y}$
Benzene	0.210	0.002
Hexane	0.750	0.008
Hydrogen	0.039	0.990

Computer Program

The complete calculation that has just been described in detail has been programmed for a 704 IBM computer. This program is presented in Table XXII.

TABLE XXII

FORTRAN PROGRAM FOR PREDICTION OF EXPERIMENTAL RESULTS

USING I.B.M. 704 DIGITAL COMPUTER

```
 1     FORMAT(9F6.0,F6.2,/6F6.0)                                       VLE00010
 2     FORMAT (8F6.2)                                                  VLE00020
 3     FORMAT(6F8.3)                                                   VLE00030
 4     FORMAT(I16,F10.2)                                               VLE00041
 5     FORMAT(7F10.4,/F10.4)                                           VLE00050
 6     FORMAT(7F10.6,/F10.6)                                           VLE00060
 7     FORMAT(F1.0)                                                    VLE00070
 8     DIMENSION B(4,4,2),S(4),AVL(4), PC(4),T(1),IRUN(4),P(4),ANU(4,4),XVLE00072
      C(8,4),XSAV(4,4),XSUV(4,4),XRKS(4,4),Y(8,4),YSAV(4,4),YSUV(4,4),YRKVLE00075
      CS(4,4),AKVALS(4,4),AKSAV(4,4),AKSUV(4,4),AKRKS(4,4),GS(4,4),GSAV(4VLE00080
      C,4),GSUV(4,4),GRKS(4,4),ANUS(4,4),ANUSAV(4,4),ANUSUV(4,4),ANURKS(4VLE00090
      C,4),FS(4,4),FSAV(4,4),FSUV(4,4),FRKS(4,4),VLS(4),VLSAV(4),VLSUV(4)VLE00100
      C,VLRKS(4),VVS(4),VVSAV(4),VVSUV(4),AKVAL(4,4),XF(4,4),SVL(4),VL(4)VLE00110
      C,VV(4),F(4,4),  TC(4),G(4,4),AKVALC(4,4),ARK(4,4),BRK(4,4),PP(4),TVLE00120
      CT(1),VP(4),ARKM(4),BM(4),XS(4,4),YS(4,4),BUVS(4,4,4),BAVS(4,4,4),AVLE00130
      C(4,4),FC(4,4),R(4,4),ERR(4),DERR(4)                             VLE00140
 9     FORMAT(27H1             RUN NUMBER    I 10,/                    VLE00150
      C27H            TEMPERATURE  F10.2,21H   DEGREES FAHRENHEIT/     VLE00160
      C27H            PRESSURE     F10.0,7H   PSIA)                    VLE00170
10     FORMAT (110H                                                    VLE00180
      C               VIRIAL EQUATION  VALUES   REDLICH-KWONG  /       VLE00190
      C106H                                                    INITIAL VLE00200
      CVALUE    ADJUSTED     UNADJUSTED       VALUES/                  VLE00210
      C55H             VOLUME OF LIQUID (CC PER GM MOLE)       F11.3,3HVLE00220
      C   F11.3,3H   F11.3,4H    F11.3,/                               VLE00230
      C55H             VOLUME OF VAPOR (CC PER GM MOLE)        F11.3,3HVLE00240
      C   F11.3,3H   F11.3)                                            VLE00250
11     FORMAT (22H                BENZENE   /                          VLE00260
      C55H             Y                                       F11.3,3HVLE00270
      C   F11.3,3H   F11.3,4H    F11.3,/                               VLE00280
      C55H             X                                       F11.3,3HVLE00290
      C   F11.3,3H   F11.3,4H    F11.3,/                               VLE00300
      C55H             K VALUE                                 F11.3,3HVLF00310
      C   F11.3,3H   F11.3,4H    F11.3)                                VLE00320
12     FORMAT(55H                 ACTIVITY COEFFICIENT,LIQUID PHASE   FVLE00330
      C11.3,3H   F11.3,3H   F11.3,4H    F11.3,/                        VLE00340
      C55H             FUGACITY,PURE                           F11.3,3HVLE00350
      C   F11.3,3H   F11.3,4H    F11.3,/                               VLE00360
      C55H             FUGACITY COEFFICIENT,VAPOR PHASE        F11.3,3HVLE00370
      C   F11.3,3H   F11.3,4H    F11.3)                                VLE00380
13     FORMAT (26H                CYCLOHEXANE  /                       VLE00390
      C55H             Y                                       F11.3,3HVLE00400
      C   F11.3,3H   F11.3,4H    F11.3,/                               VLF00410
      C55H             X                                       F11.3,3HVLE00420
      C   F11.3,3H   F11.3,4H    F11.3,/                               VLE00430
      C55H             K VALUE                                 F11.3,3HVLE00440
      C   F11.3,3H   F11.3,4H    F11.3)                                VLE00450
14     FORMAT(55H                 ACTIVITY COEFFICIENT,LIQUID PHASE   FVLE00460
      C11.3,3H   F11.3,3H   F11.3,4H    F11.3,/                        VLE00470
      C55H             FUGACITY,PURE                           F11.3,3HVLE00480
      C   F11.3,3H   F11.3,4H    F11.3,/                               VLE00490
      C55H             FUGACITY COEFFICIENT,VAPOR PHASE        F11.3,3HVLE00500
      C   F11.3,3H   F11.3,4H    F11.3)                                VLE00510
15     FORMAT (21H                HEXANE    /                          VLE00520
      C55H             Y                                       F11.3,3HVLE00530
      C   F11.3,3H   F11.3,4H    F11.3,/                               VLE00540
      C55H             X                                       F11.3,3HVLE00550
      C   F11.3,3H   F11.3,4H    F11.3,/                               VLE00560
      C55H             K VALUE                                 F11.3,3HVLE00570
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      C   F11.3,3H   F11.3,4H    F11.3)                                VLE00580
16     FORMAT(55H                 ACTIVITY COEFFICIENT,LIQUID PHASE   FVLE00590
      C11.3,3H   F11.3,3H   F11.3,4H    F11.3,/                        VLE00600
      C55H             FUGACITY,PURE                           F11.3,3HVLE00610
      C   F11.3,3H   F11.3,4H    F11.3,/                               VLE00620
      C55H             FUGACITY COEFFICIENT,VAPOR PHASE        F11.3,3HVLE00630
      C   F11.3,3H   F11.3,4H    F11.3)                                VLE00640
17     FORMAT (23H                HYDROGEN   /                         VLE00650
      C55H             Y                                       F11.3,3HVLE00660
      C   F11.3,3H   F11.3,4H    F11.3,/                               VLE00670
      C55H             X                                       F11.3,3HVLE00680
      C   F11.3,3H   F11.3,4H    F11.3,/                               VLE00690
      C55H             K VALUE                                 F11.3,3HVLE00700
      C   F11.3,3H   F11.3,4H    F11.3)                                VLE00710
18     FORMAT(55H                 ACTIVITY COEFFICIENT,LIQUID PHASE   FVLE00720
      C11.3,3H   F11.3,3H   F11.3,4H    F11.3,/                        VLE00730
      C55H             FUGACITY,PURE                           F11.3,3HVLE00740
      C   F11.3,3H   F11.3,4H    F11.3,/                               VLE00750
      C55H             FUGACITY COEFFICIENT,VAPOR PHASE        F11.3,3HVLE00760
      C   F11.3,3H   F11.3,4H    F11.3)                                VLE00770
19     FORMAT(46H                INTERACTION VIRIAL COEFFICIENTS/      VLE00780
      C69H             B(HYDROGEN-BENZENE)                             VLE00790
      C         F11.3,3H   F11.3,/                                     VLE00800
      C69H             B(HYDROGEN-CYCLOHEXANE)                         VLE00810
      C         F11.3,3H   F11.3,/                                     VLE00820
      C69H             B(HYDROGEN-HEXANE)                              VLE00830
      C         F11.3,3H   F11.3)                                      VLE00840
20     READ INPUT TAPE 7,1,B(1,1,1),B(1,2,1),B(1,3,1),B(1,4,1),B(2,2,1),BVLE00850
      C(2,3,1),B(2,4,1),B(3,3,1),B(3,4,1),B(4,4,1),B(2,1,1),B(3,1,1),B(4,VLE00860
      C1,1),B(3,2,1),B(4,2,1),B(4,3,1)                                 VLE00870
       READ INPUT TAPE 7,2,S(1),S(2),S(3),S(4),AVL(1),AVL(2),AVL(3),AVL(4VLE00880
      C)                                                               VLE00890
       READ INPUT TAPE 7,3,VP(1),VP(2),VP(3),PC(4),TC(4),TT            VLE00900
       DO 22 M=1,4                                                     VLE00910
       READ INPUT TAPE 7,4,IRUN(M),PP(M)                               VLE00921
       READ INPUT TAPE 7,5,X(1,M),X(2,M),X(3,M),X(4,M),Y(1,M),Y(2,M),Y(3,VLE00930
      CM),Y(4,M)                                                       VLE00940
22     READ INPUT TAPE 7,6,ARK(1,M),ARK(2,M),ARK(3,M),ARK(4,M),BRK(1,M),BVLE00950
      CRK(2,M),BRK(3,M),BRK(4,M)                                       VLE00960
21     READ INPUT TAPE 7,7,COND                                        VLE00965
       DO 24 M=1,4                                                     VLE00970
       DO 23 L=1,4                                                     VLE00980
       B(L,M,2)=B(L,M,1)                                               VLE00985
23     AKVAL(L,M)=Y(L,M)/X(L,M)                                        VLE00990
24     CONTINUE                                                        VLE01000
       T=(TT-32.0)/1.8+273.16                                          VLE01010
       DO 25 M=1,4                                                     VLE01020
25     P(M)=PP(M)/14.7                                                 VLE01030
27     I=1                                                             VLE01050
       K=1                                                             VLE01060
       J=1                                                             VLE01070
       DO 29 M=1,4                                                     VLE01080
       DO 28 L=1,4                                                     VLE01090
       XS(L,M)=X(L,M)                                                  VLE01100
       YS(L,M)=Y(L,M)                                                  VLE01110
28     AKVALS(L,M)=AKVAL(L,M)                                          VLE01115
29     CONTINUE                                                        VLE01120
30     DO 31 M=1,4                                                     VLE01130
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TABLE XXII CONT'D

```
      BUVS(1,4,M)=B(1,4,1)                                                  VLE01140
      BUVS(2,4,M)=B(2,4,1)                                                  VLE01150
 31   BUVS(3,4,M)=B(3,4,1)                                                  VLE01160
 32   DO 40  M=1,4                                                          VLE01165
 33   IF (X(1,M))  34,36,34                                                 VLE01170
 34   XF(4,M)=(X(1,M)/(1.0-X(4,M))+(X(4,M)*(Y(1,M)-X(1,M)))/(Y(4,M)-X(4,VLE01180
     CM))-X(1,M))/((Y(1,M)-X(1,M))/(Y(4,M)-X(4,M))+X(1,M)/(1.0-X(4,M))) VLE01200
 35   GO TO 37                                                              VLE01210
 36   XF(4,M)=(X(2,M)/(1.0-X(4,M))+(X(4,M)*(Y(2,M)-X(2,M)))/(Y(4,M)-X(4,VLE01220
     CM))-X(2,M))/((Y(2,M)-X(2,M))/(Y(4,M)-X(4,M))+X(2,M)/(1.0-X(4,M))) VLE01230
 37   XF(1,M)=X(1,M)*(1.0-XF(4,M))/(1.0-X(4,M))                            VLE01240
 38   XF(2,M)=X(2,M)*(1.0-XF(4,M))/(1.0-X(4,M))                            VLE01250
 39   XF(3,M)=X(3,M)*(1.0-XF(4,M))/(1.0-X(4,M))                            VLE01260
 40   CONTINUE                                                              VLE01270
      IF (COND-1.0)       53,73,53                                          VLE01427
 73   WRITE OUTPUT TAPE 6,191,((XF(L,M),L=1,4),M=1,4)                       VLE01428
      GO TO 53                                                              VLE01429
 53   DO 55 M=1,4                                                           VLE01430
 54   VL(M)=X(1,M)*AVL(1)+X(2,M)*AVL(2)+X(3,M)*AVL(3)+X(4,M)*AVL(4)         VLE01440
 55   SVL(M)=X(1,M)*AVL(1)*S(1)+X(2,M)*AVL(2)*S(2)+X(3,M)*AVL(3)*S(3)+X(VLE01450
     C4,M)*AVL(4)*S(4)                                                      VLE01460
 56   IF (J-2)  57,115,57                                                   VLE01470
 57   DO 62 M=1,4                                                           VLE01480
 58   BM(M)=Y(1,M)*Y(1,M)*B(1,1,K)+Y(2,M)*Y(2,M)*B(2,2,K)+Y(3,M)*Y(3,M)*VLE01490
     CB(3,3,K)+Y(4,M)*Y(4,M)*B(4,4,K)+2.0*Y(1,M)*Y(2,M)*B(1,2,K)+2.0*Y(1VLE01500
     C,M)*Y(3,M)*B(1,3,K)+2.0*Y(1,M)*Y(4,M)*B(1,4,K)+2.0*Y(2,M)*Y(3,M)*BVLE01510
     C(2,3,K)+2.0*Y(2,M)*Y(4,M)*B(2,4,K)+2.0*Y(3,M)*Y(4,M)*B(3,4,K)        VLE01520
 59   VV(M)=0.5(82.057*T/P(M)+SQRT((82.057*T/P(M))**2+328.228*T*BM(M)/P(VLE01530
     CM)))                                                                  VLE01540
 60   DO 61 L=1,4                                                           VLE01550
 61   F(L,M)=(82.057*T/(P(M)*VV(M)))*EXP((2.0/VV(M))*(Y(1,M)*B(L,1,K)+Y(VLE01560
     C2,M)                                                                  VLE01565
     C*B(L,2,K)+Y(3,M)*B(L,3,K)+Y(4,M)*B(L,4,K)))                           VLE01570
 62   CONTINUE                                                              VLE01580
 63   DO 70 M=1,4                                                           VLE01590
 64   ANU(4,M)=(PC(4)/P(M))*EXP((2.30258509)*(1.96718+(1.02972*TC(4))/T VLE01600
     C(0.054009*T)/TC(4)+0.0005288*(T/TC(4))**2+(0.008585*P(M))/PC(4))) VLE01601
 65   DO 66 L=1,3                                                           VLE01602
      FP(L,M)=VP(L)*EXP(VL(M)*(P(M)-VP(L))/(82.057*T))                      VLE01610
 66   ANU(L,M)=FP(L,M)/P(M)                                                 VLE01620
 67   DO 69 L=1,4                                                           VLE01630
      IF (COND-2.0)   68,400,68                                             VLE01635
 68   G(L,M)=(AVL(L)/VL(M))*EXP((AVL(L)*(S(L)-SVL(M)/VL(M))**2)/(1.987*TVLE11640
     C)+1.0-AVL(L)/VL(M))                                                   VLE11641
      GO TO 69                                                              VLE11642
400   G(L,M)=EXP((AVL(L)*(S(L)-SVL(M)/VL(M))**2)/(1.987*T))                 VLE11643
 69   AKVALC(L,M)=G(L,M)*ANU(L,M)/F(L,M)                                    VLE01650
 70   CONTINUE                                                              VLE01660
 71   IF(I-1)    300,72,300                                                 VLE01670
 72   DO 75 M=1,4                                                           VLE01680
      VLS(M)=VL(M)                                                          VLE01690
      VVS(M)=VV(M)                                                          VLE01700
      DO 74 L=1,4                                                           VLE01710
      GS(L,M)=G(L,M)                                                        VLE01720
      ANUS(L,M)=ANU(L,M)                                                    VLE01730
 74   FS(L,M)=F(L,M)                                                        VLE01740
 75   CONTINUE                                                              VLE01750
 76   I=I+1                                                                 VLE01760
```

```
300   DO 307  M=1,4                                                         VLE01770
301   IF(X(1,M))    303,302,303                                             VLE01775
302   AKVALC(1,M)=0.0000                                                    VLE01780
303   IF(X(2,M))    305,304,305                                             VLE01790
304   AKVALC(2,M)=0.0000                                                    VLE01800
305   IF(X(3,M))    307,306,307                                             VLE01810
306   AKVALC(3,M)=0.0000                                                    VLE01820
307   CONTINUE                                                              VLE01830
      DO 316 M=1,4                                                          VLE01865
308   ERR(M)=X(4,M)(AKVALC(4,M)-1.0)((XF(1,M)(AKVALC(1,M)-AKVALC(3,M)))/VLE01870
     C(XF(4,M)(AKVALC(1,M)-1.0)+X(4,M)(AKVALC(4,M)-AKVALC(1,M)))+(XF(2,MVLE01871
     C)(AKVALC(2,M)-AKVALC(3,M)))/(XF(4,M)(AKVALC(2,M)-1.0)+X(4,M)(AKVALVLE01872
     CC(4,M)-AKVALC(2,M))))+AKVALC(3,M)(1.0-X(4,M))+AKVALC(4,M)*X(4,M)-1VLE01873
     C.0                                                                    VLE01874
309   IF(ABSF(ERR(M))-0.0001)    313,313,310                                VLE01880
310   DERR(M)=(ERR(M)-AKVALC(3,M)+1.0)/(X(4,M))-X(4,M)(AKVALC(4,M)-1.0)(VLE01890
     C(XF(1,M)*(AKVALC(1,M)-AKVALC(3,M))(AKVALC(4,M)-AKVALC(1,M)))/((XF(VLE01891
     C4,M)(AKVALC(1,M)-1.0)+X(4,M)(AKVALC(4,M)-AKVALC(1,M)))**2)+(XF(2,MVLE01892
     C)(AKVALC(2,M)-AKVALC(3,M))(AKVALC(4,M)-AKVALC(2,M)))/((XF(4,M)(AKVVLE01893
     CALC(2,M)-1.0)+X(4,M)(AKVALC(4,M)-AKVALC(2,M)))**2))                   VLE01894
311   X(4,M)=X(4,M)-ERR(M)/DERR(M)                                          VLE01900
312   GO TO 308                                                             VLE01910
313   X(8,M)=X(4,M)                                                         VLE01920
314   X(5,M)=(X(8,M)*XF(1,M)*(AKVALC(4,M)-1.0))/(XF(4,M)(AKVALC(1,M)-1. VLE01921
     C)+X(8,M)(AKVALC(4,M)-AKVALC(1,M)))                                    VLE01922
      X(6,M)=(X(8,M)*XF(2,M)(AKVALC(4,M)-1.0))/(XF(4,M)(AKVALC(2,M)-1.0)VLE01923
     C+X(8,M)(AKVALC(4,M)-AKVALC(2,M)))                                     VLE01924
      X(7,M)=1.0-X(8,M)-X(5,M)-X(6,M)                                       VLE01925
315   Y(5,M)=AKVALC(1,M)*X(5,M)                                             VLE01930
      Y(6,M)=AKVALC(2,M)*X(6,M)                                             VLE01931
      Y(7,M)=AKVALC(3,M)*X(7,M)                                             VLE01932
316   Y(8,M)=AKVALC(4,M)*X(8,M)                                             VLE01933
      IF (COND-1.0)  85,105,85                                              VLE01841
105   WRITE OUTPUT TAPE 6,192,((X(L,M),Y(L,M),ANU(L,M),G(L,M),F(L,M),L=1VLE01842
     C,4),M=1,4)                                                            VLE01843
      GO TO 85                                                              VLE01844
 85   DO 93 M=1,4                                                           VLE01850
 86   DO 92 L=1,4                                                           VLE01860
 87   LL=L+4                                                                VLE01870
 88   IF(ABSF(X(L,M)-X(LL,M))-0.0001) 91,91,89                              VLE01880
 89   X(L,M)=X(LL,M)                                                        VLE01890
      Y(L,M)=Y(LL,M)                                                        VLE01900
 90   GO TO 53
 91   IF(ABSF(Y(L,M)-Y(LL,M))-0.0001) 92,92,89                              VLE01920
 92   CONTINUE                                                              VLE01925
 93   CONTINUE                                                              VLE01930
 94   IF (J-2)  95,120,167                                                  VLE01940
 95   DO 104 M=1,4                                                          VLE01950
      VVSUV(M)=VV(M)                                                        VLE01960
 96   VLSUV(M)=VL(M)                                                        VLE01970
 97   DO 103 L=1,4                                                          VLE01980
 98   AKSUV(L,M)=G(L,M)*ANU(L,M)/F(L,M)                                     VLE01990
 99   FSUV(L,M)=F(L,M)                                                      VLE02000
100   GSUV(L,M)=G(L,M)                                                      VLE02020
101   ANUSUV(L,M)=ANU(L,M)                                                  VLE02030
102   XSUV(L,M)=X(L,M)                                                      VLE02040
103   YSUV(L,M)=Y(L,M)                                                      VLE02050
104   CONTINUE                                                              VLE02060
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TABLE XXII CONT'D

```
108     J=J+1                                                        VLE02070
109     DO 113 M=1,4                                                 VLE02080
110     DO 112 L=1,4                                                 VLE02090
111     X(L,M)=XS(L,M)                                               VLE02100
112     Y(L,M)=YS(L,M)                                               VLE02110
113     CONTINUE                                                     VLE02120
114     IF(K-2) 53,132,53                                            VLE02130
115     DO 119 M=1,4                                                 VLE02140
116     ARKM(M)=Y(1,M)*ARK(1,M)+Y(2,M)*ARK(2,M)+Y(3,M)*ARK(3,M)+Y(4,M)*ARKVLE02150
       C(4,M)                                                        VLE02160
117     DO 118 L=1,4                                                 VLE02170
118     F(L,M)=EXP((BRK(L,M)-ARK(L,M)**2-(ARK(L,M)-ARKM(M))**2)*P(M))  VLE02180
119     CONTINUE                                                     VLE02190
        GO TO 63                                                     VLE02195
120     DO 129 M=1,4                                                 VLE02200
121     VLRKS(M)=VL(M)                                               VLE02210
122     DO 128 L=1,4                                                 VLE02220
123     XRKS(L,M)=X(L,M)                                             VLE02230
124     YRKS(L,M)=Y(L,M)                                             VLE02240
125     AKRKS(L,M)=G(L,M)*ANU(L,M)/F(L,M)                            VLE02250
126     GRKS(L,M)=G(L,M)                                             VLE02260
127     ANURKS(L,M)=ANU(L,M)                                         VLE02270
128     FRKS(L,M)=F(L,M)                                             VLE02280
129     CONTINUE                                                     VLE02290
130     K=K+1                                                        VLE02300
131     GO TO 108                                                    VLE02310
132     DO 138 M=1,4                                                 VLE02320
133     DO 137 L=1,4                                                 VLE02330
134     G(L,M)=GS(L,M)                                               VLE02340
135     ANU(L,M)=ANUS(L,M)                                           VLE02350
136     AKVAL(L,M)=AKVALS(L,M)                                       VLE02360
137     FC(L,M)=G(L,M)*ANU(L,M)/AKVAL(L,M)                           VLE02370
138     CONTINUE                                                     VLE02380
139     DO 142 M=1,4                                                 VLE02390
        A(4,M)=VV(M)/2.0*ELOG(FC(4,M)*P(M)*VV(M)/(82.057*T))-Y(4,M)*B(4,4,VLE02400
       CK)                                                           VLE02401
140     DO 141 L=1,3                                                 VLE02402
220     R(L,M)=FC(L,M)*P(M)*VV(M)/(82.057*T)                         VLE02403
200     IF(X(1,M))   202,201,202                                     VLE02405
201     R(1,M)=1.0000                                                VLE02406
202     IF(X(2,M))   204,203,204                                     VLE02407
203     R(2,M)=1.0000                                                VLE02408
204     IF(X(3,M))   141,205,141                                     VLE02400
205     R(3,M)=1.0000                                                VLE02410
141     A(L,M)=VV(M)/2.0*ELOG(R(L,M))-Y(1,M)*B(L,1,K)-Y(2,M)*B(L,2,K)-Y(3,VLE02420
       CM)*B(L,3,K)                                                  VLE02430
142     CONTINUF                                                     VLE02435
209     DO 217 M=1,4                                                 VLE02440
210     IF(X(1,M))   212,211,212                                     VLE02441
211     A(1,M)=0.0000                                                VLE02442
212     IF(X(2,M))   214,213,214                                     VLE02443
213     A(2,M)=0.0000                                                VLE02444
214     IF(X(3,M))   217,215,217                                     VLE02445
215     A(3,M)=0.0000                                                VLE02446
217     CONTINUE                                                     VLE02448
218     AD=0.00                                                      VLE02450
        DO 143 M=1,4                                                 VLE02460
        AD=AD+Y(4,M)*A(1,M)+Y(1,M)*A(4,M)                            VLE02470
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143     CONTINUE                                                     VLE02480
        BD=0.00                                                      VLE02490
        DO 144 M=1,4                                                 VLE02500
        BD=BD+Y(4,M)*A(2,M)+Y(2,M)*A(4,M)                            VLE02510
144     CONTINUE                                                     VLE02520
        CD=0.00                                                      VLE02530
        DO 145 M=1,4                                                 VLE02540
        CD=CD+Y(4,M)*A(3,M)+Y(3,M)*A(4,M)                            VLE02550
145     CONTINUE                                                     VLE02560
        AA=0.00                                                      VLE02570
        DO 146 M=1,4                                                 VLE02580
        AA=AA+Y(4,M)**2+Y(1,M)**2                                    VLE02585
146     CONTINUE                                                     VLE02590
        AB=0.00                                                      VLE02595
        DO 147 M=1,4                                                 VLE02600
        AB=AB+Y(1,M)*Y(2,M)                                          VLE02605
147     CONTINUE                                                     VLE02610
        AC=0.00                                                      VLE02615
        DO 148 M=1,4                                                 VLE02620
        AC=AC+Y(1,M)*Y(3,M)                                          VLE02625
148     CONTINUE                                                     VLE02630
        BA=0.00                                                      VLE02635
        DO 149 M=1,4                                                 VLE02640
        BA=BA+Y(1,M)*Y(2,M)                                          VLE02645
149     CONTINUE                                                     VLE02650
        BB=0.00                                                      VLE02655
        DO 150 M=1,4                                                 VLE02660
        BB=BB+Y(4,M)**2+Y(2,M)**2                                    VLE02665
150     CONTINUE                                                     VLE02670
        BC=0.00                                                      VLE02675
        DO 151 M=1,4                                                 VLE02680
        BC=BC+Y(3,M)*Y(2,M)                                          VLE02685
151     CONTINUE                                                     VLE02690
        CA=0.00                                                      VLE02695
        DO 152 M=1,4                                                 VLE02700
        CA=CA+Y(1,M)*Y(3,M)                                          VLE02705
152     CONTINUE                                                     VLE02710
        CB=0.00                                                      VLE02715
        DO 153 M=1,4                                                 VLE02720
        CB=CB+Y(2,M)*Y(3,M)                                          VLE02725
153     CONTINUE                                                     VLE02730
        CC=0.00                                                      VLE02735
        DO 154 M=1,4                                                 VLE02740
        CC=CC+Y(4,M)**2+Y(3,M)**2                                    VLE02745
154     CONTINUE                                                     VLE02750
155     EA=AA*BB*CC+AB*BC*CA+AC*CB*BA-AC*3B*CA-BA*AB*CC-AA*CB*BC     VLE02760
156     EB=AD*BB*CC+AB*BC*CD+AC*CB*BD-AC*BB*CD-BD*AB*CC-AD*CB*BC     VLE02770
157     EC=AA*BD*CC+AD*BC*CA+AC*CD*BA-AC*BD*CA-BA*AD*CC-AA*CD*BC     VLE02780
158     ED=AA*BB*CD+AB*BD*CA+AD*CB*BA-AD*BB*CA-BA*AB*CD-AA*CB*BD     VLE02790
159     B(1,4,2)=EB/EA                                               VLE02800
160     B(2,4,2)=EC/EA                                               VLE02810
161     B(3,4,2)=ED/EA                                               VLE02820
162     DO 163 M=1,4                                                 VLE02830
        BAVS(1,4,M)=B(1,4,2)                                         VLE02840
        BAVS(2,4,M)=B(2,4,2)                                         VLE02850
        BAVS(3,4,M)=B(3,4,2)                                         VLE02860
        B(4,1,2)=B(1,4,2)                                            VLE02861
        B(4,2,2)=B(2,4,2)                                            VLE02862
```

TABLE XXII CONT'D

```
163    B(4,3,2)=B(3,4,2)                                                 VLE02863
165    K=K+1                                                             VLE02870
166    GO TO 109                                                         VLE02880
167    DO 177 M=1,4                                                      VLE02890
168    VVSAV(M)=VV(M)                                                    VLE02900
169    VLSAV(M)=VL(M)                                                    VLE02910
170    DO 176 L=1,4                                                      VLE02920
171    AKSAV(L,M)=G(L,M)*ANU(L,M)/F(L,M)                                 VLE02930
172    FSAV(L,M)=F(L,M)                                                  VLE02940
173    GSAV(L,M)=G(L,M)                                                  VLE02950
174    ANUSAV(L,M)=ANU(L,M)                                              VLE02960
175    XSAV(L,M)=X(L,M)                                                  VLE02970
176    YSAV(L,M)=Y(L,M)                                                  VLE02980
177    CONTINUE                                                          VLE02990
178    DO 189 M=1,4                                                      VLE02995
179    WRITE OUTPUT TAPE 6,9,IRUN(M),TT,PP(M)                            VLE03000
180    WRITE OUTPUT TAPE 6,10,VLS(M),VLSAV(M),VLSUV(M),VLRKS(M),VVS(M),VVVLE03010
      CSAV(M),VVSUV(M)                                                   VLE03020
181    WRITE OUTPUT TAPE 6,11,YS(1,M),YSAV(1,M),YSUV(1,M),YRKS(1,M),XS(1,VLE03030
      CM),XSAV(1,M),XSUV(1,M),XRKS(1,M),AKVALS(1,M),AKSAV(1,M),AKSUV(1,M)VLE03040
      C,AKRKS(1,M)                                                       VLE03050
182    WRITE OUTPUT TAPE 6,12,GS(1,M),GSAV(1,M),GSUV(1,M),GRKS(1,M),ANUS(VLE03060
      C1,M),ANUSAV(1,M),ANUSUV(1,M),ANURKS(1,M),FS(1,M),FSAV(1,M),FSUV(1,VLE03070
      CM),FRKS(1,M)                                                      VLE03080
183    WRITE OUTPUT TAPE 6,13,YS(2,M),YSAV(2,M),YSUV(2,M),YRKS(2,M),XS(2,VLE03090
      CM),XSAV(2,M),XSUV(2,M),XRKS(2,M),AKVALS(2,M),AKSAV(2,M),AKSUV(2,M)VLE03100
      C,AKRKS(2,M)                                                       VLE03110
184    WRITE OUTPUT TAPE 6,14,GS(2,M),GSAV(2,M),GSUV(2,M),GRKS(2,M),ANUS(VLE03120
      C2,M),ANUSAV(2,M),ANUSUV(2,M),ANURKS(2,M),FS(2,M),FSAV(2,M),FSUV(2,VLE03130
      CM),FRKS(2,M)                                                      VLE03140
185    WRITE OUTPUT TAPE 6,15,YS(3,M),YSAV(3,M),YSUV(3,M),YRKS(3,M),XS(3,VLE03150
      CM),XSAV(3,M),XSUV(3,M),XRKS(3,M),AKVALS(3,M),AKSAV(3,M),AKSUV(3,M)VLE03160
      C,AKRKS(3,M)                                                       VLE03170
186    WRITE OUTPUT TAPE 6,16,GS(3,M),GSAV(3,M),GSUV(3,M),GRKS(3,M),ANUS(VLE03180
      C3,M),ANUSAV(3,M),ANUSUV(3,M),ANURKS(3,M),FS(3,M),FSAV(3,M),FSUV(3,VLE03190
      CM),FRKS(3,M)                                                      VLE03200
187    WRITE OUTPUT TAPE 6,17,YS(4,M),YSAV(4,M),YSUV(4,M),YRKS(4,M),XS(4,VLE03210
      CM),XSAV(4,M),XSUV(4,M),XRKS(4,M),AKVALS(4,M),AKSAV(4,M),AKSUV(4,M)VLE03220
      C,AKRKS(4,M)                                                       VLE03230
188    WRITE OUTPUT TAPE 6,18,GS(4,M),GSAV(4,M),GSUV(4,M),GRKS(4,M),ANUS(VLE03240
      C4,M),ANUSAV(4,M),ANUSUV(4,M),ANURKS(4,M),FS(4,M),FSAV(4,M),FSUV(4,VLE03250
      CM),FRKS(4,M)                                                      VLE03260
189    WRITE OUTPUT TAPE 6,19,BAVS(1,4,M),BUVS(1,4,M),BAVS(2,4,M),BUVS(2,VLE03270
      C4,M),BAVS(3,4,M),BUVS(3,4,M)                                      VLE03280
190    GO TO 20                                                          VLE03290
191    FORMAT (1H 8F6.5/1H08F6.5//)                                      VLE03300
192    FORMAT(1H 8F7.5//)                                                VLE03310
```

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