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THE WATER CONTENT OF LIQUID ETHANE AND PROPANE
IN TWO-PHASE EQUILIBRIUM WITH HYDRATE

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A thesis submitted to the Faculty and the Board-of Trustees of the Colorado School of Mines in partial fulfilment of the requirements for the degree of Master of Science in Chemical and Petroleum-Refining Engineering.

Golden, Colorado

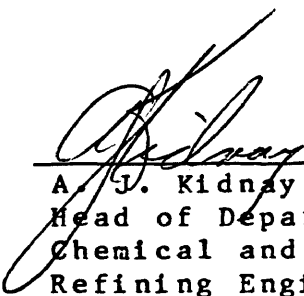
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T-2809

DEDICATED TO MY FATHER JAMES S. SPARKS

ABSTRACT

An experimental method was developed and used to determine the water concentration of liquid ethane and liquid propane in equilibrium with hydrate. The reported data of this work represent the first taken with the intent of measuring liquid hydrocarbon-hydrate equilibrium.

An a priori prediction method was generated, which uses the existing van der Waals and Platteeuw hydrate model for three phase (vapor-aqueous liquid-hydrate) predictions, together with an equation of state interaction parameter determined from vapor-liquid equilibrium data.

The predictions show close agreement with the experimental data.

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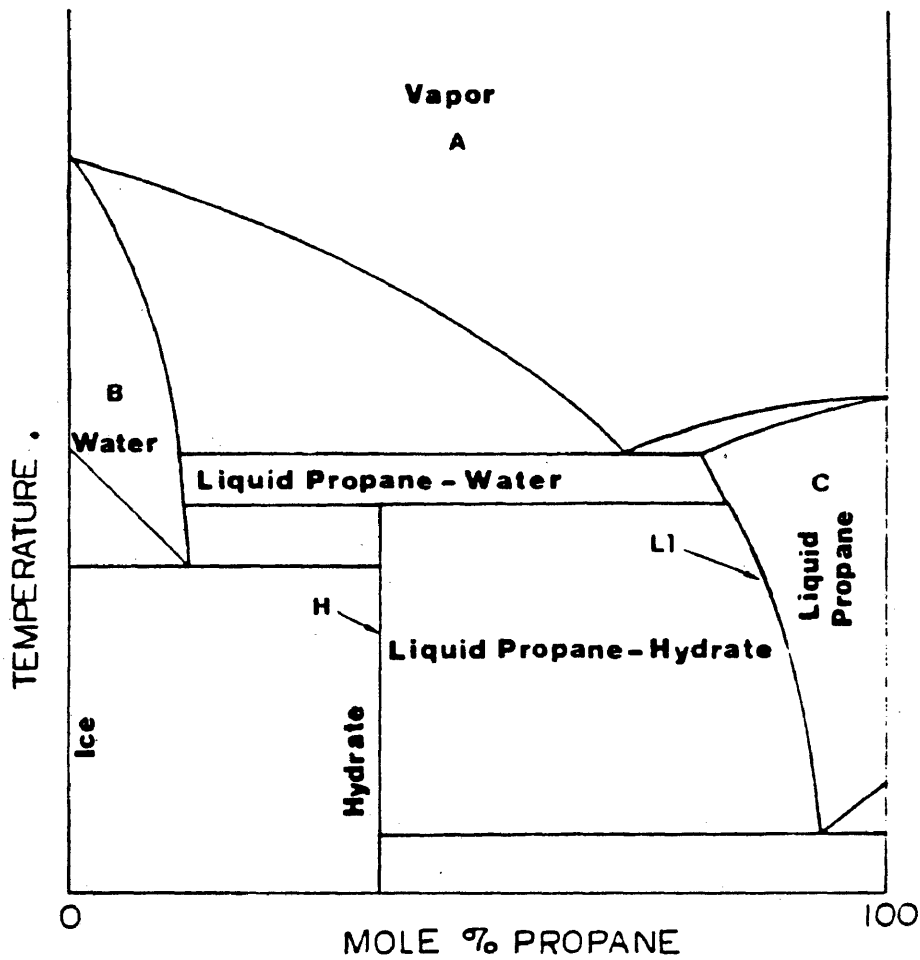
To the Gas Processors Association for their financial support.

INTRODUCTION

The primary objective of this work was to measure the maximum amount of water in a single hydrocarbon fluid phase. The two hydrocarbons studied were ethane and propane as a function of temperature and pressure.

The experimental work may best be understood by considering the qualitative isobaric propane-water phase diagram of Figure 1, originally formulated by Kobayashi (1951) through the use of the Phase Rule of J. W. Gibbs. This diagram has four single phase regions: a vapor area marked A, a liquid water-rich area, marked B, a liquid propane-rich area, marked C, and a hydrate boundary, marked H. In this experiment two-phase equilibrium existed between regions H and C. The water concentration along line Ll was measured as a function of temperature for both ethane and propane, and the effect of pressure on line Ll was determined to be relatively negligible. Such measurements give the NGL processor an indication of how dry the liquid hydrocarbon must be to prevent hydrate formation.

An experimental method based upon oscillometry (the study of dielectric properties) was generated to measure low water concentrations in a liquid hydrocarbon at a hydrate phase boundary. The extension of the method to NGL mixtures is planned in the future.



Propane-Water Phase Diagram Above the Quadruple Point (82.8 psia) and Below the Three-Phase Critical Point (637 psia) as Seen Along a Plane of Constant Pressure

Propane-Water Phase Diagram

Figure 1

BACKGROUND

HISTORY OF GAS HYDRATES

Water clathrates are a crystalline-like structure composed of cavities, formed by water molecules, which are stabilized by the inclusion of a "guest" molecule within each cavity. Clathrates are generally regarded as nonstoichiometric compounds since all of the internal cavities need not be occupied by a guest.

Hydrates were first discovered in 1810, by Sir Humphrey Davy (1811). Gas hydrates were found to be the cause of plugged gas transmission lines in 1934, by Hammerschmidt (1934).

NATURAL OCCURING GAS HYDRATES

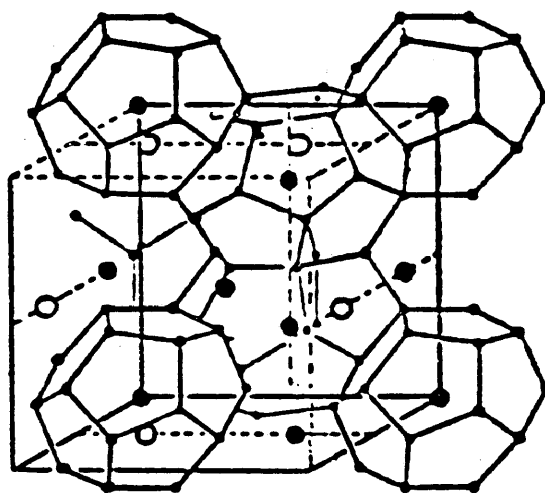
Natural occurring gas hydrates are currently being investigated. Although they have normally been considered a hindrance to the gas processing industry, Trofimuk (1979) optimistically predicted that the ultimate natural gas hydrate reserve is approximately three times greater than the remaining combustible fuel reserve. Kvenvolden and McMenamin (1980) present a rather detailed review of the geological occurrence of hydrates.

Natural hydrates form initially from biogenic gas, mostly methane, in near-surface unconsolidated muds

containing 40-70 percent water according to Hunt (1979). These naturally occurring hydrate deposits are currently being considered as possible natural gas sources. Unfortunately the technology for the drilling and optimum recovery of gas from gas hydrates is still in the early stages of development.

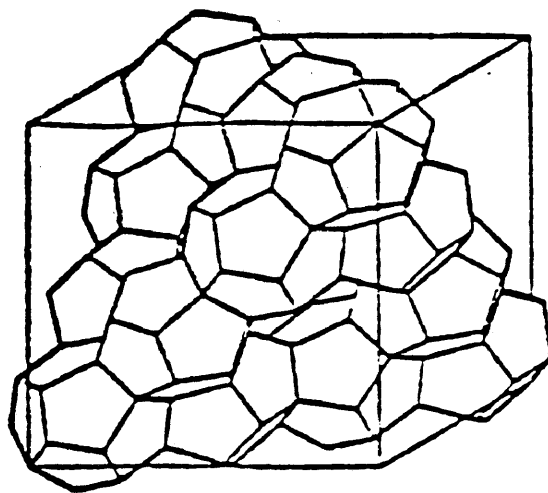
PHYSICAL STRUCTURE OF HYDRATES

Gas hydrates crystallize in one of two cubic structures. The unit cell of Structure I hydrates is shown in Figure 2. Figure 3 illustrates the unit cell of Structure II hydrates. The basis for each structure is a pentagonal dodecahedron as shown in Figure 4. The remaining polyhedron involved in the Structure I hydrate configuration is the tetradecahedron, also shown in Figure 4. The hexadecahedron given in Figure 4 is also involved in the configuration of the Structure II hydrate lattice. Propane enters only the large cavities of Structure II hydrate. All other cavities are too small to be significantly stabilized by propane. Ethane enters only the large cavities of Structure I hydrate, however it will enter the large cavities of Structure II hydrate if propane is present in a large enough concentration. Table 1 presents the physical properties of the hydrate lattice. An excellent review of the physiochemical aspects of hydrates is given by Davidson



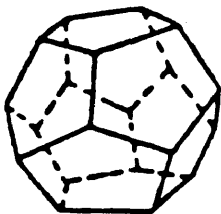
Structure I Unit Cell

Figure 2

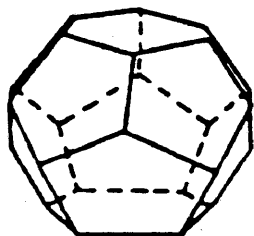


Structure II Unit Cell

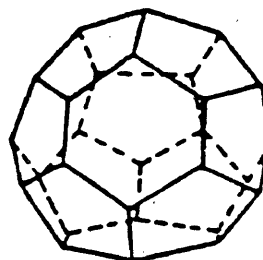
Figure 3



Pentagonal Dodecahedron



Tetradecahedron (Structure I)



Hexadecahedron (Structure II)

Hydrate Cavity Types

Figure 4

Table 1
 PHYSICAL PROPERTIES
 OF THE
 HYDRATE LATTICE

	Structure I	Structure II
Water molecules per unit cell	46	136
Cavities per unit cell		
Small	2	16
Large	6	8
Cavity radius (Å)		
Small	3.94	3.91
Large	4.30	4.73
Typical pure gases which form this structure	Methane	Propane
	Ethane	i-Butane
	Ethylene	

(1973).

HYDROCARBON-HYDRATE EQUILIBRIUM

Recently two-phase hydrocarbon-hydrate equilibrium (without a free-water phase) has become an area of increased interest. The optimum utilization of low-temperature, gas processing and transport lines, such as the dense-phase transport lines through Canada and the North Sea, is dependent on the accurate determination of two-phase hydrate equilibrium conditions.

There are currently two laboratories investigating this phenomenon; the laboratory of Kobayashi at Rice University, and this laboratory under the guidance of E. D. Sloan. The major problem involved in this type of experimental work involves the extremely low water concentrations encountered, often less than 0.001 on a mole fraction basis. The three primary experimental difficulties, cited in increasing order, are: 1) the metastability of hydrate formation, 2) the conversion of all the free-water to hydrate, and 3) the measurement of the extremely low water concentrations.

The work of Kobayashi involves a flow method in which hydrocarbon flows past a condensed (hydrate) phase until equilibrium is established. The water content of the hydrocarbon is determined as it leaves the equilibrium chamber. The details of this method are presented by Sloan,

Khoury, and Kobayashi (1976). It is important to note that this method has generally only been applied to gas-hydrate equilibrium systems, however the apparatus is being modified to allow liquid-hydrate equilibrium data to be obtained.

The pioneering work of Johnson (1981) indicated that oscillometry, the study of dielectric behavior, was a promising in situ technique for the determination of two-phase liquid-hydrate equilibrium formation conditions. Johnson (1981) originally considered calibrating a capacitance cell against known water concentrations. This method was not considered in this work. Instead, the dielectric behavior of the liquid hydrocarbon-water mixture at hydrate equilibrium conditions was utilized in the determination of the hydrate equilibrium temperature for a given hydrocarbon-water mixture at a specified pressure. The details of this generated experimental technique are given subsequently.

THEORETICAL PREDICTION

The x-ray diffraction work of von Stackelberg (1954) in the early 1950s and the resulting determination of the molecular structure of gas hydrates allowed the statistical thermodynamic model of clathrate compounds to be developed in 1959, by van der Waals and Platteeuw (1959). The model for the chemical potential difference of water between the empty and filled hydrate for a single hydrate former which fills only one type of cavity is:

$$\Delta\mu_w^H = RTV_i \ln[1 - \theta_{ij}] \quad (1)$$

where V_i is the number of type i cavities per water molecule in the hydrate lattice, specifically 1/17 for the propane-hydrate system and 2/23 for the ethane-hydrate system. The fraction of type i cavities filled by guest j is:

$$\theta_{ij} = C_{ij}f_j / (1 + C_{ij}f_j) \quad (2)$$

where C_{ij} is the Langmuir constant and f_j is the fugacity of gas component j .

The determination of the Langmuir constant requires the evaluation of the configurational properties of the gas-water interactions within the hydrate cavity. Most

often a spherically symmetric cell potential is assumed for for the host potential field. Tse and Davidson (1982) have shown that the spherical cell approximation (when compared to the Monte Carlo integration scheme employed by Tester (1972) to account for the asymmetric structure of the hydrate cages) provides a reasonably good approximation to the more detailed summation of discrete guest-water binary interactions in gas hydrates.

Van der Waals and Platteeuw using the Lennard-Jones-Devonshire Cell Theory obtained the following expression for the Langmuir constant:

$$C_{ij} = 4\pi/kT \int_0^R \exp(-w(r)/kT) r^2 dr \quad (3)$$

k = Boltzmann's constant

$w(r)$ = spherically symmetric cell potential

r = radial coordinate

This study employs the most commonly used potential function in hydrate prediction, the Kihara potential with a spherical core. McKoy and Sinanoglu (1963) derived the following expression for the spherically symmetric cell potential using the Kihara potential:

$$w(r) = 2Z_m \epsilon \left[\frac{\sigma^{12}}{R^{11} r} \left(\delta^{10} + \frac{a}{R} \delta^{11} \right) - \frac{\sigma^6}{R^5 r} \left(\delta^4 + \frac{a}{R} \delta^5 \right) \right] \quad (4)$$

$$\delta^N = \left[\left\{ 1 - r/R - a/R \right\}^{-N} - \left\{ 1 + r/R - a/R \right\}^{-N} \right] / N \quad (5)$$

Z_m = coordination number

ϵ = characteristic energy

a = core radius

R = cell radius

σ = location of zero potential

N = 4, 5, 10, or 11 in Equation (4)

The Langmuir constant can also be approximated by the empirical relation proposed by Parrish and Prausnitz (1972):

$$C_{ij} = (A_{ij}/TK) \exp(B_{ij}/TK) \quad (6)$$

The Kihara parameters for the hydrate-gas interactions and the constants in the empirical equation for the ethane-hydrate system and the propane-hydrate system were taken from Dharmawardhana (1980) and are given in Tables 2 and 3.

The fugacity of the liquid hydrocarbon, f_j , was evaluated using both the Peng-Robinson equation of state (1976) and the Soave-Redlich-Kwong equation of state (1972).

Sloan et.al. (1976) showed that the chemical potential difference of water in the filled and empty hydrate structure can be related to the fugacity of water in the

Table 2
LANGMUIR CONSTANT PARAMETERS
KIHARA POTENTIAL

Component	ϵ / K	$\sigma \text{ \AA}$	$a \text{ \AA}$
Ethane	177.01	3.2444	0.5651
Propane	208.45	3.3111	0.6502

Table 3

LANGMUIR CONSTANT PARAMETERS

$$C_{ij} = (A_{ij} / T(K)) \exp(B_{ij} / T(K))$$

Between 260 K and 300 K

Component	Structure I			
	small cavities		large cavities	
	$A_{ij} \times 10^3$	B_{ij}	$A_{ij} \times 10^2$	B_{ij}
Ethane	0.0	0.0	0.4071	3820.7119
Propane	0.0	0.0	0.0	0.0

Component	Structure II			
	small cavities		large cavities	
	$A_{ij} \times 10^3$	B_{ij}	$A_{ij} \times 10^2$	B_{ij}
Ethane	0.0	0.0	2.9157	3277.9254
Propane	0.0	0.0	1.3212	4506.9810

hydrate phase by the following equation:

$$f_w^H = f_w^{MT} \exp(\Delta\mu_w^H/RT) \quad (7)$$

where f_w^{MT} is an experimentally determined parameter related to the hypothetical vapor pressure of the empty hydrate.

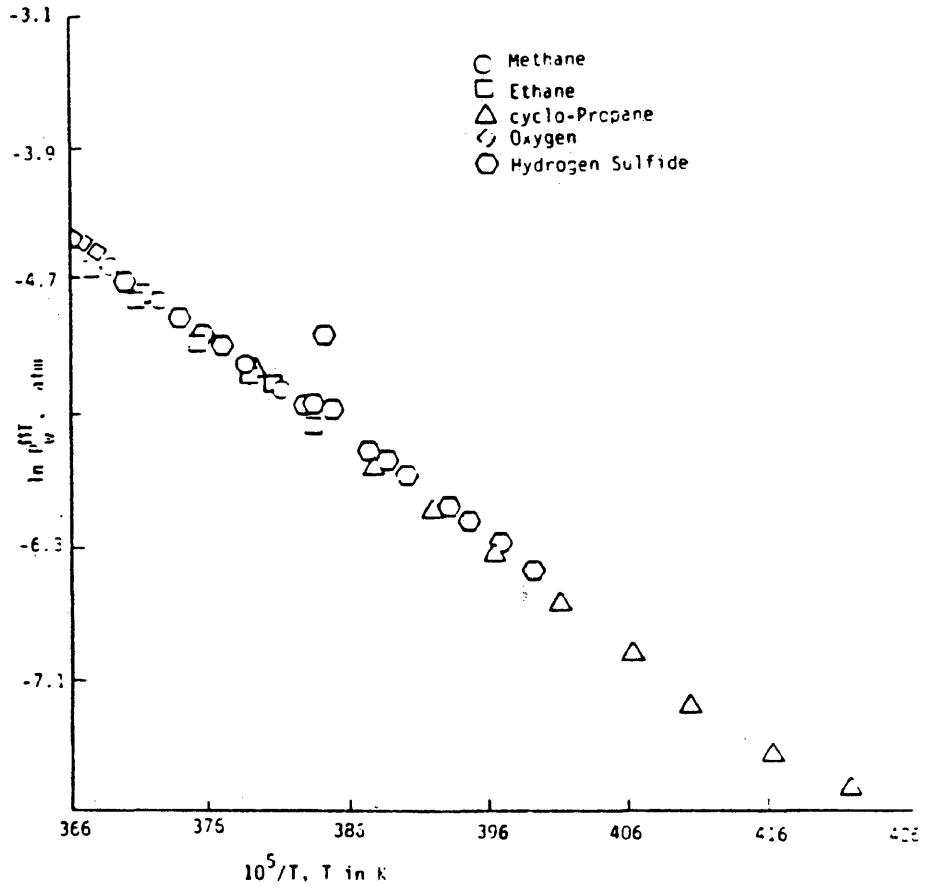
DETERMINING f_w^{MT} BY THE METHOD OF DHARMAWARDHANA

By equating the fugacity of hydrate to ice in three-phase data, Dharmawardhana (1980) showed that f_w^{MT} can be expressed as an empty hydrate vapor pressure as follows:

$$P_{ice}^{vap} \Phi_{ice}^{vap} \exp \int_{P_{ice}^{vap}}^P \frac{V_{ice}}{RT} dP = P_w^{MT} \Phi_w^{MT} \exp \int_{P_w^{MT}}^P \frac{V_w}{RT} dP \exp(\Delta\mu_w^H/RT) \quad (8)$$

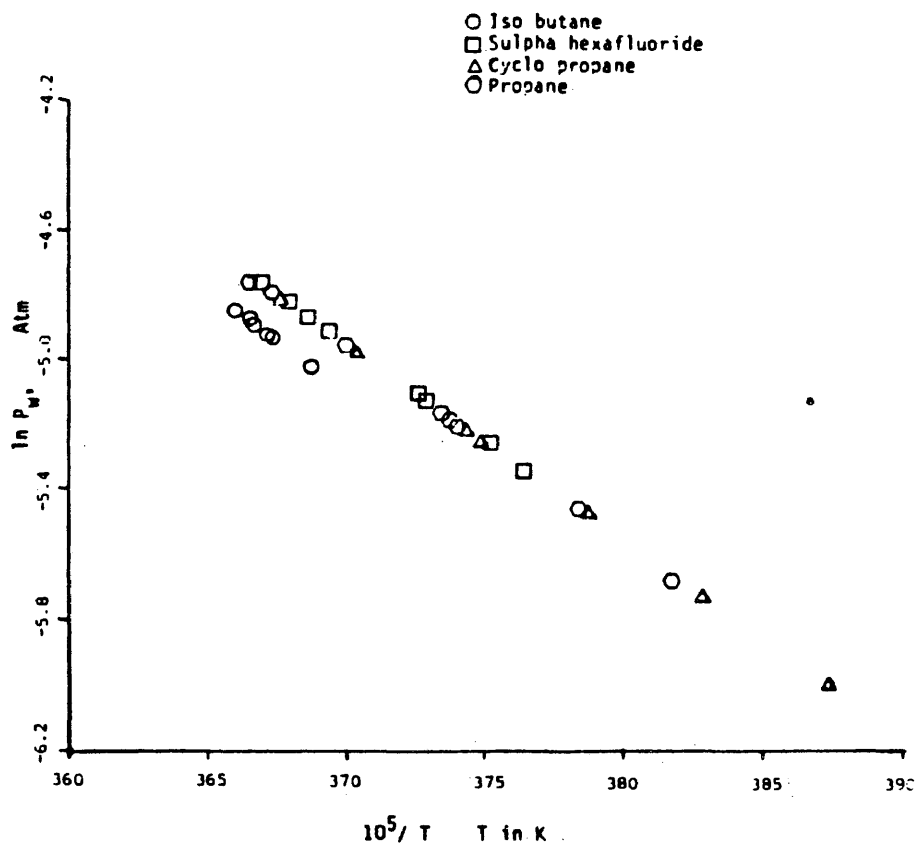
In the above equation, all of the ice properties are well known, the $\Delta\mu_w^H$ is obtained from three phase data. The only unknown in P_w^{MT} which was fit to a number of hydrate's three-phase data below 273 K and found to be a single function of temperature. Figure 5 shows the empty hydrate vapor pressure for Structure I hydrate formers. A similar plot for Structure II hydrate formers is shown in Figure 6.

The empty hydrate vapor pressure can be expressed as follows:



Structure I Empty Hydrate Vapor Pressure

Figure 5



Structure II Empty Hydrate Vapor Pressure

Figure 6

for Structure I hydrate

$$\ln P_w^{MT} = 17.440 - 6003.925/T \quad (9a)$$

for Structure II hydrate

$$\ln P_w^{MT} = 17.332 - 6017.635/T \quad (9b)$$

where: P_w^{MT} in atm, T in K

The empty hydrate fugacity coefficient may be determined using a virial coefficient by:

$$\Phi_w^{MT} = \exp(B_w P/RT) \quad (10)$$

In most cases Φ_w^{MT} is within one percent of unity. Tabulated second virial coefficients for water are given in Table 4. Values for the exponential term $\exp \int_{P_w^{MT}}^P \frac{V_H^{MT}}{RT} dP$ (Poynting correction factor) are presented in Table 5, for various pressures and both hydrate structures.

DETERMINING f_w^{MT} BY THE METHOD OF NG AND ROBINSON

An alternate method for the determination of the fugacity of water in the empty hydrate, f_w^{MT} , was developed by Ng and Robinson (1980) who report expressions for f_w^{MT} obtained by fitting the vapor-hydrate data of Kobayashi and coworkers. The expression for the fugacity of water in the empty hydrate follows:

Table 4

SECOND VIRIAL COEFFICIENT OF WATER
AS A FUNCTION OF TEMPERATURE
DYMOND (1980)

Temp. K.	B_w cc/gmol
323.15	-838.3
373.15	-451.0
423.15	-283.5

Table 5

POYNTING CORRECTION FACTOR

Temperature K	Pressure psia	PCF	
		Structure I	Structure II
273.15	14.7	1.001000	1.001020
	100	1.006890	1.007013
	500	1.034960	1.035590
	1000	1.071124	1.072427
	5000	1.408445	1.417025
253.15	14.7	1.001086	1.001106
	100	1.007425	1.007558
	500	1.037679	1.038360
	1000	1.076750	1.078162
	5000	1.445692	1.455195

$$\ln f_w^{MT} = \ln f_{w,0}^{MT} + \left(\frac{d \ln f_w^{MT}}{dP} \right)_T P(\text{atm}) \quad (11)$$

The expressions for each structure follow:

$$\ln f_{w,0}^{MT} = 14.269 - 5393/TK \quad (12a)$$

$$\left(\frac{d \ln f_w^{MT}}{dP} \right)_T = 0.00036TK - 0.1025 \quad (13a)$$

for Structure I, and

$$\ln f_{w,0}^{MT} = 18.062 - 6512/TK \quad (12b)$$

$$\left(\frac{d \ln f_w^{MT}}{dP} \right)_T = 0.0001109TK - 0.03192 \quad (13b)$$

for Structure II.

The prediction of hydrate equilibrium, specifically in the two-phase, liquid-hydrate region can be reduced to the equating of the fugacity of the water in the liquid phase to the fugacity of the water in the hydrate phase as shown in the following equation:

$$X_w \Phi_w P = f_w^{MT} \exp(\Delta \mu_w^H / RT) \quad (14)$$

In this study the fugacity coefficient of water in the liquid, Φ_w , was determined using both the Peng-Robinson

equation of state and the Soave-Redlich-Kwong equation of state. The binary interaction parameter, k_{ij} , used in the determination of the fugacity coefficient was taken from vapor-liquid equilibrium data, specifically that reported by Peng and Robinson (1976) who fit interaction parameters to these data. The interaction parameters used with the Soave-Redlich-Kwong equation of state were optimized to reproduce the results predicted using the Peng-Robinson equation of state. The interaction parameters used in the prediction are shown in Table 6.

Table 6

INTERACTION PARAMETER

SYSTEM	k_{ij} EQUATION OF STATE	
	PENG-ROBINSON	SRK
Ethane-Water	0.50	0.516
Propane-Water	0.48	0.496

EXPERIMENTAL METHOD

In measurements of the water content of liquid hydrocarbon phases in equilibrium with hydrates, typically water mole fractions of 0.001 or less are encountered. Currently two methods exist for such measurements.

FLOW METHOD

In the flow method liquid hydrocarbon is withdrawn from a cell in which equilibrium with hydrate has been obtained. The water content of the liquid is determined as it leaves the equilibrium chamber. The details of this method are presented by Sloan, Khoury, and Kobayashi (1976).

IN SITU MEASUREMENT

The method generated and employed in this work involves the use of oscillometry for the determination of hydrate formation conditions in a hydrocarbon-rich liquid phase. The method has the advantage of measurement without sample withdrawal, thus reducing cost and error introduced in the sampling procedure.

The experimental procedure involves the monitoring of the liquid hydrocarbon-water mixture's dielectric in regard to system temperature and pressure. The dielectric of a material is defined as the capacitance of the material divided by the corresponding capacitance of the assembly

under a vacuum. It is a measure of the mixture's polarizability. Its behavior is used to determine the hydrate formation temperature.

The relationship between the dielectric constant of a condensed phase and its polarizability has not yet been rigorously derived, however it has been approximated by Debye (1929). Traditionally this formulation was only considered valid for nonpolar liquids, although it has been extended to a dilute solution of a polar solute (component 2) in a relatively nonpolar solvent (component 1). The resulting relation given by Davidson (1962) is often used along with measurements of the dielectric constants of dilute solutions for the calculation of dipole moments of polar molecules. The expression is shown below:

$$\frac{\epsilon - 1}{\epsilon + 2} = \frac{4\pi}{3} \left\{ N_1 \alpha_1 + N_2 \left[\alpha_2 + \frac{\mu_2^2}{3kT} \right] \right\} \quad (15)$$

- N_2 = the number of solute molecules per unit volume
- N_1 = the number of solvent molecules per unit volume
- α_1 = polarizability of component 1
- α_2 = polarizability of component 2
- μ_2 = dipole moment of component 2
- k = Boltzmann's constant
- ϵ = dielectric constant of mixture
- T = absolute temperature

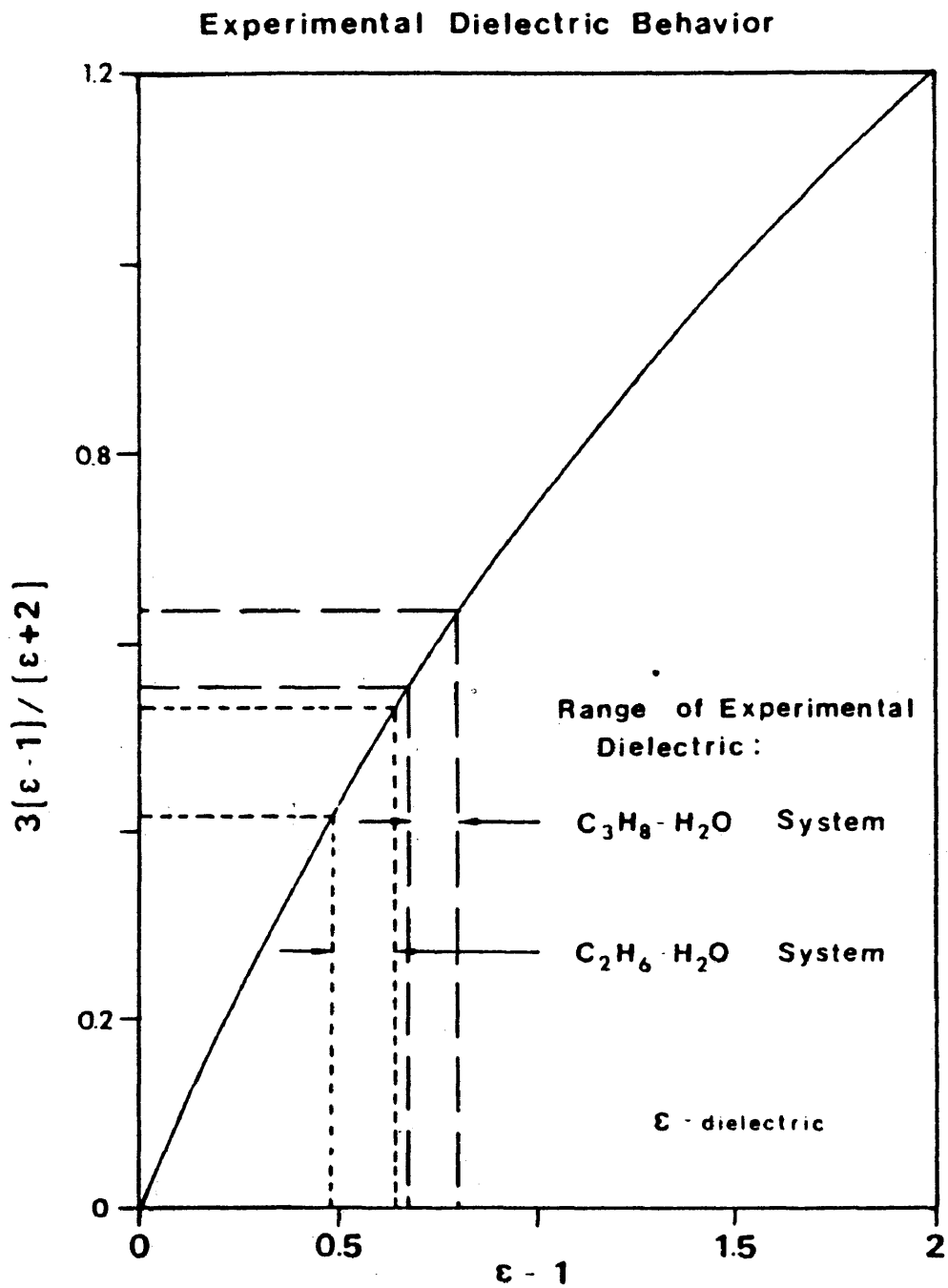
$$\frac{\epsilon-1}{\epsilon+2} = \text{modified Clausius-Mosotti function}$$

It is evident from the above relation that the modified Clausius-Mosotti function is inversely proportional to absolute temperature, assuming the equation adequately describes the dielectric behavior of the system.

The behavior of the modified Clausius-Mosotti function in regard to the dielectric is shown in Figure 7. The observed ranges of dielectric measurements for both the liquid ethane-water system and the liquid propane-water system are also shown in Figure 7.

The maximum error observed between the true value of the modified Clausius-Mosotti function and that approximated by a truncated, after the first term, Taylor series expansion of the function about the mean of each system was 0.32% for the liquid ethane-water system and 0.12% for the liquid propane-water system. Therefore it is the contention of this work that the modified Clausius-Mosotti function is essentially proportional to the actual dielectric over the ranges observed experimentally. Thus it can be shown that the dielectric constant is also practically inversely proportional to absolute temperature.

The experimental procedure involves the loading of the



Experimental Dielectric Behavior

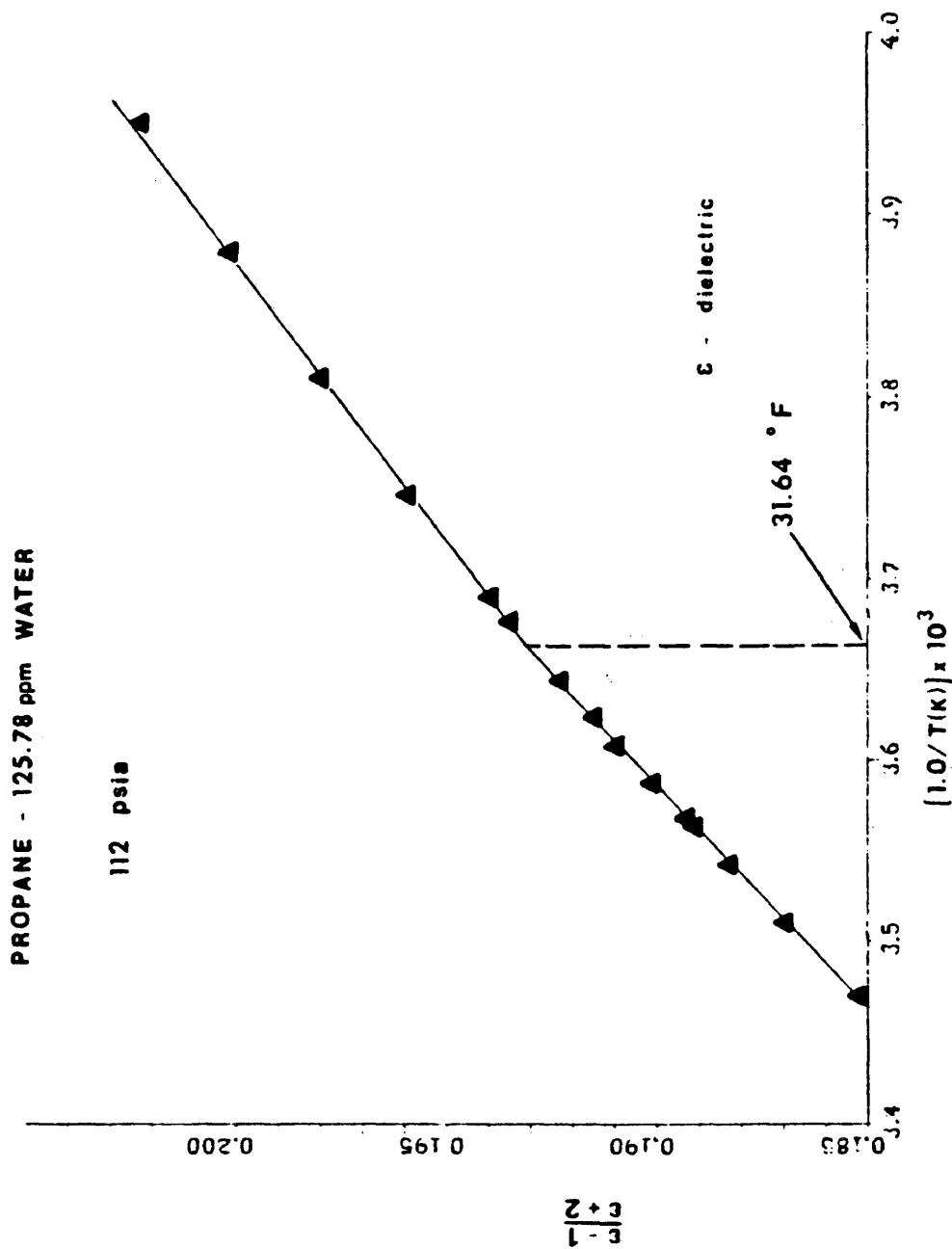
Figure 7

capacitance cell with a liquid hydrocarbon-water mixture of known concentration, specifically in the single phase region, marked C, in Figure 1. The dielectric of the mixture is then measured as a function of temperature.

The basis of the data analysis employed in this study involves the fact that the concentration of water in the liquid phase changes abruptly when the hydrate phase boundary is crossed. This translates to a change in slope of the polarizability as plotted against inverse temperature. The modified Clausius-Mosotti function is shown plotted against inverse temperature in Figure 8. Figure 9 shows the dielectric constant plotted against inverse temperature. Both plots involve the same set of data, specifically that of November 5, 1982.

Although the formation of a hydrate from a single phase is considered impossible by a few individuals, the formation of a hydrate from a single vapor phase has been demonstrated by Cady (1981). Therefore, it is the contention of this work that the formation of a hydrate from a single liquid phase is also possible.

The data reduction routine employs the response of the dielectric measurement in regard to absolute temperature. The regression routine is outlined subsequently.

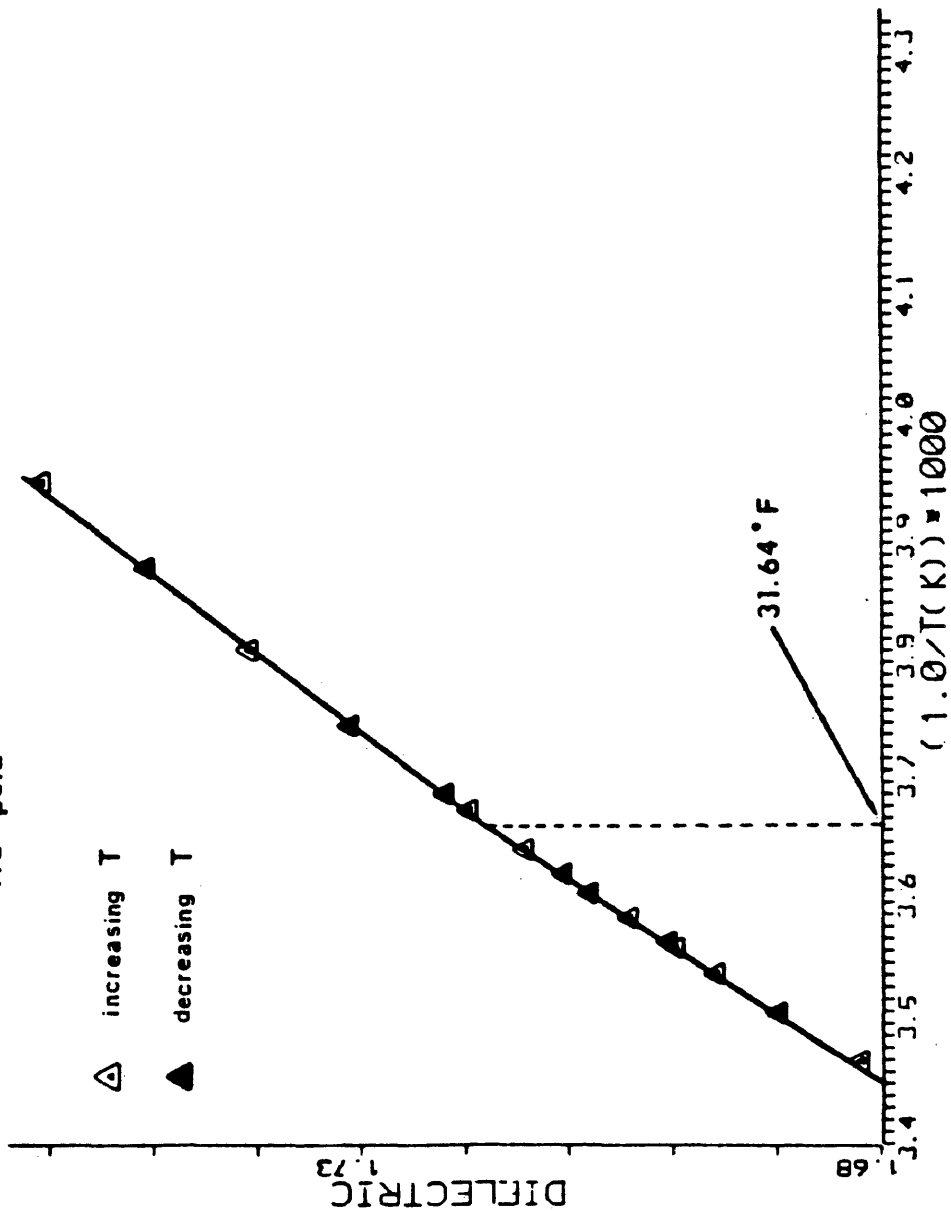


Modified Clausius-Mosotti Function Versus Inverse Temperature

Figure 8

PROPANE - 125.78 ppm WATER

112 psia



Dielectric Versus Inverse Temperature

Figure 9

EXPERIMENTAL APPARATUS

The experimental apparatus consisted of two systems. The low pressure system is shown in Figure 10. It is designed to load the capacitance cell with known amounts of water. Figure 11 shows the high pressure experimental apparatus used: 1) to load the condensed hydrocarbon into the capacitance cell and 2) to measure the dielectric constant of the liquid phase within the cell.

The experimental apparatus is essentially identical to that used and described by Johnson (1981), with the exception of the modification of the capacitance cell and the addition of a high pressure Heise guage capable of measuring the higher pressures encountered with the liquid ethane-water system.

CAPACITANCE CELL

The capacitance cell used in this study is shown in detail in Figure 12. The ultrasonic oscillator was a recent modification of the oscillometric equilibrium cell. It was designed to keep the contents of the cell well mixed, while also to minimize the degree of occlusion and metastability encountered at hydrate formation conditions. The capacitor is identical to that described by Pan, Mady, and Miller (1975), a slightly modified version of that described by

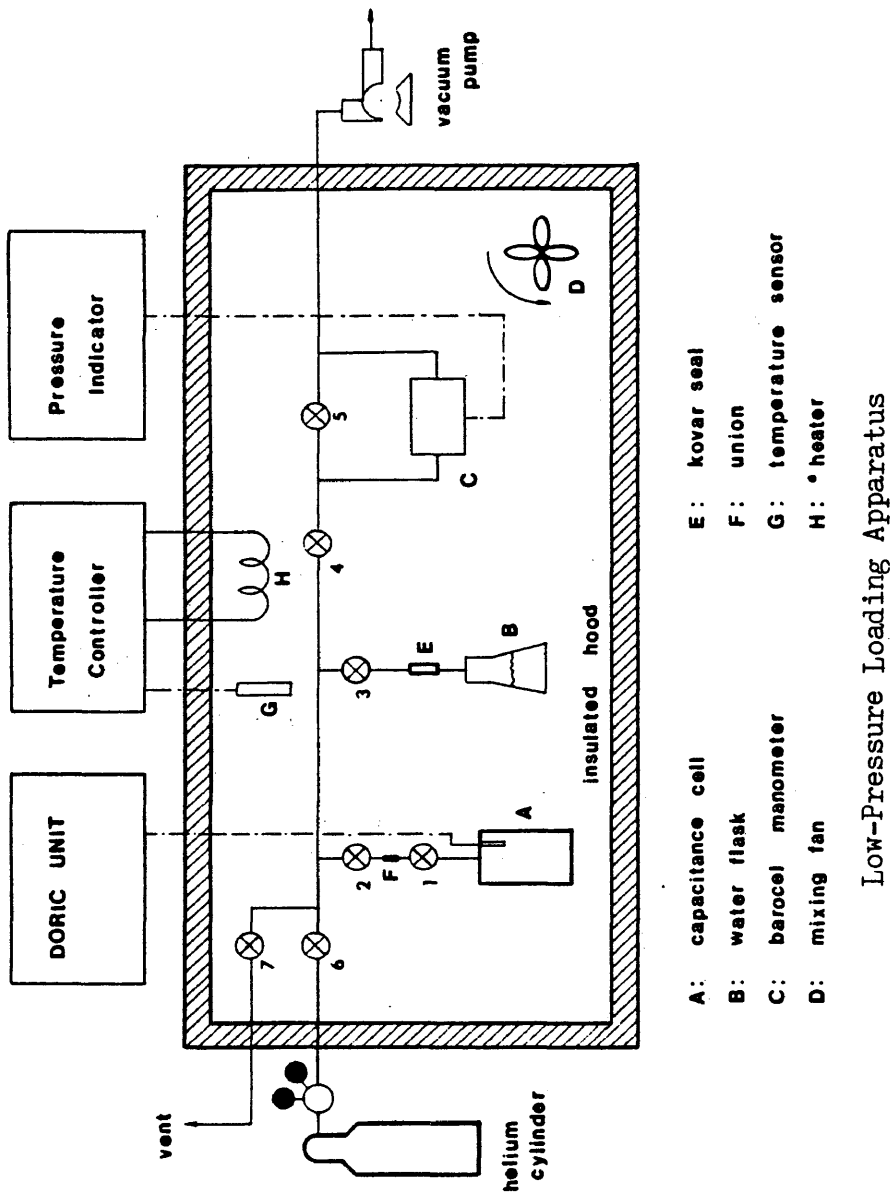
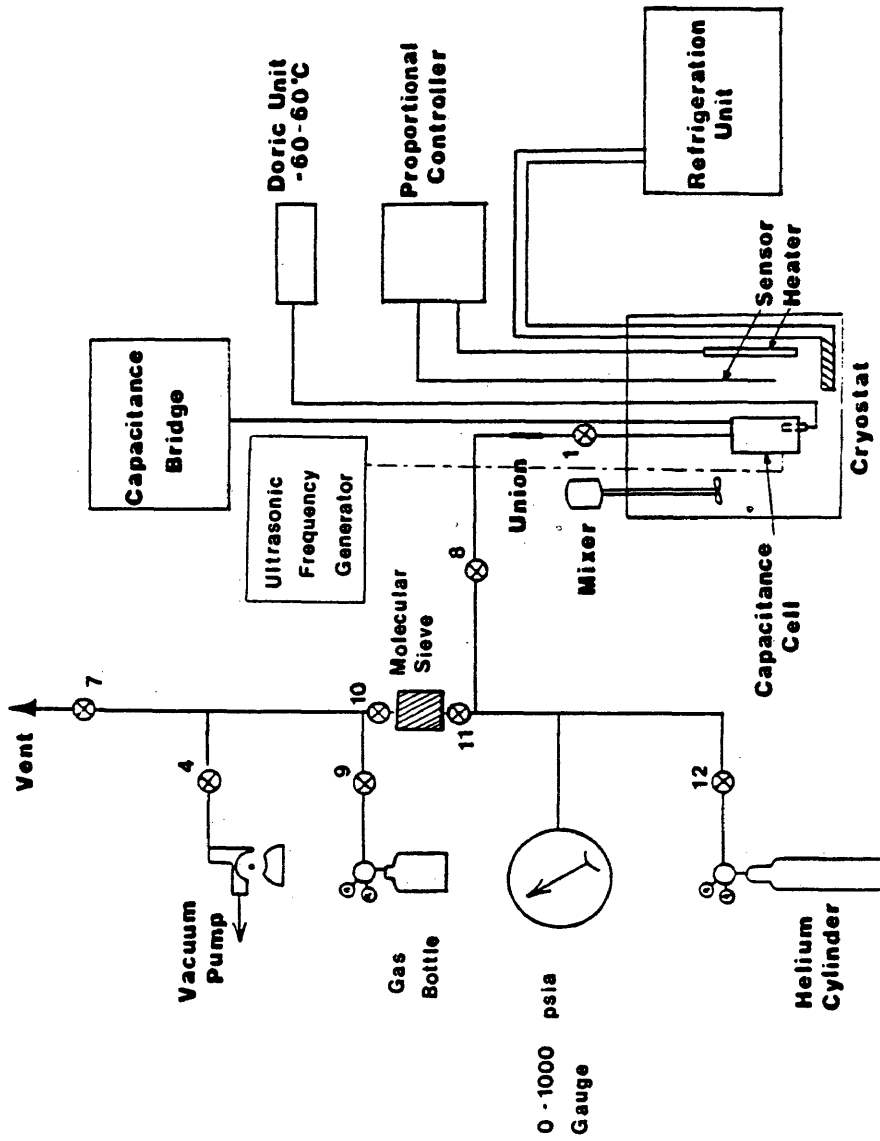


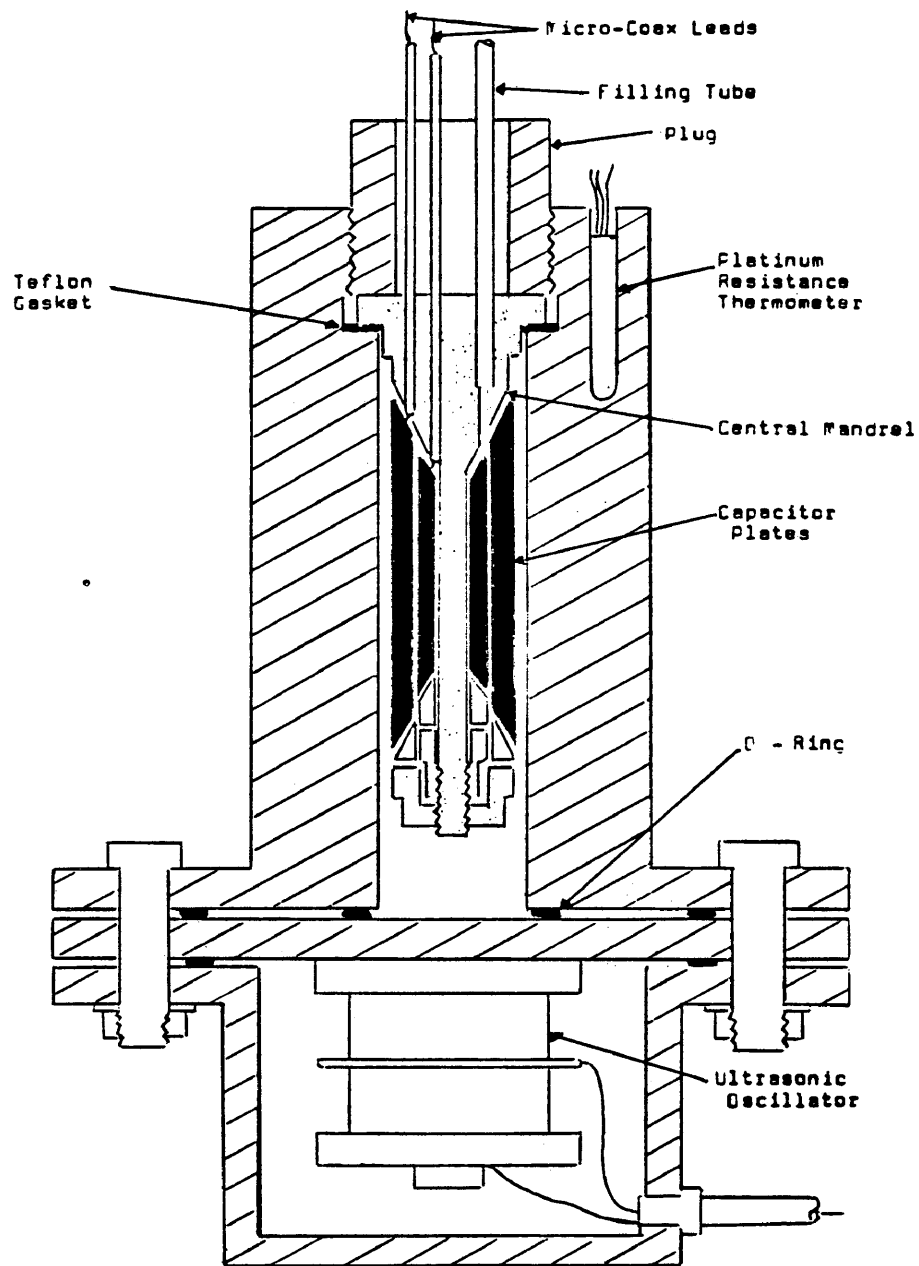
Figure 10

Low-Pressure Loading Apparatus



High-Pressure Experimental Apparatus

Figure 11



Capacitance Cell

Figure 12

Younglove and Straty (1970). The cell volume, 15.12 cm^3 , was determined by helium expansion. The standard deviation of the measured cell volume was approximately 0.1 cm^3 . A good description of the original capacitance assembly is given by Johnson (1981), Thompson (1978), and Luo (1979). The assembly was modified to include an ultrasonic agitator on the bottom of the cell closure.

The ultrasonic agitation system consisted of an ultrasonic transducer attached to the lower plate of the capacitance cell and an ultrasonic generator. The ultrasonic agitation equipment is identical to that described by Zerpa (1977).

LOW PRESSURE SYSTEM

The low pressure system is shown diagrammatically in Figure 10. The insulated hood was designed to allow the temperature of the entire contents of the hood to be raised to maximum of approximately $70 \text{ }^\circ\text{C}$, well above ambient conditions. The hood was heated with three 660 W coil heaters. A rheostat was used in conjunction with two of the heaters to provide constant heat. The third heater was controlled by an Omega Model 4201 RTD proportional temperature controller. Temperature stability within the hood was estimated to be on the order of $\pm 0.2 \text{ K}$.

HIGH PRESSURE SYSTEM

The high pressure system is shown diagrammatically in Figure 11. The oscillometric equilibrium cell was suspended within a cryostat bath. The cryostat bath consisted of a Neslab size B U-Tainer with an internal volume of 7500 cc. It has a seamless stainless steel reservoir which is insulated by polyurethane foam. The bath was filled with Dow Corning 200 fluid (dimethylpolysiloxane) which has a quoted viscosity of five centistokes at 0 °C. Refrigeration was continuously provided from a Neslab Cryocool Model CC100 mechanical refrigeration system through a flexible immersion probe. The quoted continuous load capacity of the refrigeration unit is in excess of 160 W at 228 K. A 1550 RPM Lightnin Model L stirrer with a three blade impeller 5 cm in diameter was employed for the mixing of the bath fluid. Bath temperature was controlled by a Neslab Exatrol 30 LT proportional controller in conjunction with a 250 W immersion heater. Temperature stability of the cryostat bath was on the order of ± 0.01 K.

PRESSURE MEASUREMENT

The high pressure system pressures were measured with two different gauges depending on the system being evaluated. Propane-water system pressures were measured using a zero to three hundred psig Heise gauge calibrated

with a Ruska Air Dead Weight Tester by Johnson (1981). Ethane-water system pressures were measured using a zero to one thousand psia Heise guage calibrated by Giussani (1981).

The low pressure measurements required in the loading of water into the capacitance cell were achieved through the use of a Datametrics Barocel Pressure Sensor Model 570 D used in conjunction with a Datametric Electronic Manometer Model 1173. A Datametrics Thermal Base Type 525 was employed to enhance the sensitivity of the Barocel and to prevent condensation within the sensor.

The quoted absolute accuracy of the Heise guages is 0.1% of full scale. The Barocel pressure sensor has a quoted absolute accuracy of 0.4%, although a value of 5% was used in the error analysis as a means of compensating for the error introduced by the the adsorption of water in the cell during the loading procedure.

TEMPERATURE MEASUREMENT

A platinum resistance thermometer mounted in the top of the capacitance cell was used for measuring temperatures in both the high and low pressure systems. A nominal 100 ohm Omega Model PR-11-2-100-1/8-2E PRT was used in conjunction with a Model DS-100-T5A Doric Digital Thermometer. The Doric temperature measuring apparatus was calibrated against

a Leeds & Northrup platinum resistance thermometer by Johnson (1981).

The quoted absolute accuracy of the Doric digital thermometer is 0.023%.

CAPACITANCE MEASUREMENT

A three-lead General Radio Type 1620-A Capacitance Measuring Assembly was used to measure the experimental capacitance. The assembly consisted of a 1615-A Capacitance Bridge, 1311-A Oscillator, and a 1232-A Tuned Amplifier and Null Detector. The capacitance bridge and its corresponding electrical connections are further outlined by Johnson (1981).

The quoted absolute accuracy of the capacitance bridge is $0.01\% \pm 0.00003$ pF at 1kHz, with a resolution of 1 ppm for capacitances above 1 pF.

VACUUM SYSTEM

A Welch Duo-Seal Vacuum Pump model 1399 with a quoted ultimate McLeod gauge pressure of 0.015 mm of mercury was used to evacuate both the low pressure system and the high pressure system. A glass cold trap maintained at liquid nitrogen temperatures was used in conjunction with the vacuum pump in order to prevent condensibles from entering the pump and to prevent the residual pump oil vapor from

entering the low pressure system. The vacuum pump discharge was vented to the atmosphere.

EXPERIMENTAL PROCEDURE

LOADING WATER INTO THE CAPACITANCE CELL

Water is introduced into the capacitance cell as a vapor. Its temperature and pressure are measured and the cell is subsequently valved shut. An accurate determination of the amount of water loaded into the cell is made using the ideal gas law and the known cell volume. The applicability of the ideal gas law was determined experimentally. The pressure-temperature behavior of water vapor was studied in regard to the vapor pressure of water at the various loading temperatures. The results of this experimental study are shown in Figure 13. The behavior of the water vapor loaded at a pressure of 8.2% of the total saturation pressure appear linear as does the behavior of helium loaded into the cell. The compressibility factor for the water vapor was also determined using the low pressure virial equation approximation:

$$Z = 1 + B_w P / RT \quad (16)$$

The second virial coefficients for water vapor were taken from Dymond (1980). The compressibility factors are given in Table 7. Typically pressures of 25 torr or less were required in the loading of water into the equilibrium cell. The optimum loading region for water vapor is shown in

Figure 13

P-T Behavior at Water Loading Conditions

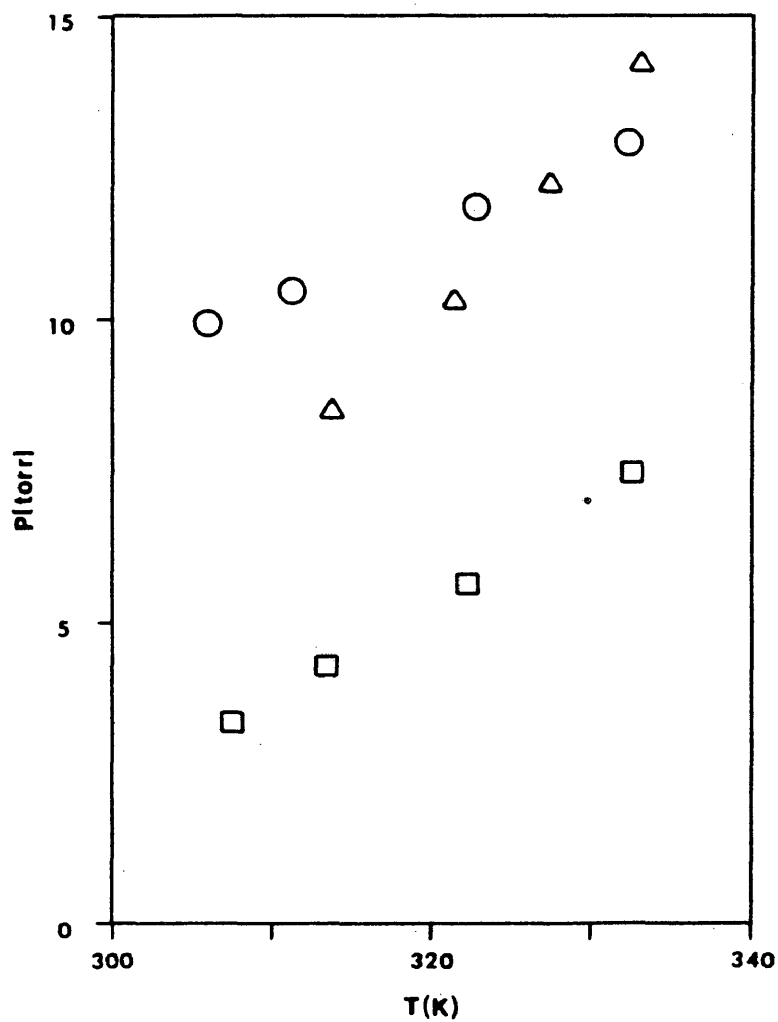


Table 7

COMPRESSIBILITY FACTOR OF WATER
AT A PRESSURE OF 25 TORR

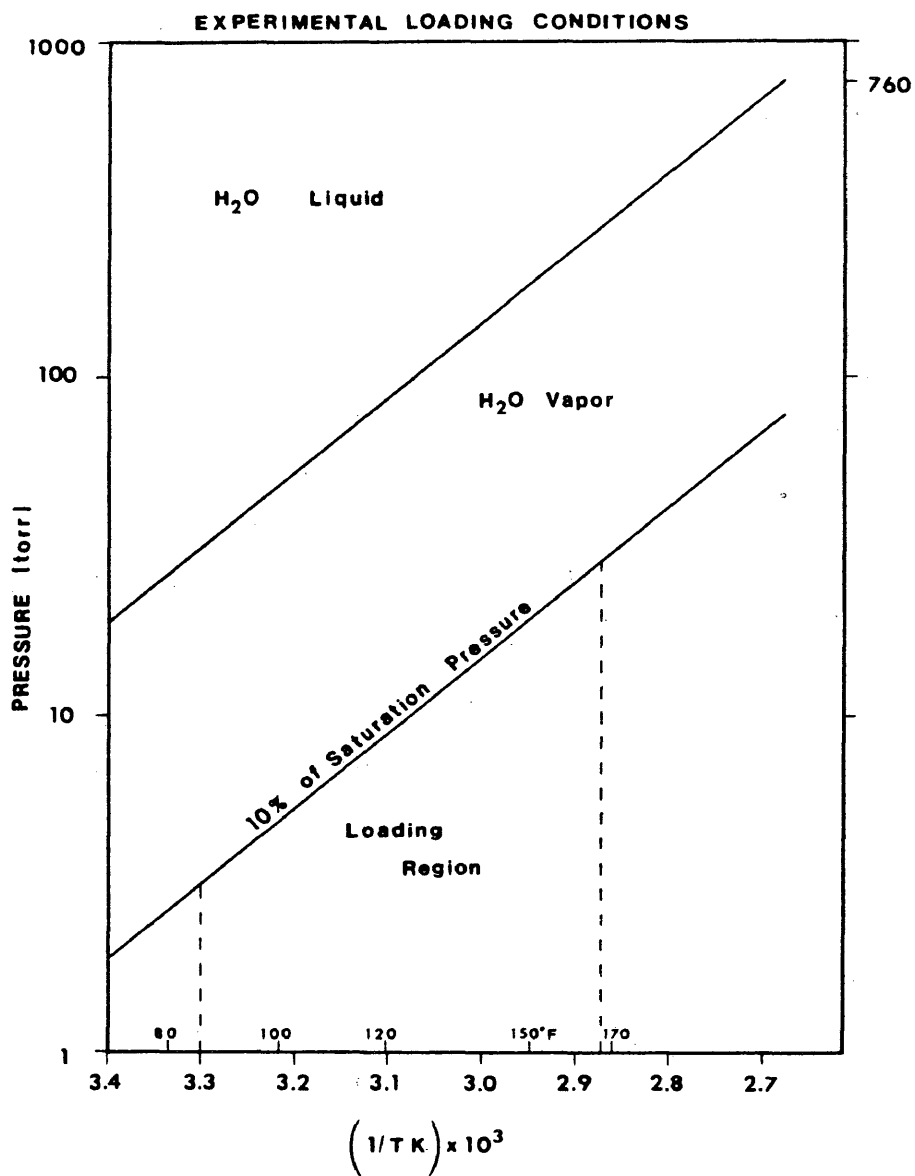
Temp. K.	Z	% Diff. From Unity
323.15	0.99896	0.104
373.15	0.99952	0.048
423.15	0.99973	0.027

Figure 14. As an attempt to minimize adsorption errors, loading pressures were generally limited to a maximum of ten percent of the vapor pressure of water at the loading temperature. This maximum of ten percent was arrived upon after careful consideration of the range of water concentrations required and the extreme limitations of the low pressure loading apparatus in regard to its upper temperature limit.

LOADING CONDENSED HYDROCARBON INTO THE CAPACITANCE CELL

The capacitance cell, once loaded with the desired amount of water, is installed into the high pressure system. The cell is cooled to approximately 5 °C, and the hydrocarbon at ambient temperature and its corresponding vapor pressure, is condensed directly into the cell. The pressure range is limited by the pressure of the hydrocarbon reservoir. Helium was used to pressurize the system when pressures higher than the hydrocarbon's ambient vapor pressure were required.

The water concentration of the mixture loaded into the capacitance cell was always less than the concentration of water in the saturated liquid water-liquid hydrocarbon system as reported by the data of Poettman (1946), Pollin (1982), Kahre (1964), and Kobayashi (1951). This ensured a single phase within the capacitance cell, for the water



Experimental Loading Conditions

Figure 14

concentration loaded into the cell would be impossible to determine if more than one phase existed within the cell.

MEASURING THE DIELECTRIC OF THE MIXTURE

Once the capacitance cell is loaded with the desired liquid propane-water or ethane-water mixture, the ultrasonic agitation equipment is turned on and the cell is subsequently cooled to approximately $-35\text{ }^{\circ}\text{C}$. System pressure is maintained at a constant value by adjusting the amount of vapor above the liquid mixture. This is done by carefully either venting excess vapor or adding it directly from the hydrocarbon reservoir. It was determined by Johnson (1981) that the amount of water that could possibly flash into the vapor phase above the liquid was negligible in respect to the amount of water in the liquid phase within the capacitance cell. Johnson (1981) also determined that the level of liquid in the fill tube of the capacitance cell had a negligible effect on the loaded water concentration.

Once the cell reaches the desired temperature, the ultrasonic agitator is shut off and the cell is allowed to come to thermal equilibrium with the cryostat bath. Capacitance measurements are made until they no longer change with time. The dielectric is then calculated by dividing the measured capacitance by the corresponding vacuum capacitance. The vacuum capacitance was found to be

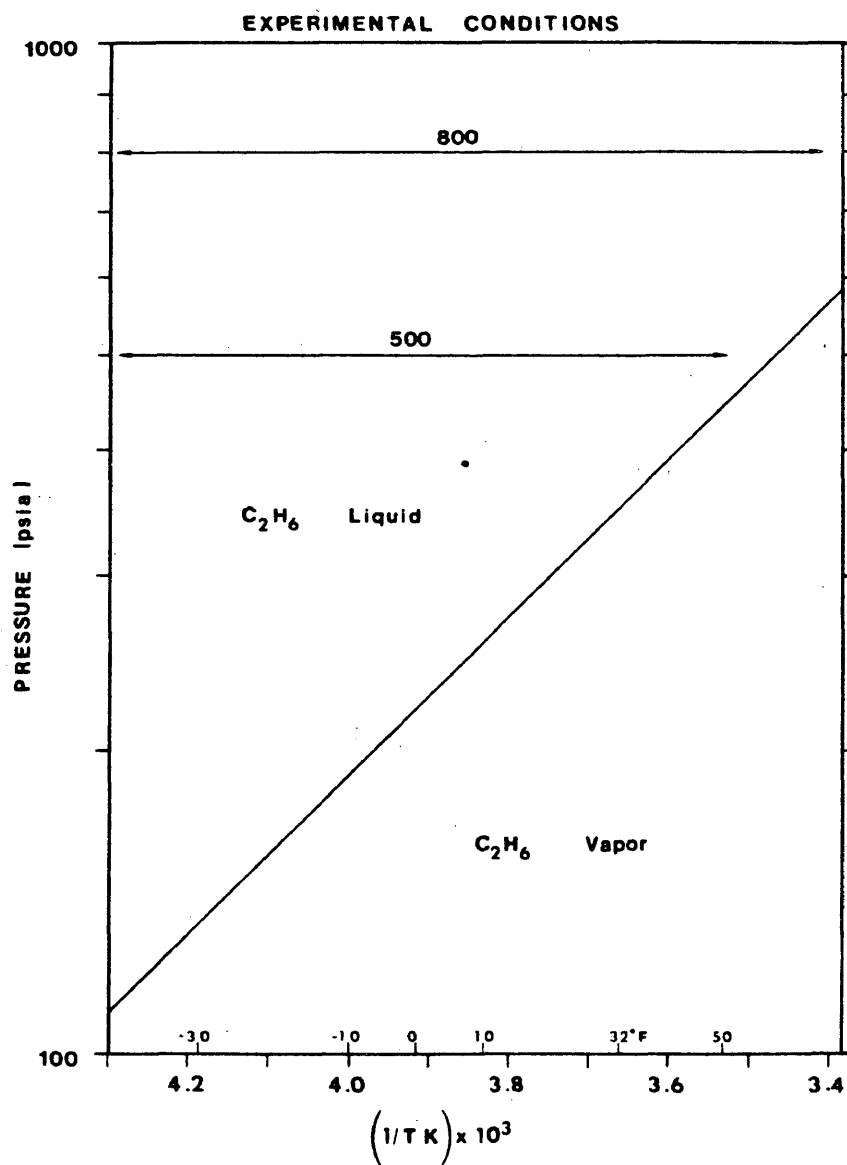
linearly related to temperature by the relation:

$$C_0(\text{pF}) = 4.22479 + 0.005294197 \times T(^{\circ}\text{C}) \quad (17)$$

The difference between the smoothed vacuum capacitance and the experimental vacuum capacitance was found to be insignificant.

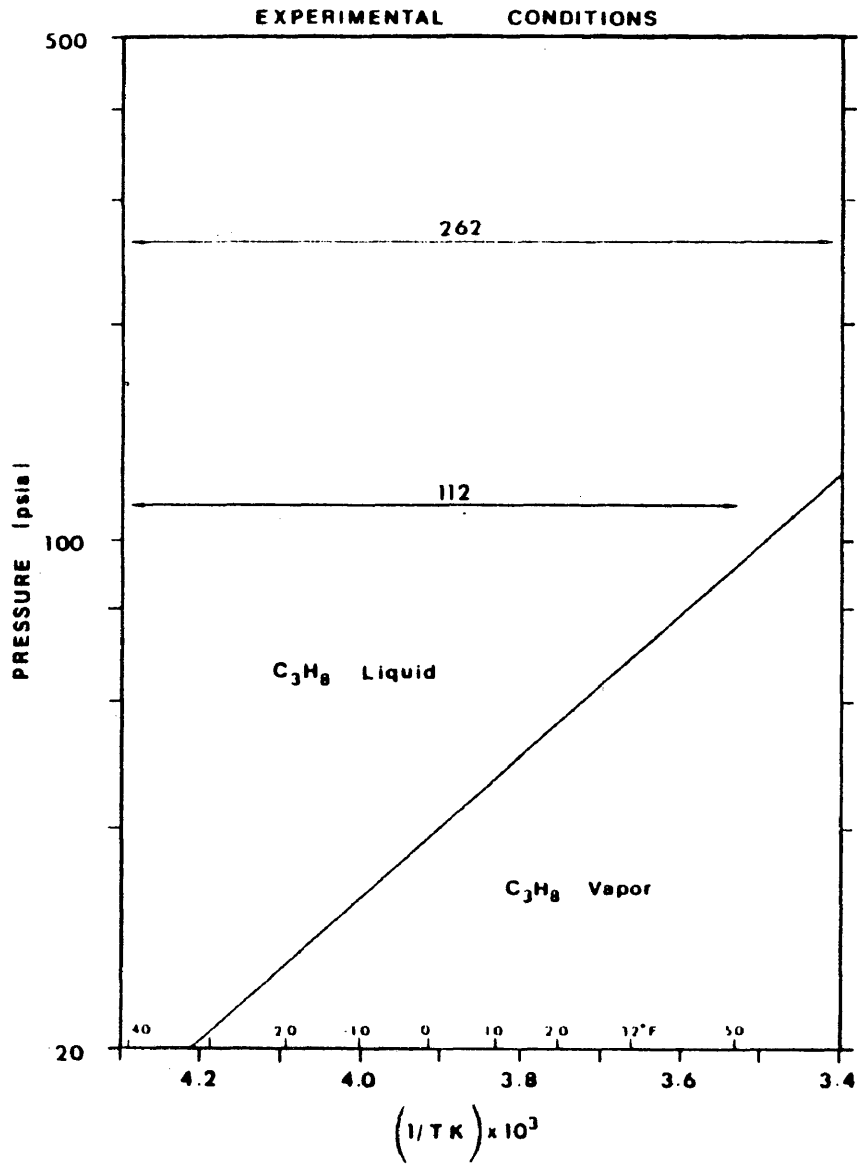
The ultrasonic agitation is again turned on and the bath temperature is raised, where again the same procedure is followed for the measurement of the dielectric constant of the liquid mixture. Normally it would take approximately 60 minutes for the cell to stabilize once the ultrasonic agitation equipment had been turned off.

Hysteresis was never observed in the experimental procedure when temperature cycling was employed. The temperature and pressure range examined in this work, relative to the condensed hydrocarbon bubble points are shown in Figures 15 and 16.



Ethane-Water Experimental Conditions

Figure 15



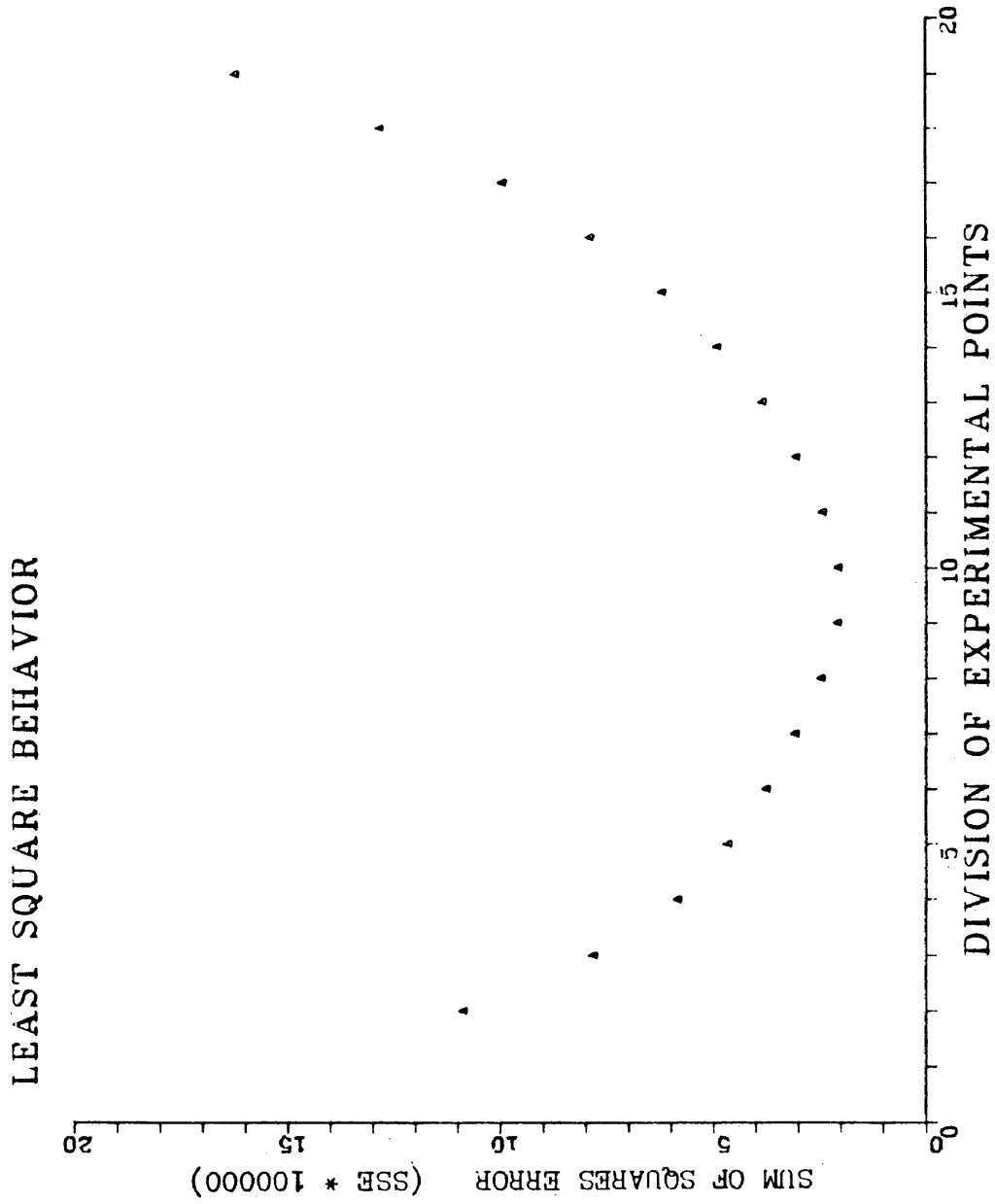
Propane-Water Experimental Conditions

Figure 16

DATA REDUCTION

The basis of the data analysis employed in this study involves the fact that as the new hydrate phase forms, the concentration of water in the liquid phase changes abruptly. This translates to a change in slope of the dielectric as plotted against inverse temperature. An example of this is shown in Figure 9. The point at which the change in slope occurs corresponds to the hydrate equilibrium temperature for the specific concentration initially loaded into the equilibrium cell. Hysteresis does not appear to occur as indicated by Figure 9.

The determination of the "break" point involves the fitting of the data with two straight lines. The solution is obtained by looking at every possible division of experimental points to the first and second lines, estimating the parameters by linear least squares and evaluating the residual sum of squares for each division. The division and set of parameters that give rise to the smallest of all the residual sum of squares is then chosen as the appropriate description of the experimental data. This technique is described by Draper and Smith (1966). An example of the behavior of the sum of squares error is illustrated in Figure 17. The resulting two lines are then equated, allowing the determination of the experimental



Least Square Behavior of Regression Routine Employed for the Determination of the "Break" Temperature

Figure 17

"break" temperature.

The "break" temperature corresponds to the hydrate equilibrium temperature. The equilibrium temperature is used along with the system pressure to calculate the density of the liquid hydrocarbon being evaluated. Two methods were employed to approximate the density of the liquid hydrocarbon: 1) a method based upon corresponding states formulated by Chueh and Prausnitz as outlined by Reid, Prausnitz, and Sherwood (1977), and 2) the method formulated by Goodwin (1976,1977) at the National Bureau of Standards. Tables 8 and 9 give the comparison of these two methods. It should be noted that the method outlined by Goodwin is relatively difficult to solve and requires a good initial guess for the liquid density. The initial guess is provided by the method of corresponding states.

The volume of the water loaded into the cell was considered negligible in the determination of the amount of hydrocarbon liquid loaded into the cell, since the maximum water concentration in this work was approximately 180 parts per million on a molar basis.

Table 8

LIQUID ETHANE DENSITY CALCULATION
AT A PRESSURE OF 500 PSIA

Temperature (°C)	CSP (gmole/l)	NBS (gmole/l)	% Difference
0	13.44913	13.49256	-0.3219
-10	14.17274	14.25043	-0.5455
-20	14.80395	14.89913	-0.6388
-30	15.38263	15.47769	-0.6142
-40	15.92492	16.00697	-0.5126

CSP - Method of Chueh and Prausnitz

NBS - Method of Goodwin (1976)

% Difference = ((CSP - NBS)/NBS) x 100

Table 9

LIQUID PROPANE DENSITY CALCULATION
AT A PRESSURE OF 112 PSIA

Temperature (°C)	CSP (gmole/l)	NBS (gmole/l)	% Difference
0	11.95497	11.99612	-0.3430
-10	12.28235	12.29882	-0.1339
-20	12.59326	12.58718	0.0483
-30	12.88767	12.86398	0.1842
-40	13.16462	13.13135	0.2534

CSP - Method of Chueh and Prausnitz

NBS - Method of Goodwin(1977)

% Difference = ((CSP - NBS)/NBS) x 100

EXPERIMENTAL ACCURACY

PURITY OF MATERIALS

Ultra high purity ethane was purchased from the Matheson Company bearing a stated purity of 99.99% plus.

Research Grade propane donated from Phillips Petroleum Company with a stated purity of 99.98%, the only measureable impurity being trace ethane, was used along with degassed triple distilled water in all the experiments.

The hydrocarbon liquids were dried over a molecular sieve with an effective pore size of 4 Å before being loaded into the capacitance cell.

PRECISION

The dielectric of pure propane was measured and compared with the pure propane data of Haynes as reported by Johnson (1981). The experimental data was not smoothed as an attempt to duplicate the "exact" conditions reported by Haynes. The results are given in Table 10.

As an attempt to determine the precision of the loading procedure, a propane-methanol mixture was prepared using the same loading procedure used in the loading of propane-water mixtures. Luo (1979) reports a linear relationship between the dielectric of a propane-methanol mixture and its methanol concentration, specifically between zero and two

Table 10

COMPARISON OF THE MEASURED DIELECTRIC CONSTANT
OF LIQUID PROPANE AT 111.96 psia

Temperature(°C)	This Work	Haynes	Difference(%)
-30.005	1.78139	1.77940	-0.140
-20.015	1.76109	1.75881	-0.129
-10.005	1.73960	1.73744	-0.124
0.000	1.71740	1.71519	-0.129
10.005	1.69409	1.69194	-0.127

hundred parts per million (ppm) methanol on a mole basis. The experimental dielectric measurement of a 128 ppm methanol in propane mixture was within 0.0215% of the smoothed data of Luo (1979).

METHOD OF ACCURACY ESTIMATION

This study employed two methods for the estimation of the uncertainty of the experimental water concentration at hydrate formation conditions. The traditional propagation of error was evaluated utilizing numerically approximated partial derivatives to estimate the variance of the experimental dependent variable. A Monte Carlo type error analysis was used because of its ability to generate information regarding the probability distribution of the dependent variable. The two methods give identical results in regard to the variance of the dependent variable if the error in the cell volume is assumed to be zero. The reported error bars in the experimental results correspond to a confidence interval of 99.9 percent assuming the error to be normally distributed.

MONTE CARLO ERROR ANALYSIS

This study employed two Monte-Carlo type error analyses. The first being a study of the statistical behavior of the hydrate formation temperature determined

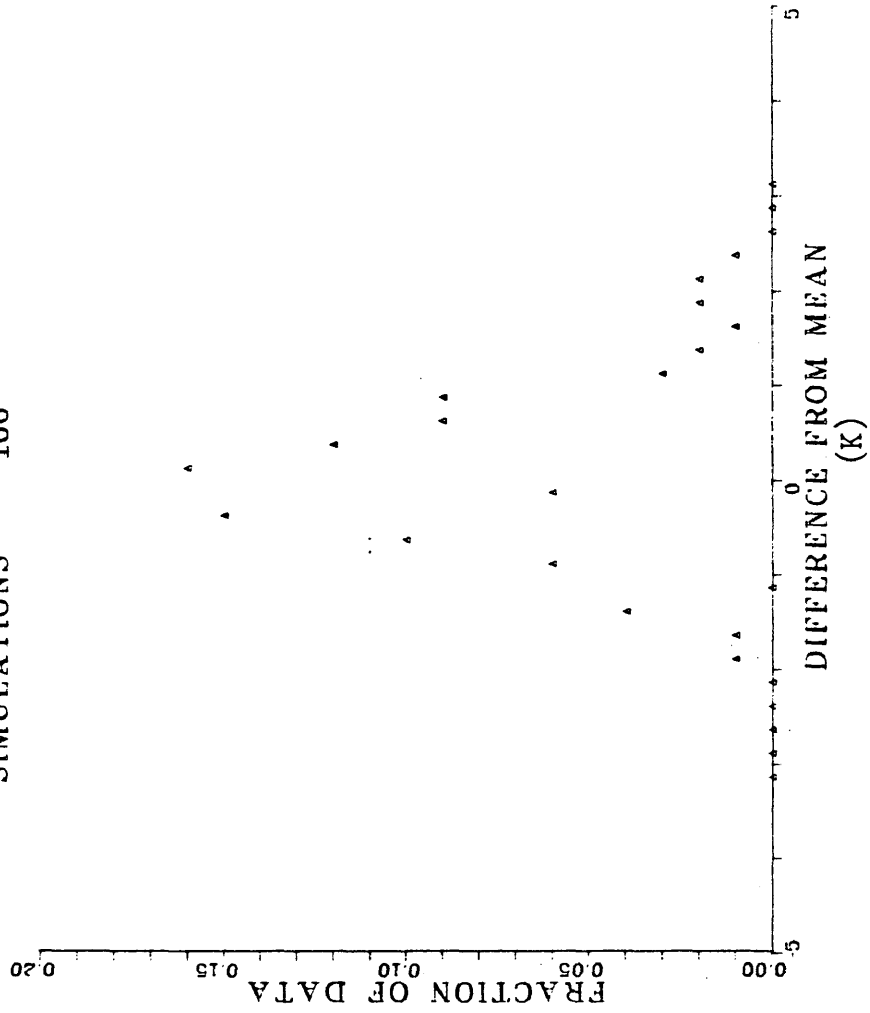
from the least squares regression routine.

The resulting intercepts and slopes along with the standard deviations obtained from the regression analysis are used in the Monte Carlo program to generate a number of "mean" dielectric measurements for each of the two lines. The dielectrics are generated using a number of temperatures at one degree intervals on each side of the "break" temperature. The "mean" dielectric measurements are then used, along with their corresponding standard deviation obtained from the regression routine, to generate random normally distributed measurements around each mean. A linear regression routine is then employed to refit the generated data to a new line. The resulting two new lines are then similarly analyzed to generate a new "break" temperature about its mean. Finally, one can repeat the procedure many times, thus allowing the corresponding variance of the experimentally determined hydrate equilibrium temperature to be estimated. Figures 18, 19, 20, and 21, show the distribution of a "break" temperature for a single experimental point as a function of the number of simulations.

The variance of the water concentration of the liquid hydrocarbon in equilibrium with hydrate was determined using a second Monte Carlo type error analysis and the resulting

Figure 18

REGRESSION TEMPERATURE DISTRIBUTION
SIMULATIONS - 100



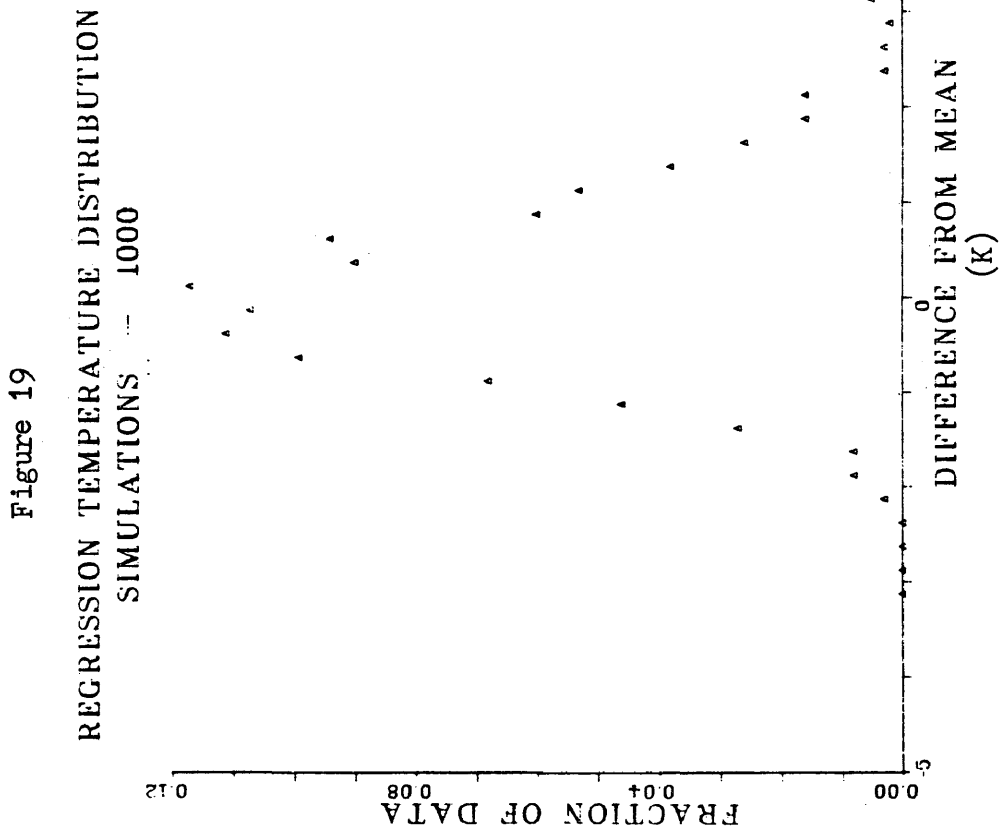


Figure 20

REGRESSION TEMPERATURE DISTRIBUTION
SIMULATIONS - 10000

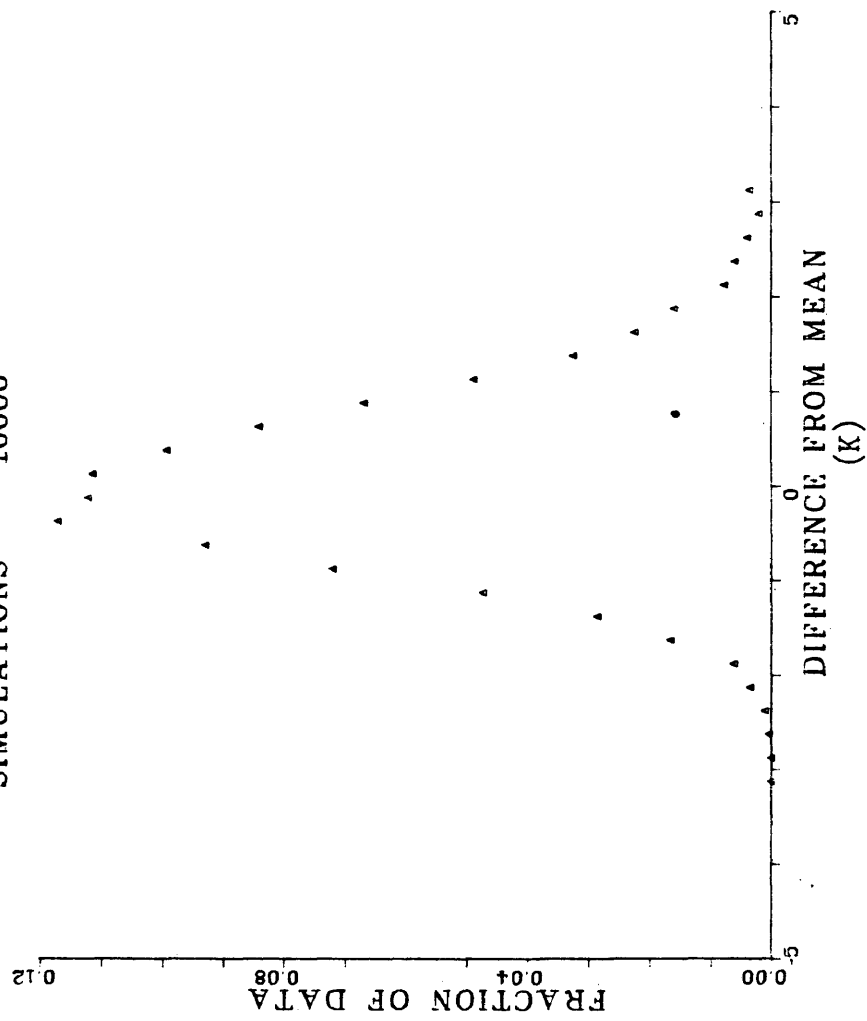
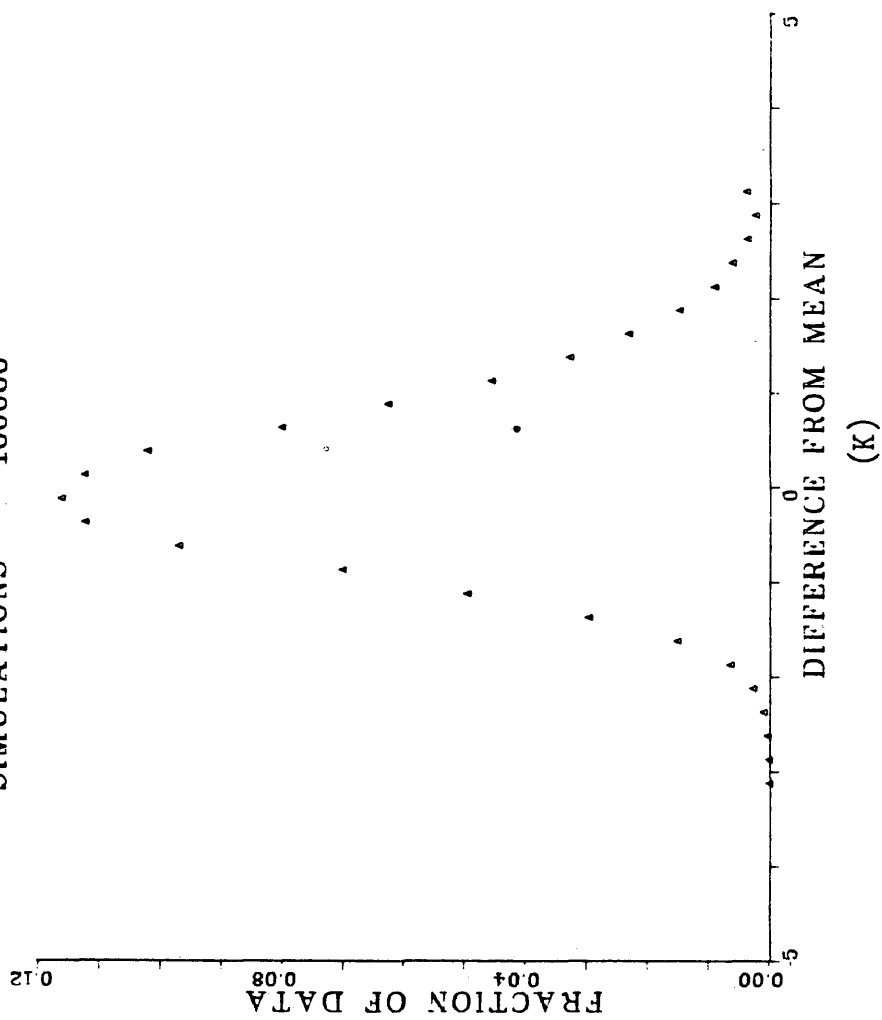


Figure 21

REGRESSION TEMPERATURE DISTRIBUTION
SIMULATIONS - 100000



standard deviation of the "break" temperature found from the first Monte Carlo routine. The water concentration calculation is performed many times using estimated variances of the measured system variables assuming each to be normally distributed with a mean of the actual measured value. The resulting concentration distribution for a single experimental point is shown as a function of the number of simulations in Figures 22, 23, 24, and 25. It is important to note that the standard deviation obtained from this analysis is identical to that obtained using the traditional propagation of errors.

The generation of random normally distributed variables is discussed by Martin (1968) and Weiler (1983). Additional information regarding Monte Carlo type analyses is presented by Hammersley (1964).

SENSITIVITY ANALYSIS

The effect each independent variable contributed to the error of the dependent variable, the water concentration, was evaluated using the Monte Carlo routine used in determining the total error of the dependent variable. The sensitivity was studied by setting the variance of each independent variable equal to zero, except for the variable being studied. The results of the sensitivity analysis are shown in Figure 26.

Figure 22

CONCENTRATION DISTRIBUTION
SIMULATIONS - 100

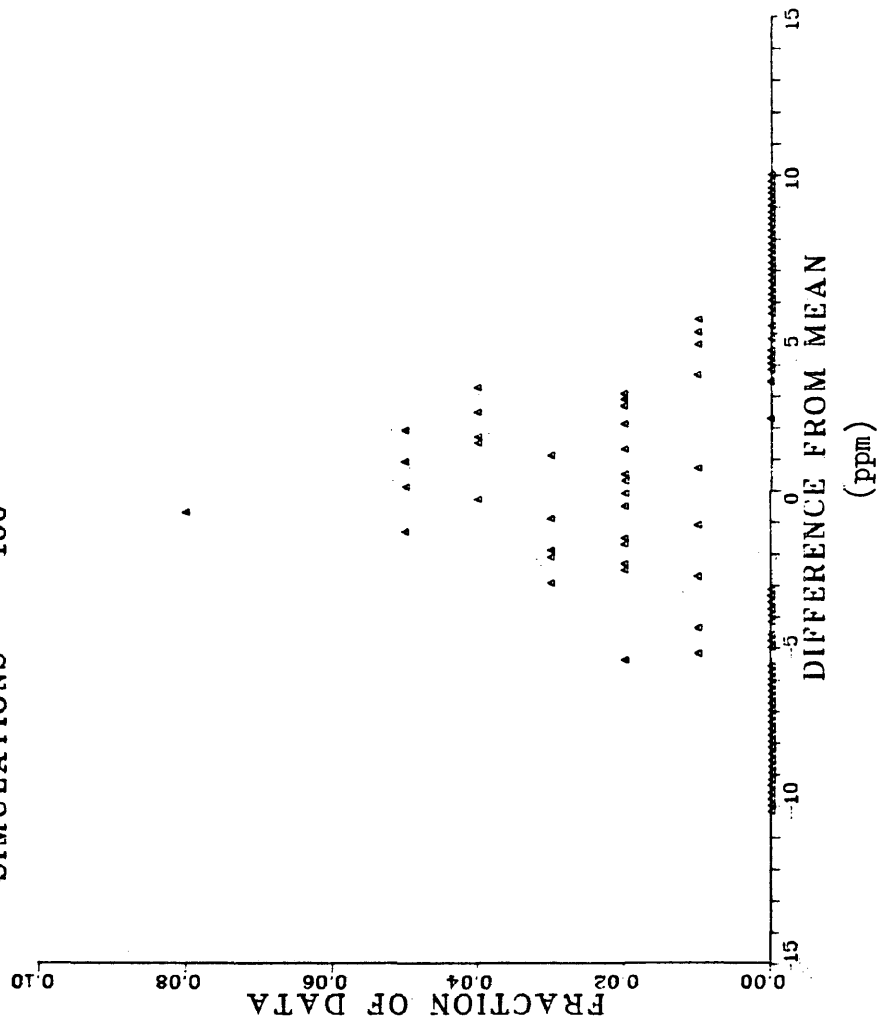


Figure 23

CONCENTRATION DISTRIBUTION
SIMULATIONS - 1000

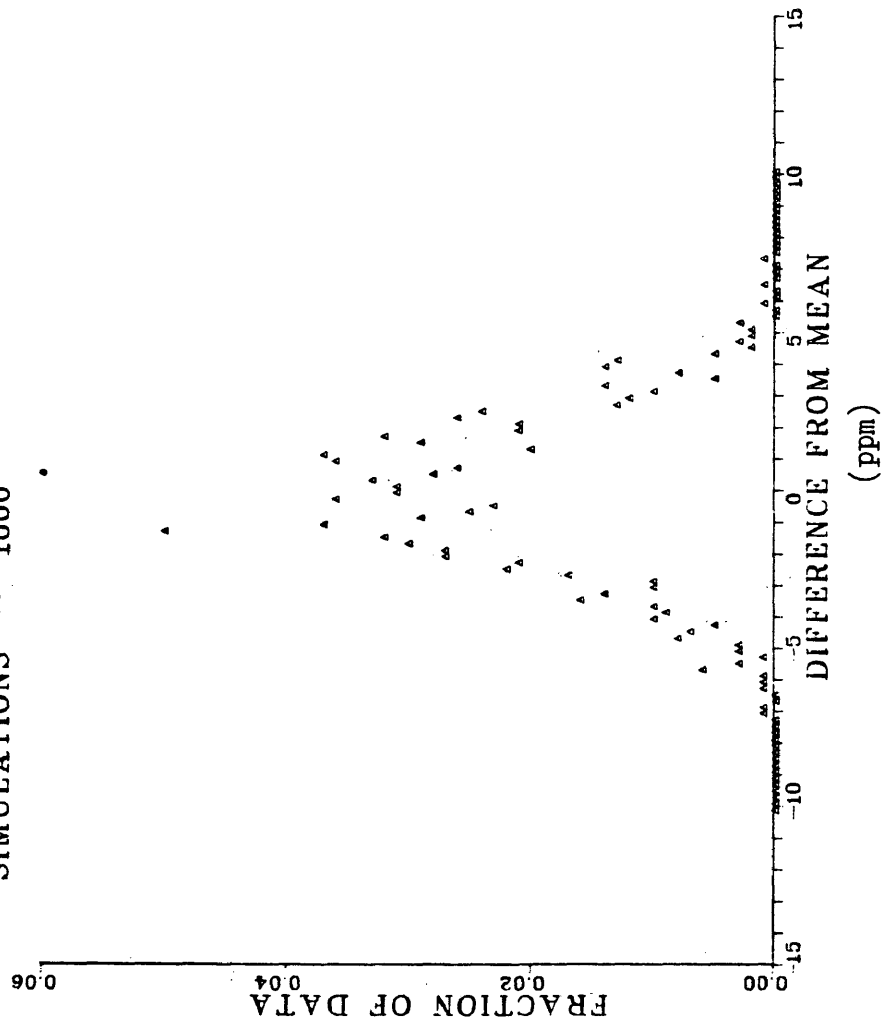


Figure 24

CONCENTRATION DISTRIBUTION
SIMULATIONS - 10000

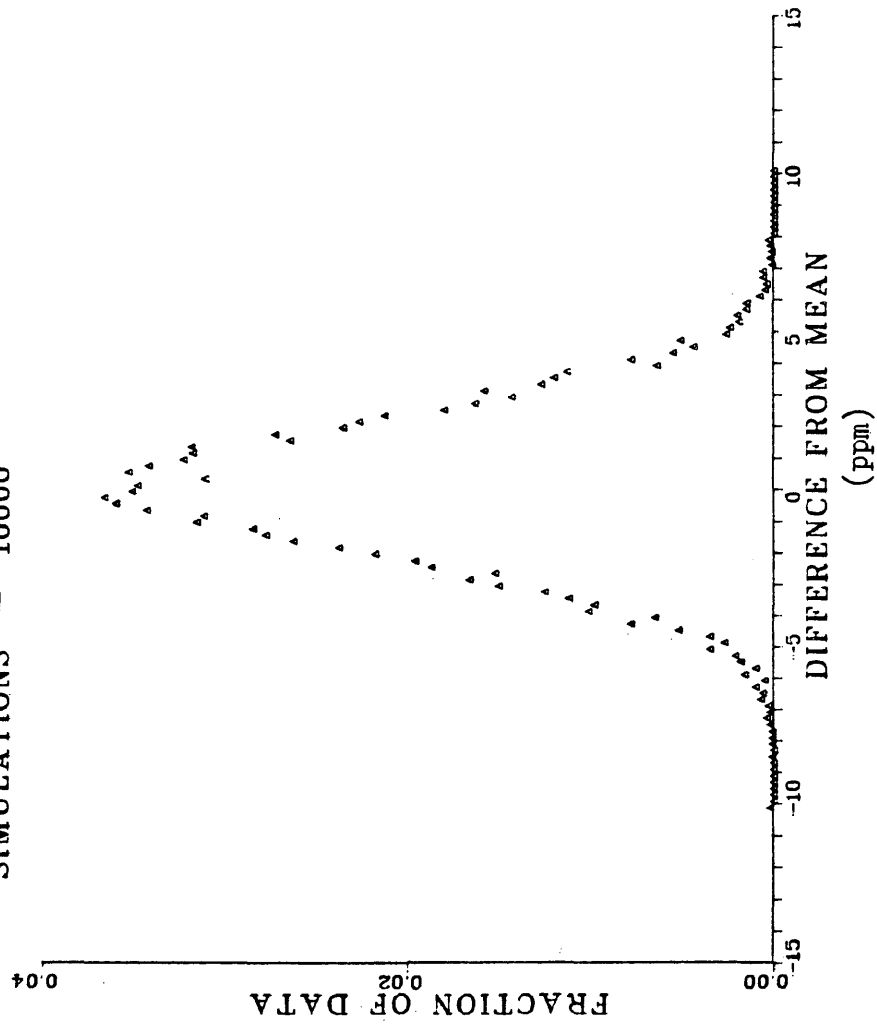


Figure 25

CONCENTRATION DISTRIBUTION
SIMULATIONS - 100000

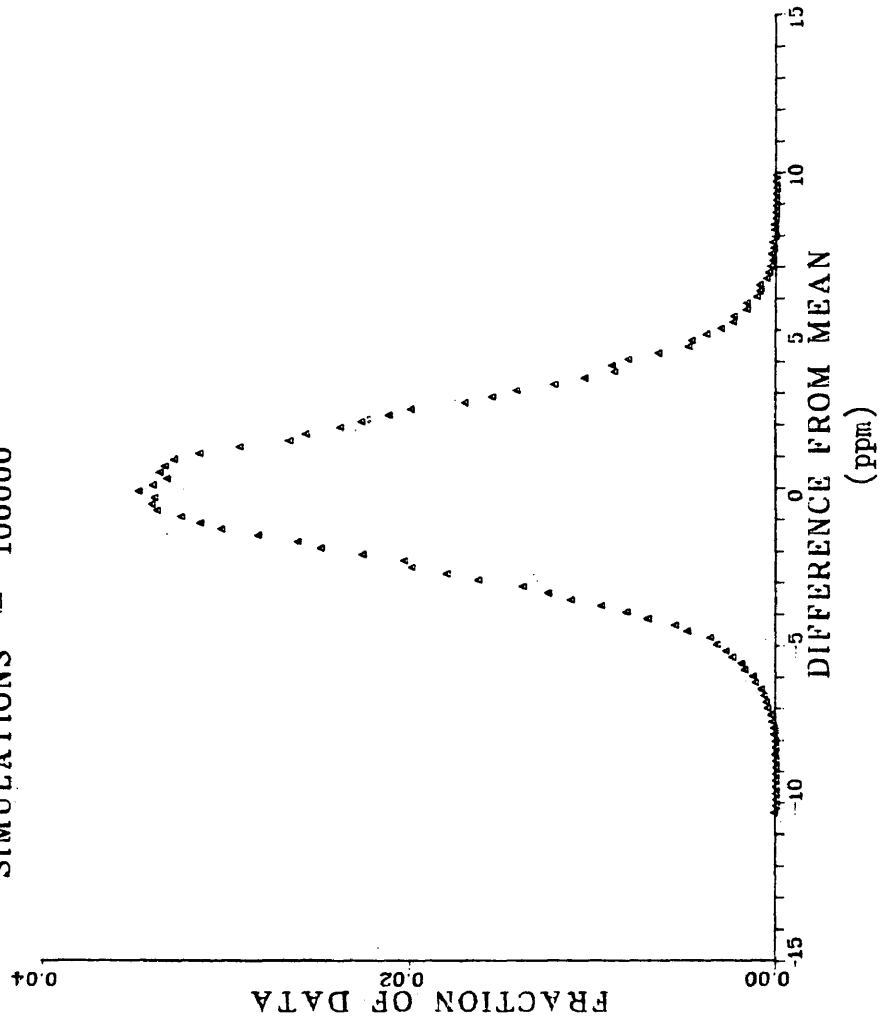
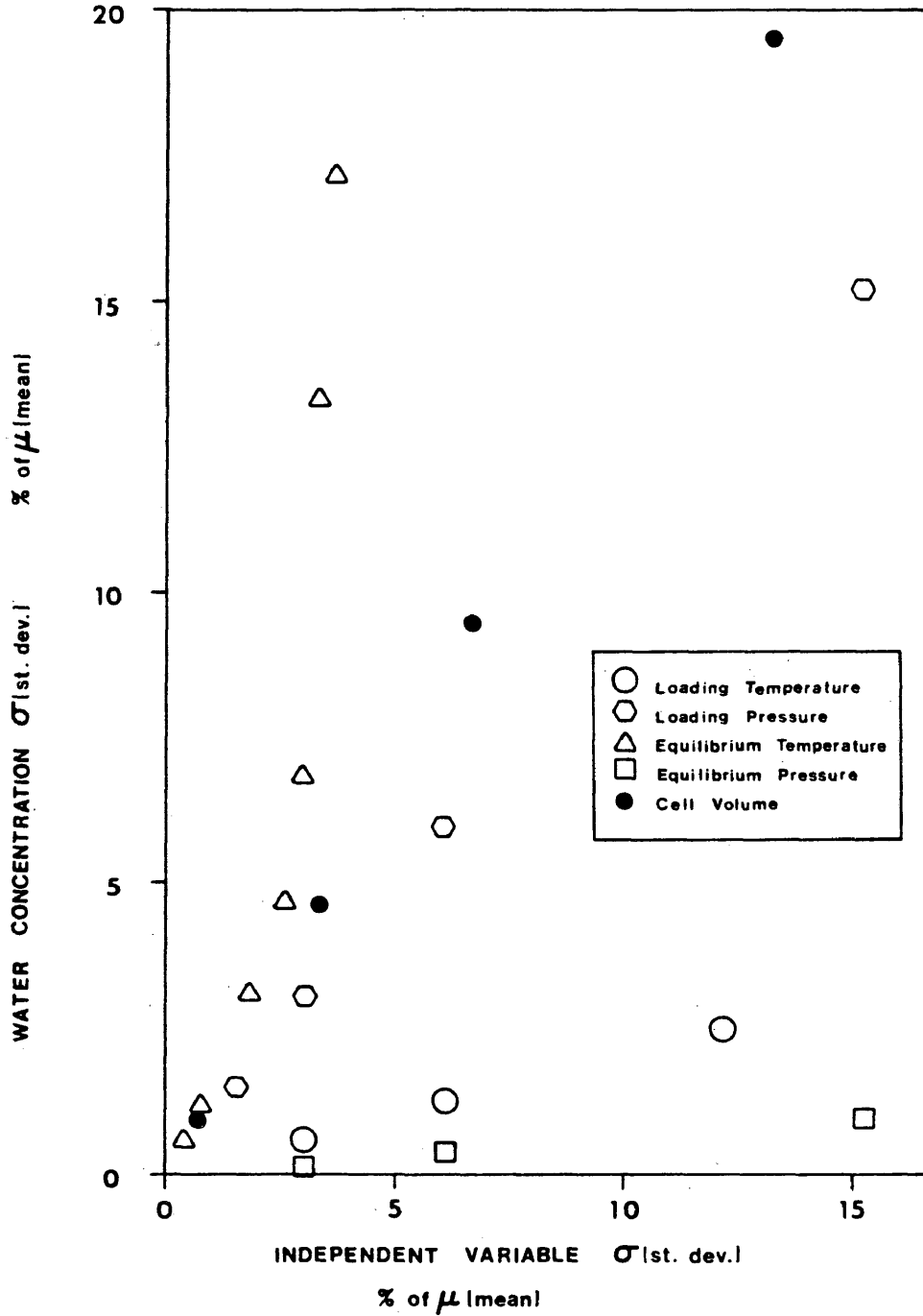


Figure 26

SENSITIVITY OF CONCENTRATION ERROR

Monte-Carlo Analysis (5000 simulations)



RESULTS

The reported data represent the first taken with the intent of measuring the water content of liquid hydrocarbon in equilibrium with hydrate. The importance of this objective is discussed subsequently. Table 11 and Figure 27 present the experimental water content of condensed ethane in equilibrium with Structure I hydrate. Table 12 and Figure 28 present the experimental water content of condensed propane in equilibrium with Structure II hydrate. The solid lines represent the predicted values. A simple empirical equation best representing the isobaric water concentration data for both experimental systems on a molar basis is given as follows:

Ethane-Water System (500 psia)

$$\log_{10} X(\text{ppm}) = 10.8943 - 2426.900/T(\text{K}) \quad (18a)$$

Temperature Range: 271 K to 259 K

Propane-Water System (112 psia)

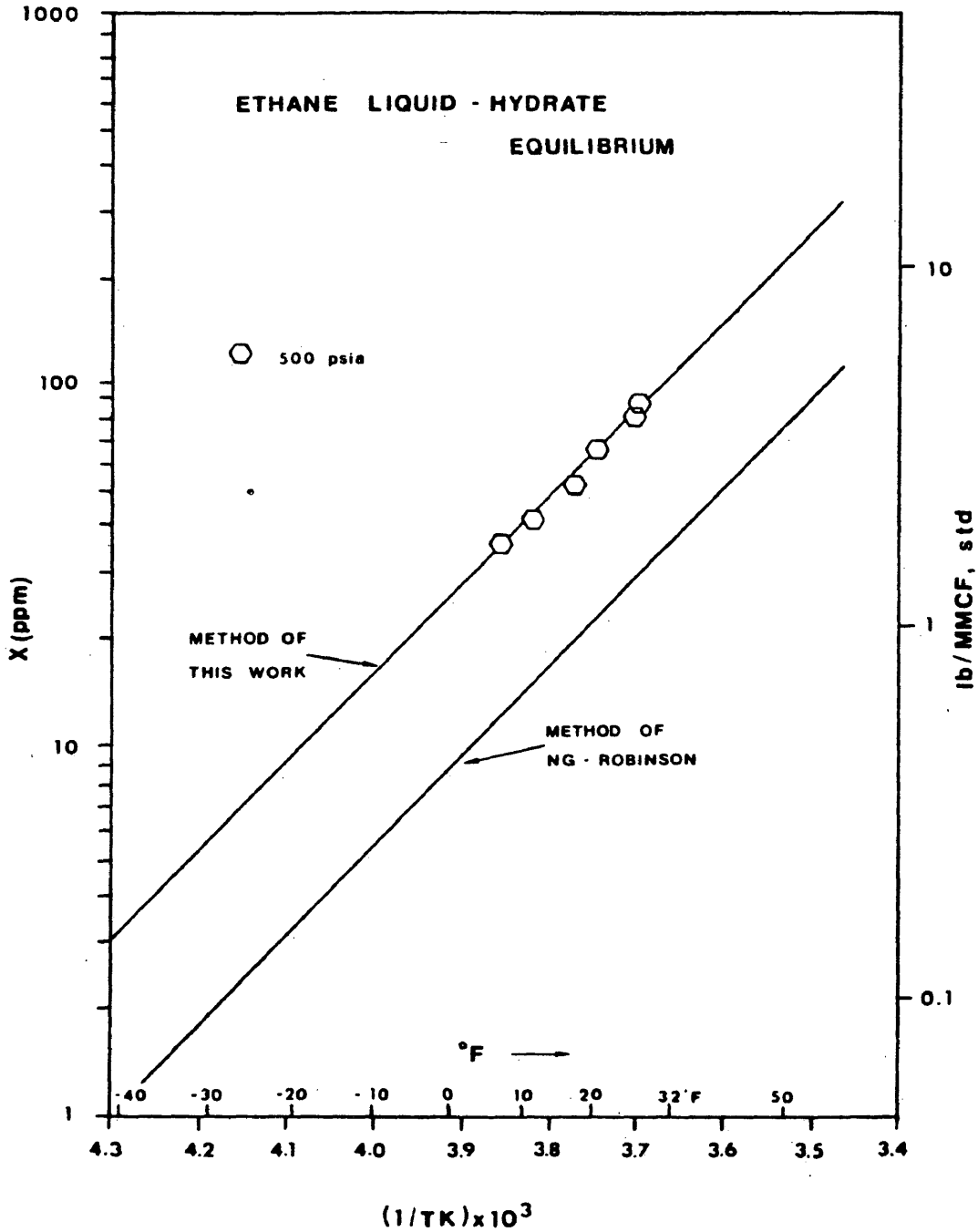
$$\log_{10} X(\text{ppm}) = 10.4573 - 2276.296/T(\text{K}) \quad (18b)$$

Temperature Range: 277 K to 246 K

An elevated pressure data point, specifically at 262 psia, was measured for the propane-water system, which was not statistically different from that at low pressure. Two

Table 11
ETHANE LIQUID - HYDRATE EQUILIBRIUM
System Pressure
500 psia(3447 kPa)

TEMPERATURE K / °F		EXPERIMENTAL CONCENTRATION (PPM)	PREDICTED CONCENTRATION (PPM)
270.45	/ 27.14	86.21 ± 5.38	82.31
270.00	/ 26.33	79.99 ± 4.98	79.57
266.70	/ 20.39	62.71 ± 3.93	61.88
264.87	/ 17.10	50.90 ± 3.15	53.73
261.74	/ 11.46	41.60 ± 2.59	42.07
259.1	/ 6.78	34.79 ± 2.16	34.21

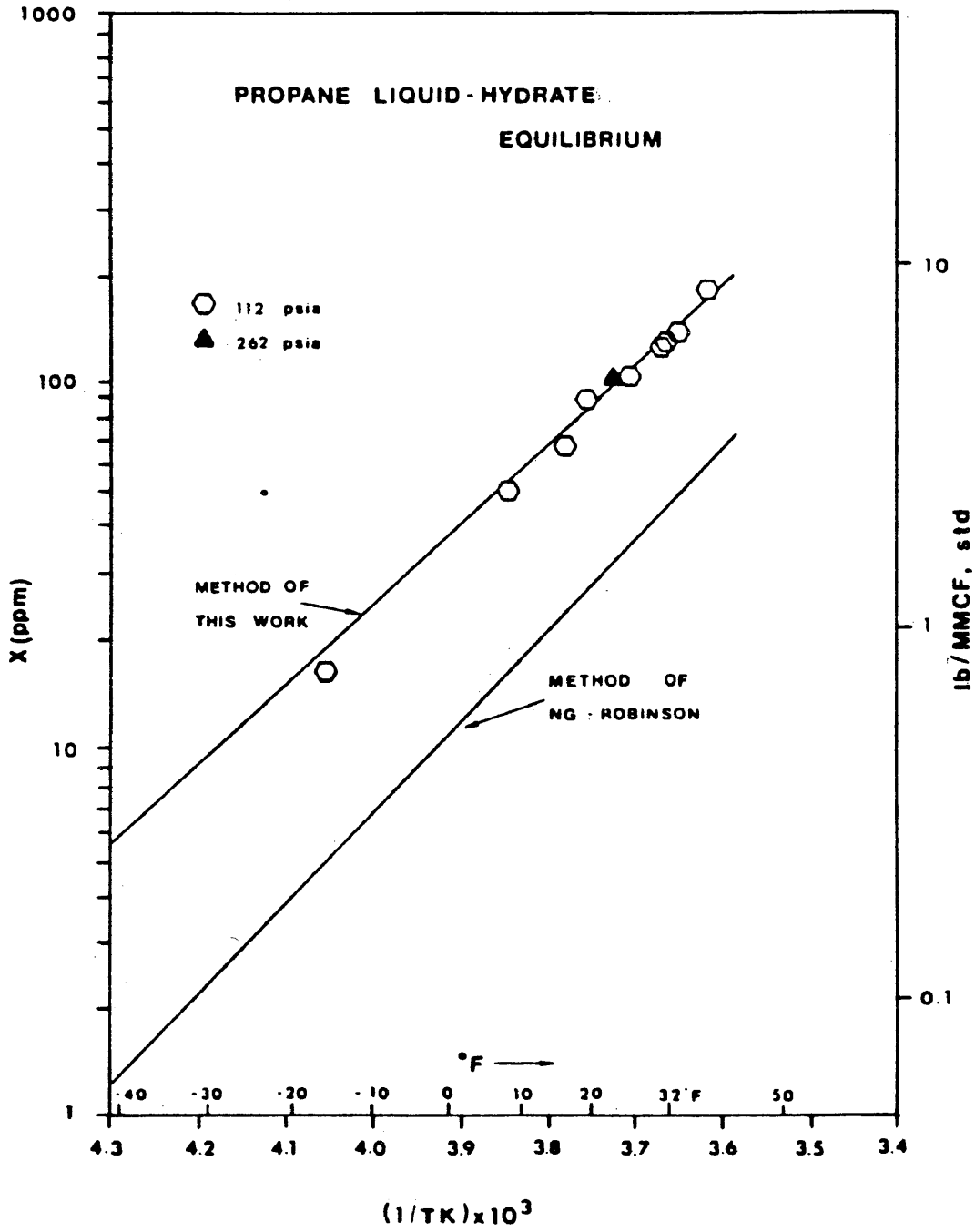


Ethane Liquid-Hydrate Equilibrium

Figure 27

Table 12
 PROPANE LIQUID - HYDRATE EQUILIBRIUM
 System Pressure
 112 psia(772 kPa)

TEMPERATURE K / °F	EXPERIMENTAL CONCENTRATION (PPM)	PREDICTED CONCENTRATION (PPM)
276.43 / 37.90	176.06 ± 10.60	168.29
273.94 / 33.42	136.89 ± 8.20	142.24
272.95 / 31.64	125.78 ± 7.54	132.95
272.16 / 30.22	123.92 ± 7.46	125.94
269.87 / 26.10	102.50 ± 6.29	107.47
266.00 / 19.13	87.62 ± 5.39	81.78
264.32 / 16.11	65.68 ± 4.03	72.48
259.88 / 8.11	50.45 ± 3.08	52.35
246.66 / -15.68	16.92 ± 1.81	18.73
268.50 / 23.63	101.92 ± 6.25	96.60



Propane Liquid-Hydrate Equilibrium

Figure 28

attempts were made at measuring the pressure effect on the ethane-water system, specifically at 800 psia, but dielectric measurement problems were encountered. The predicted pressure effect for the ethane-water system is small, similar to that measured and predicted for the propane-water system.

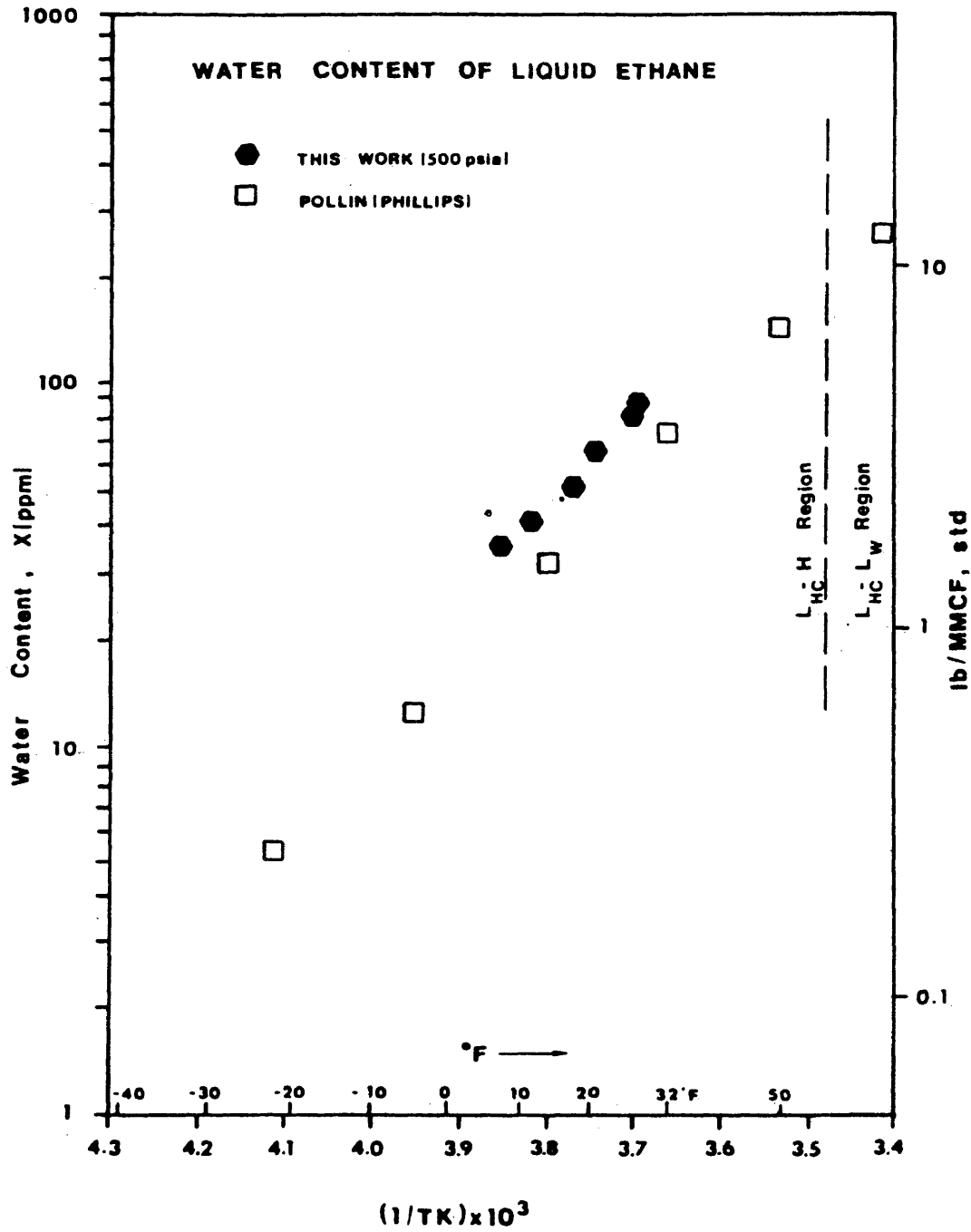
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DISCUSSION

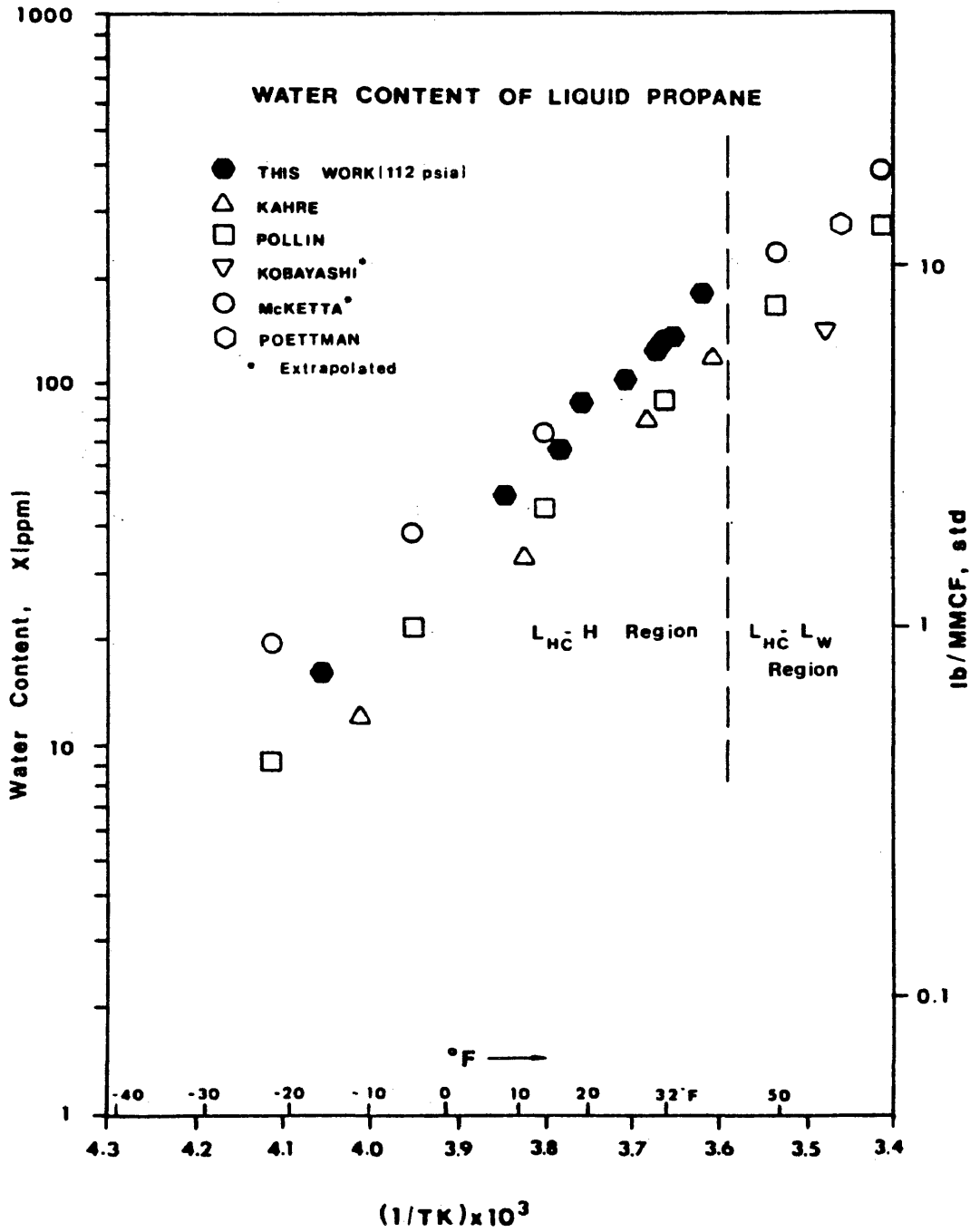
The purpose of this experimental work was to determine the water content of liquid ethane and propane in two-phase equilibrium with hydrate. The knowledge of this data enables one to avoid hydrate formation in the various aspects of natural gas liquid processing.

Water solubility data exist which inadvertently extend into the two-phase, liquid hydrocarbon-hydrate region. The data are shown in Figures 29 and 30. The propane data of Kahre (1964) and the ethane and propane data of Pollin et. al. (1982), both of Phillips Petroleum Company were taken without explicit planning for the possible existence of hydrate equilibrium, especially with regard to possible metastability and occlusion. Kobayashi and Katz (1955) indicate that without careful planning for hydrate equilibrium, experimental error can occur. No conclusive reason has been found to explain why the data of Phillips investigators fall below the data of this work.

The water solubility data of Pollin (1982) are presented in Table 13. Table 14, presents the solubility data of Kahre (1964). Portions of the data of Pollin and Kahre extend into the metastable hydrate region. Kobayashi's (1951) data concerning the concentration of water in the saturated propane-rich liquid phase in



Water Content of Liquid Ethane
 Figure 29



Water Content of Liquid Propane
Figure 30

Table 13
WATER SOLUBILITY OF LIQUID ETHANE & PROPANE
Parrish, Pollin, and Schmidt (1982)

Temp. °C.	Water Mole Fraction(ppm)	
	Ethane	Propane
-30	5.2	9.2
-20	12.6	21.2
-10	32.0	44.5
0	72	88
10	142	160
20	258	265
25	324	354
30	415	452

Table 14
SOLUBILITY OF WATER IN LIQUID PROPANE
Kahre (1964)

Temp. °C.	Water Mole Fraction(ppm)
-24	12
-12	33
-1.5	80
4	118

equilibrium with a water-rich liquid phase and a propane-rich vapor phase are given in Table 15. Table 16, gives the Poettman (1946) data of the water content of saturated liquid propane. The data of McKetta (1957) was presented graphically and is therefore not shown separately in this work.

In Figure 30, for propane the data of McKetta and coworkers (1957) was extrapolated from the liquid-liquid region into the liquid-hydrate region. From this extrapolation, two things can be noted: 1) the data of the present work fall below the McKetta data as they should, and 2) the straight line of the data of this work in the liquid-hydrate region intersects the straight line of the extrapolated McKetta data at the quadrupole point temperature, the dashed line in Figure 30. The results of Poettman and Dean (1946) appear to confirm the data of this work in a similar manner. The Phillips data lie below the McKetta data, and the data of this work. In Figure 30 the single data point of Kobayashi was extrapolated from a concentration 82 ppm higher.

The prediction of the two-phase hydrate equilibrium using the predictive method of this work shows satisfactory agreement with the experimental data as shown in Tables 11 and 12. The results using the method of Ng and Robinson

Table 15
CONCENTRATION OF WATER IN THE
SATURATED PROPANE-RICH LIQUID PHASE
Kobayashi (1951)

Temperature (°F)	Pressure (psia)	Mole Fraction Water (ppm)
58.4	107.1	136.8
78.5	142.5	334.0
101.9	195.0	614
128.5	272	1368
144.6	330	1995
170.0	438	3555
171.0	443	3682

Table 16
WATER CONTENT OF PROPANE
Poettman and Dean (1946)
Saturated Liquid Phase

Temp. °F.	Mole Percent Water
60	0.0269
80	0.0469
100	0.0682
100	0.0745
140	0.1569
177	0.4700
180	0.4597
184	0.4829
187	0.5399

(1980) to determine f_w^{MT} predict values systematically lower than the data of this work.

CONCLUSIONS

The following conclusions are based on the results of this experimental work.

1. The water content of liquid ethane in equilibrium with Structure I hydrate at a pressure of 500 psia has been successfully determined.
2. The water content of liquid propane in equilibrium with Structure II hydrate at a pressure of 112 psia has been successfully determined.
3. A two-phase hydrate prediction program has been written and tested using both the method formulated by Ng and Robinson (1980) and the method formulated by Dharmawardhana (1980) for the determination of the fugacity of water in the empty hydrate.
4. The predictions based upon the work of Dharmawardhana (1980) show close agreement with the experimentally determined values.
5. The predictions based upon the work of Ng and Robinson (1980) are systematically low in regard to the experimental values.
6. The oscillometric methods formulated in this work, for the determination of two-phase liquid hydrocarbon-water hydrate equilibrium conditions, has been successfully tested.

RECOMMENDATIONS

The following recommendations are based upon this experimental work.

1. The addition of a Ruska type hand pump would eliminate the vapor phase above the liquid mixture and allow the pressure of the system to be more accurately controlled.
2. The addition of an electronic pressure transducer to the capacitance cell would allow one to minimize the volume above the cell previously required for the measurement of system pressure.
3. The extension of this experimental method to NGL mixtures would allow one to examine the results of currently existing two-phase hydrate prediction techniques involving mixtures.
4. The method formulated by Dharmawardhana (1980) should be used for determining the fugacity of water in the empty hydrate.

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APPENDIX A

INSTRUMENT CALIBRATION

.

TEMPERATURE CALIBRATION

The Doric temperature sensor was calibrated against a Leeds and Northrup 4-lead nominal 25 ohm platinum resistance thermometer in conjunction with a Leeds and Northrup model 8069 Mueller Bridge. A fourth order polynomial was generated by Johnson (1981) to correct the temperature as measured by the Doric instrumentation. The relationship is given below:

$$T = T_m + 0.994377E-2 + 0.29582E-2 \times T_m \\ - 0.66030E-4 \times T_m^2 - 0.17229E-5 \times T_m^3 \\ + 0.27143E-7 \times T_m^4$$

T = Actual Temperature (°C)

T_m = Measured Temperature (°C)

PRESSURE CALIBRATION

The Barocel Pressure Sensor used in conjunction with the Datametrics Electronic Manometer was recalibrated against a high quality mercury manometer. The reference ports of the Barocel manometer and the mercury manometer were joined together with stainless steel tubing. The entire system was evacuated and differential pressures were obtained by injecting air into one side of the calibration assembly. A high precision cathatometer was used to measure

the mercury levels of the mercury manometer. The density of mercury was adjusted to 0 °C. The results of the calibration are shown in Figure 31. The following linear equations describe the calibration of the Barocel pressure sensor:

Range	Equation
0 - 30 torr	$P = P_m \times 0.985978 + 0.207593$
30 - 60 torr	$P = P_m \times 0.964443 + 1.459493$
60 - 100 torr	$P = P_m \times 0.990453 + 0.344983$
100 - 150 torr	$P = P_m \times 0.993366 - 0.034710$

P = Actual Pressure (torr)

P_m = Measured Pressure (torr)

The zero to three hundred psig Heise Bourdon tube pressure guage was calibrated with a Ruska Air Dead Weight Tester Model 2465-751-00 by Johnson (1981). The calibration was fit as a second order polynomial as shown below:

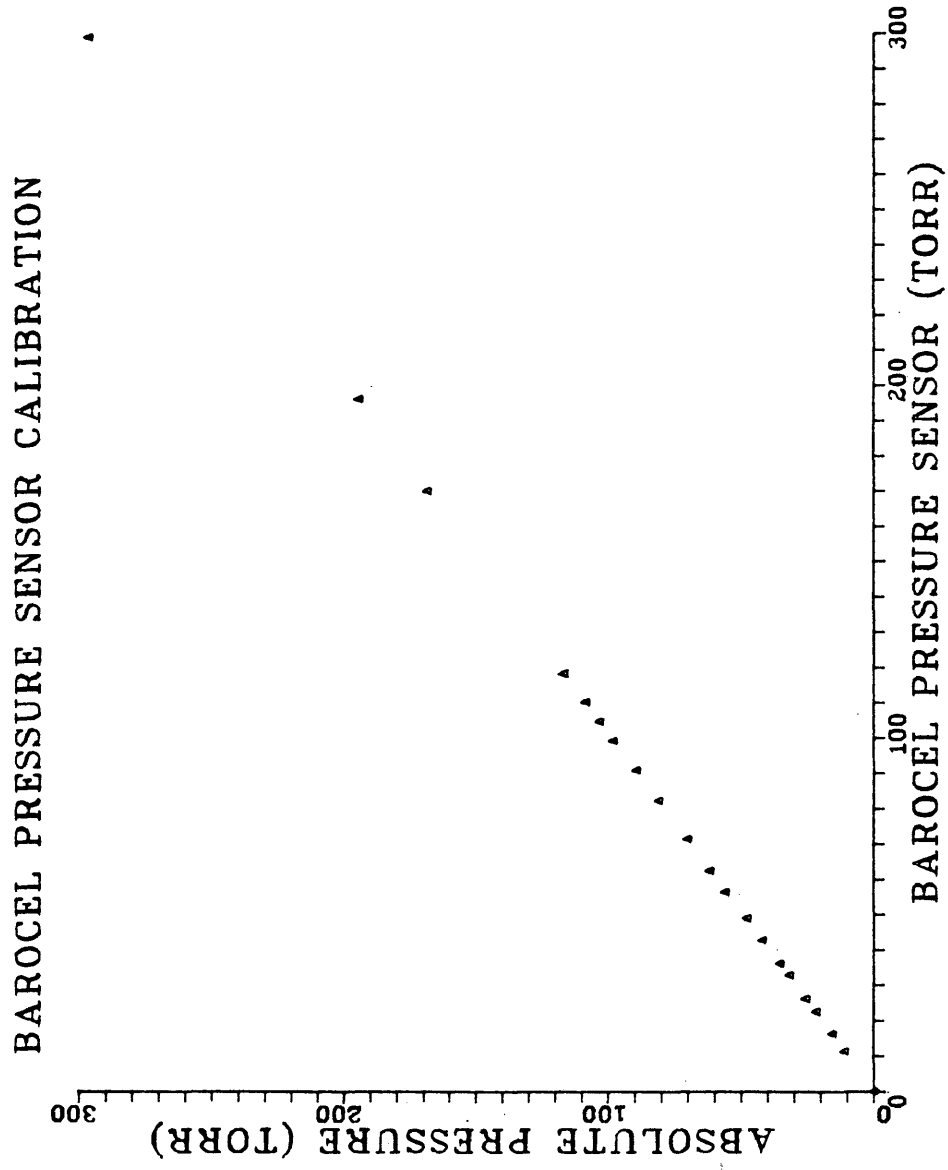
$$P = P_m - 0.20677 + 0.2953E-2 \times P_m - 0.43444E-5 \times P_m^2$$

P = Actual Pressure (psig)

P_m = Measured Pressure (psig)

The zero to one thousand psia Heise guage was

Figure 31



calibrated by Giussani (1981). The resulting calibration was fit to a second order polynomial. The expression is shown below:

$$P = 0.6801342 + 0.9936020 \times P_m + 0.0000073 \times P_m^2$$

P = Actual Pressure (psia)

P_m = Measured Pressure (psia)

CAPACITANCE MEASURING ASSEMBLY

The capacitance measuring assembly was calibrated against a General Radio Type 1404-B reference standard capacitor with a capacitance of 100.0001 ± 0.0005 pF. The capacitance measuring assembly was checked regularly with a General Radio Type 1404-C reference standard capacitor with a capacitance of 10.00005 ± 0.00005 pF.

APPENDIX B

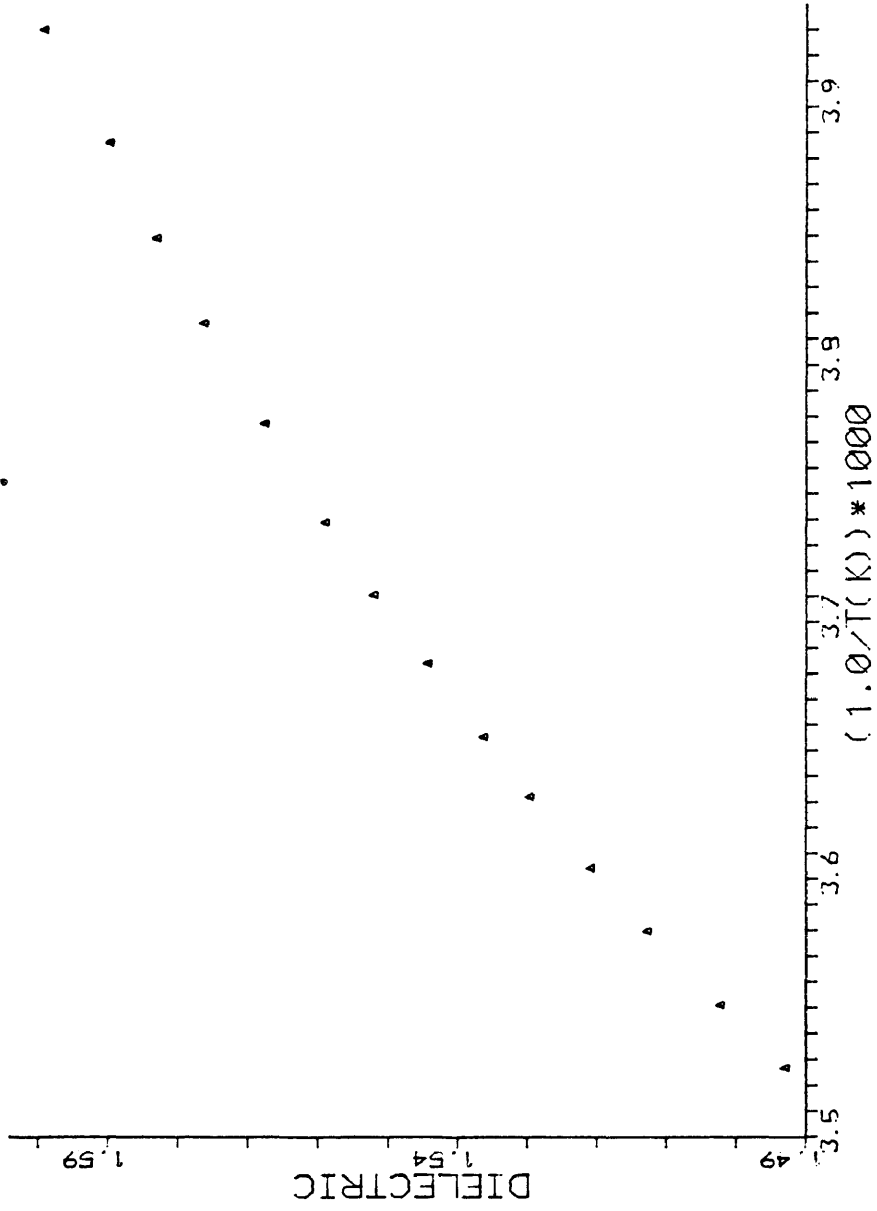
LIQUID ETHANE-WATER EXPERIMENTAL DATA

ETHANE-WATER (500 psia) Date: January 12, 1983
Water Loading System Temperature(°C) 72.01
Water Loading System Pressure(torr) 25.45

TEMPERATURE(K)	DIELECTRIC
283.55	1.49302
281.62	1.50227
279.37	1.51285
277.47	1.52099
275.34	1.52981
273.59	1.53639
271.45	1.54451
269.50	1.55223
267.48	1.55912
264.78	1.56771
262.08	1.57644
259.83	1.58317
257.35	1.58989
254.46	1.59926

ETHANE - 86.21 PPM WATER

500 psia (1-12-83)

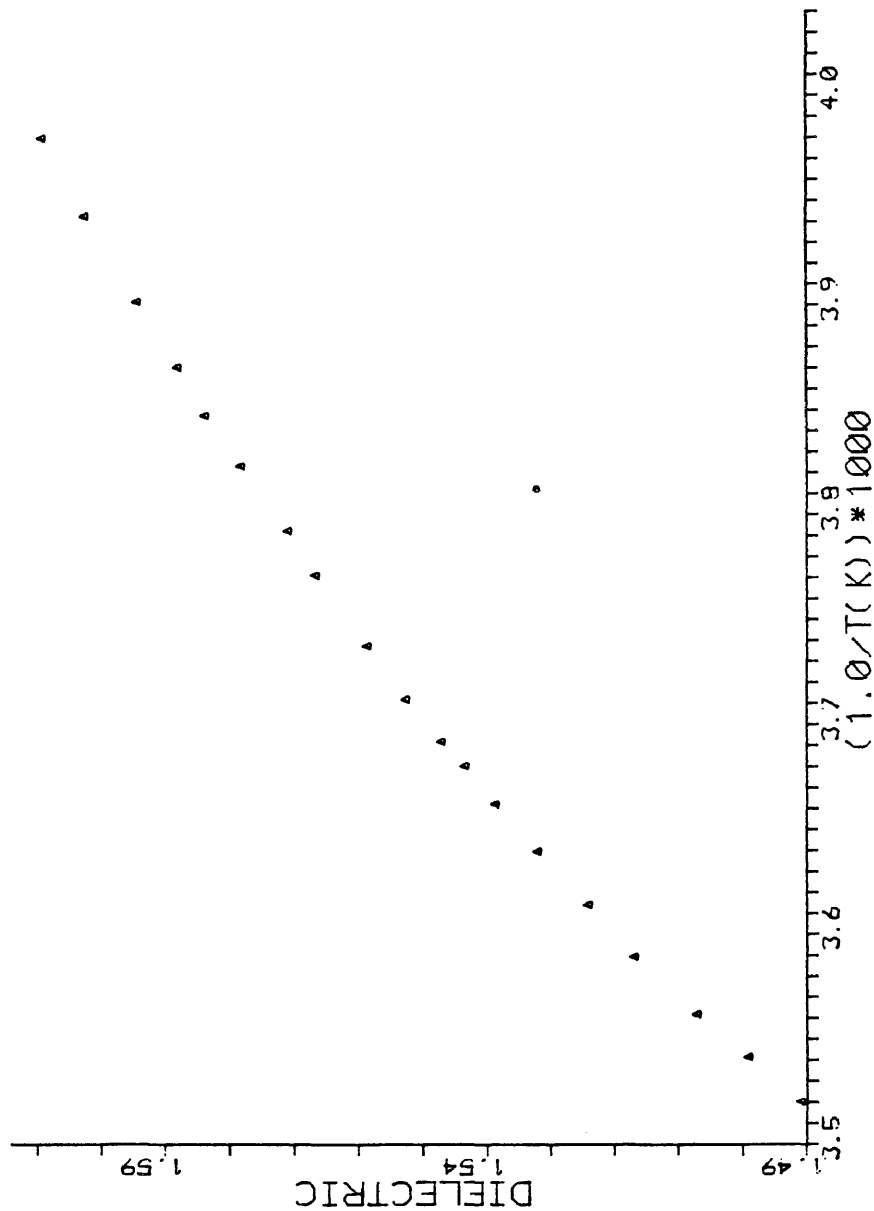


ETHANE-WATER (500 psia) Date: January 20, 1983
Water Loading System Temperature(°C) 71.31
Water Loading System Pressure(torr) 23.62

TEMPERATURE(K)	DIELECTRIC
284.08	1.49096
282.38	1.49915
280.78	1.50718
278.62	1.51700
276.71	1.52423
274.77	1.53218
273.08	1.53881
271.74	1.54363
270.88	1.54730
269.42	1.55278
267.59	1.55880
265.20	1.56682
263.72	1.57107
261.59	1.57850
259.94	1.58404
258.38	1.58829
256.33	1.59462
253.66	1.60275
251.32	1.60942

ETHANE - 79.99 PPM WATER

500 psia (1-20-83)



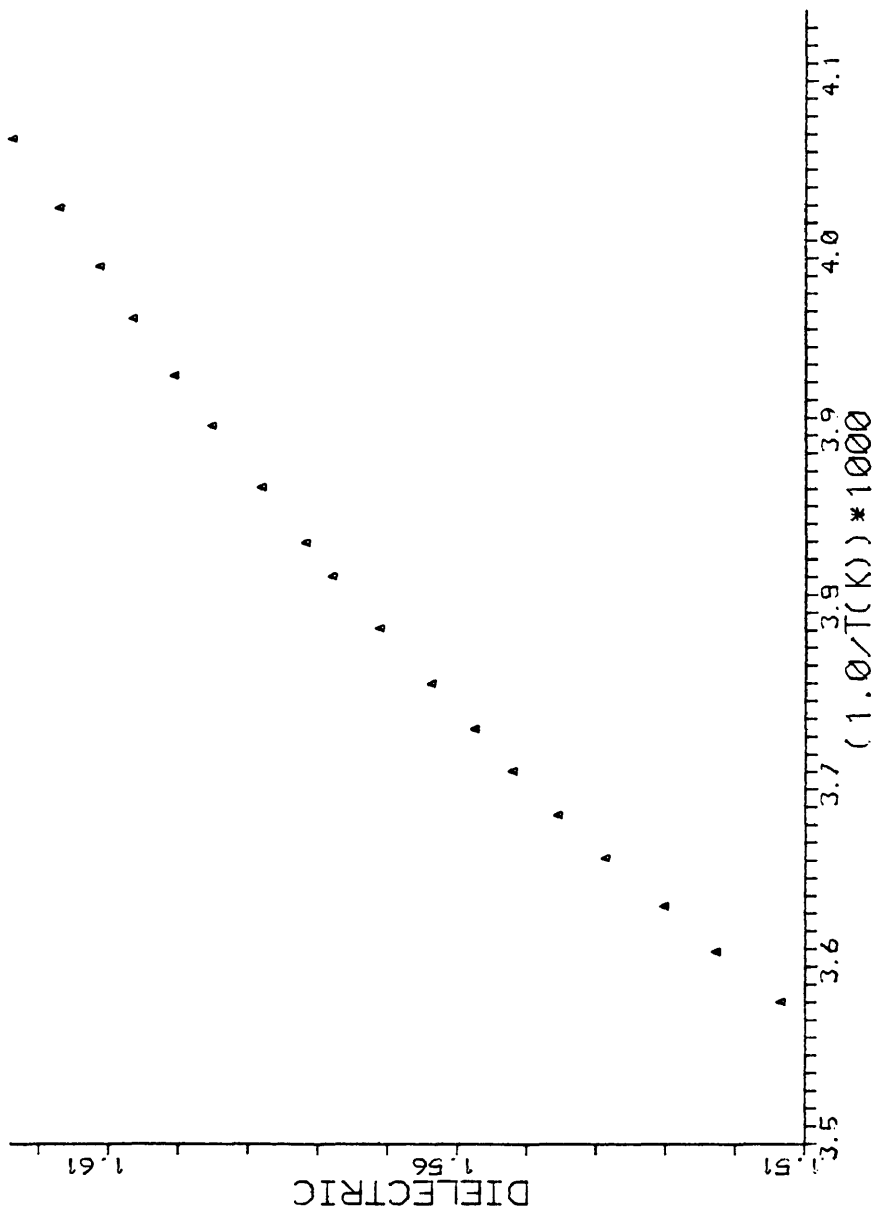
ETHANE-WATER (500 psia) Date: January 27, 1983
Water Loading System Temperature(°C) 72.64
Water Loading System Pressure(torr) 15.51

TEMPERATURE(K) DIELECTRIC

279.33	1.51342
277.15	1.52278
275.20	1.53020
273.15	1.53871
271.36	1.54554
269.55	1.55211
267.82	1.55761
266.00	1.56385
263.80	1.57121
261.77	1.57810
260.47	1.58189
258.38	1.58821
256.09	1.59526
254.26	1.60070
252.21	1.60666
250.35	1.61144
248.28	1.61721
245.90	1.62394

ETHANE - 50.9 PPM WATER

500 psia (1-27-83)



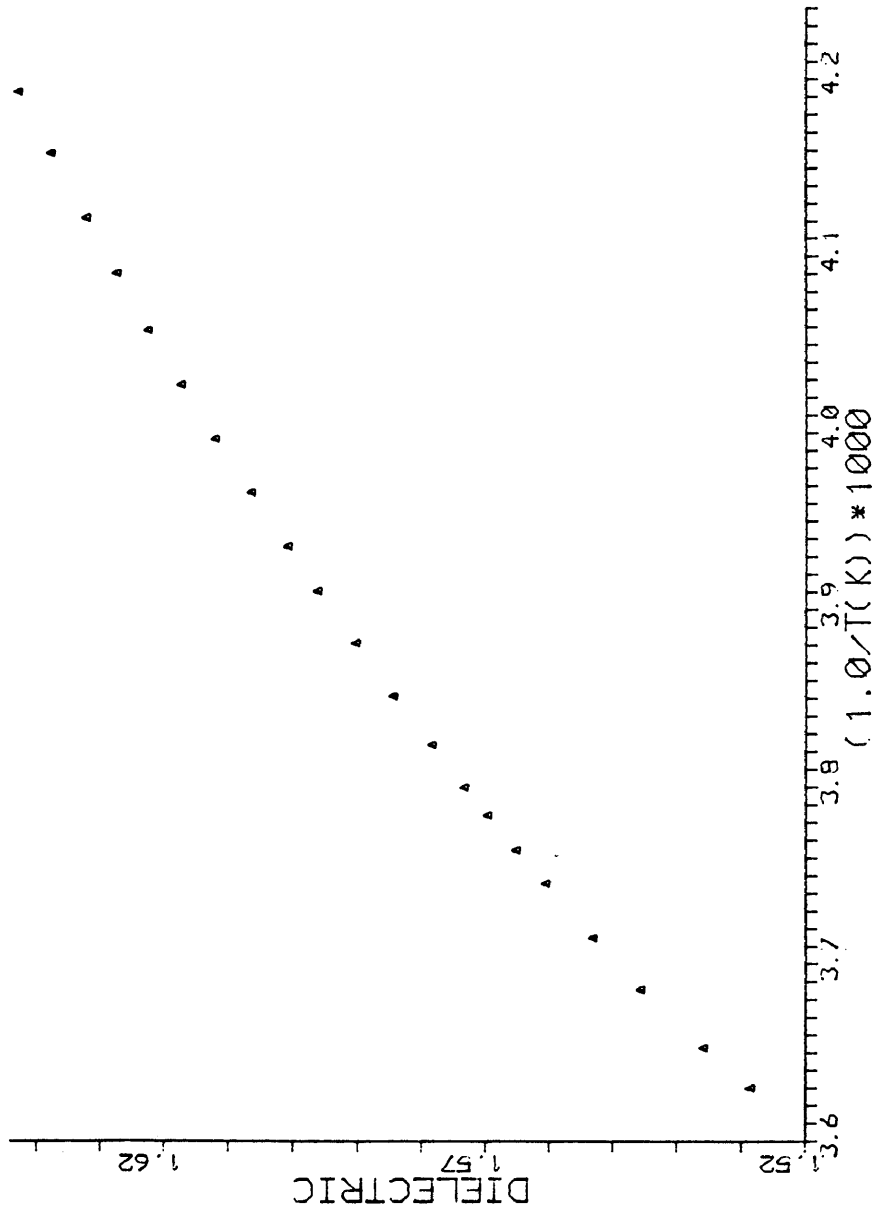
ETHANE-WATER (500 psia) Date: February 3, 1983
Water Loading System Temperature(°C) 73.94
Water Loading System Pressure(torr) 10.94

TEMPERATURE(K) DIELECTRIC

275.48	1.52863
273.77	1.53591
271.33	1.54569
269.20	1.55318
266.97	1.56060
265.64	1.56525
264.26	1.56976
263.16	1.57341
261.51	1.57851
259.66	1.58455
257.66	1.59036
255.74	1.59623
254.11	1.60090
252.16	1.60666
250.24	1.61227
248.33	1.61757
246.44	1.62276
244.49	1.62763
242.63	1.63244
240.50	1.63801

ETHANE -- 34.79 PPM WATER

500 psia (2-3-83)



ETHANE - WATER (500 psia) Date: February 16, 1983

Water Loading System Temperature(°C) 71.08

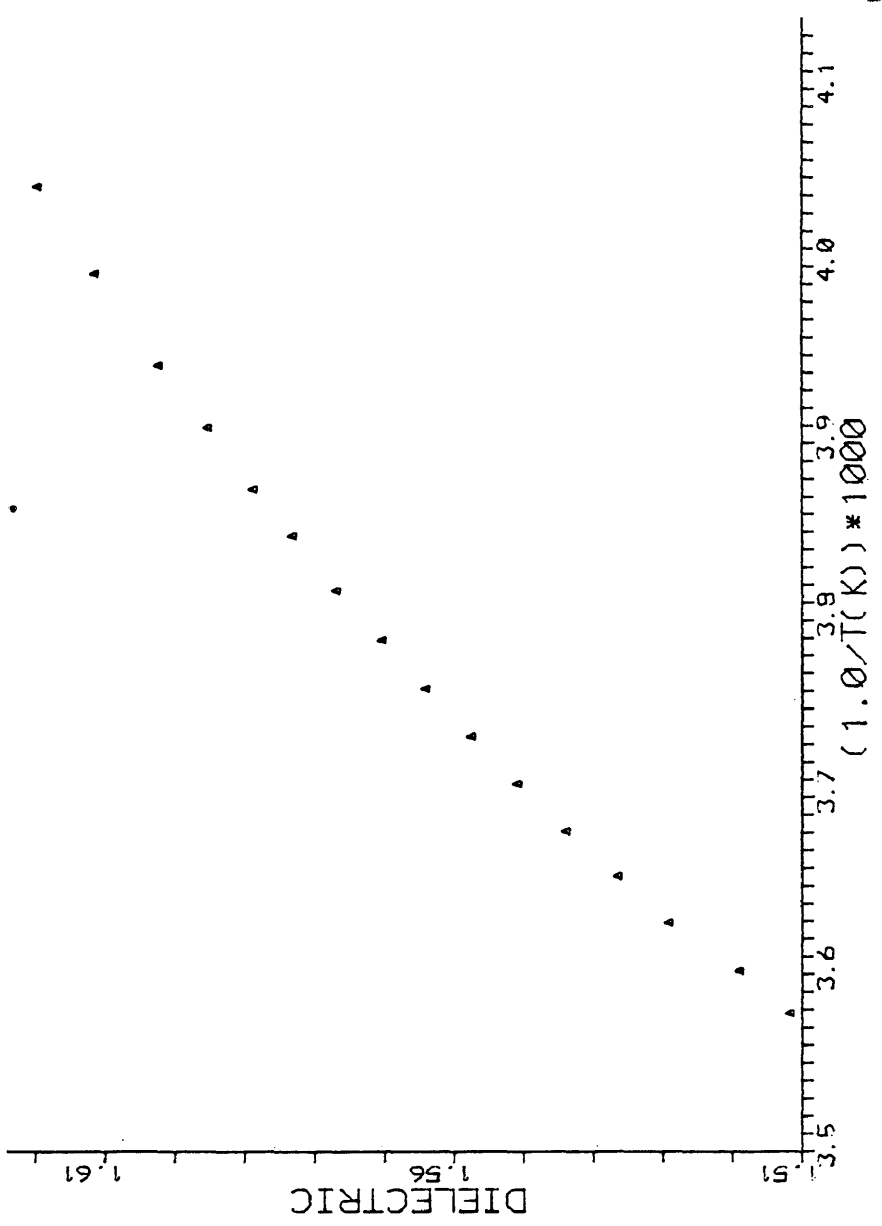
Water Loading System Pressure(torr) 18.84

TEMPERATURE(K) DIELECTRIC

279.50	1.51175
277.64	1.51896
275.56	1.52918
273.59	1.53653
271.70	1.54398
269.74	1.55098
267.80	1.55760
265.89	1.56427
263.96	1.57052
262.02	1.57705
259.91	1.58330
258.15	1.58900
255.85	1.59551
253.60	1.60247
250.31	1.61162
247.27	1.61986

ETHANE - 62.71 PPM WATER

500 psia (2-16-83)

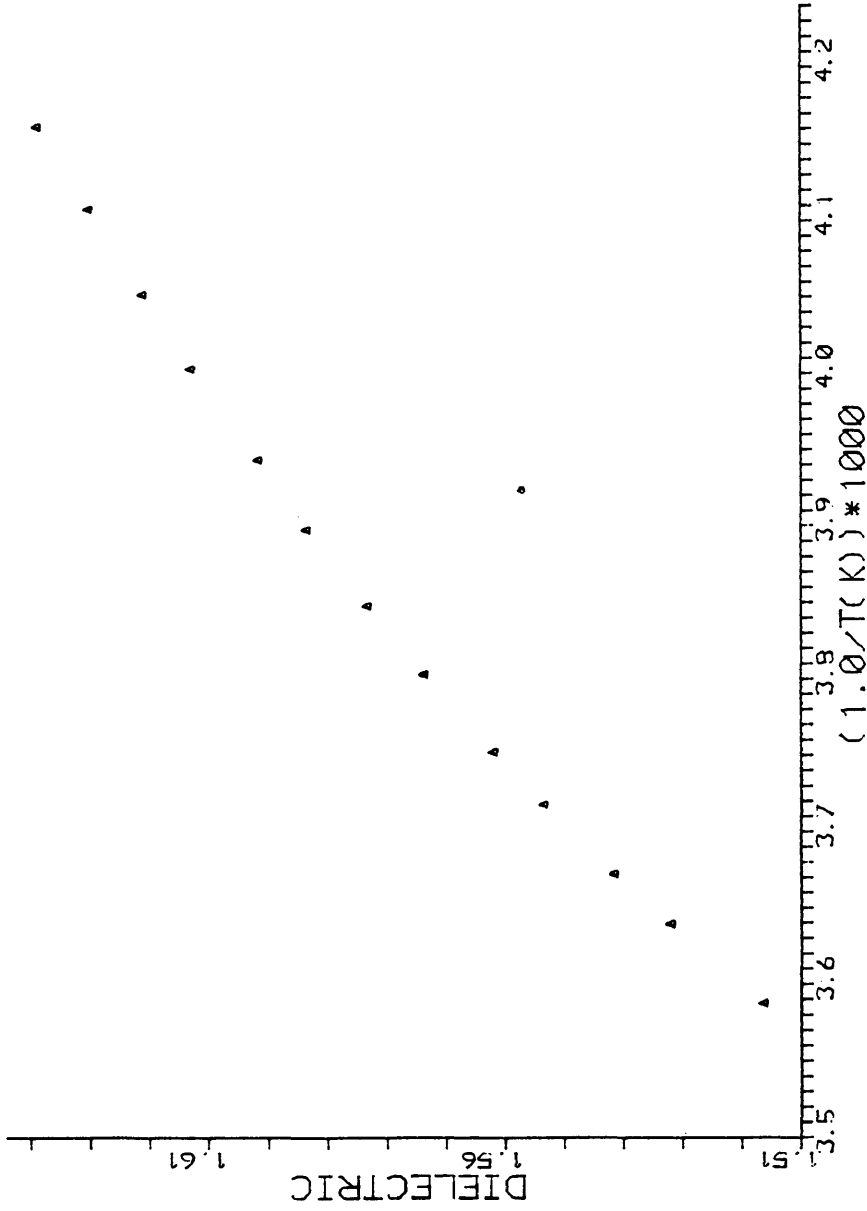


ETHANE - WATER (500 psia) Date: March 3, 1983
Water Loading System Temperature(°C) 74.93
Water Loading System Pressure(torr) 12.96

TEMPERATURE(K)	DIELECTRIC
278.74	1.51648
274.78	1.53217
272.32	1.54172
268.97	1.55363
266.50	1.56212
262.95	1.57395
259.90	1.58357
256.59	1.59369
253.62	1.60188
249.84	1.61316
246.82	1.62130
243.44	1.63036
240.29	1.63899

ETHANE - 41.60 PPM WATER

500 psia (3-3-83)



APPENDIX C

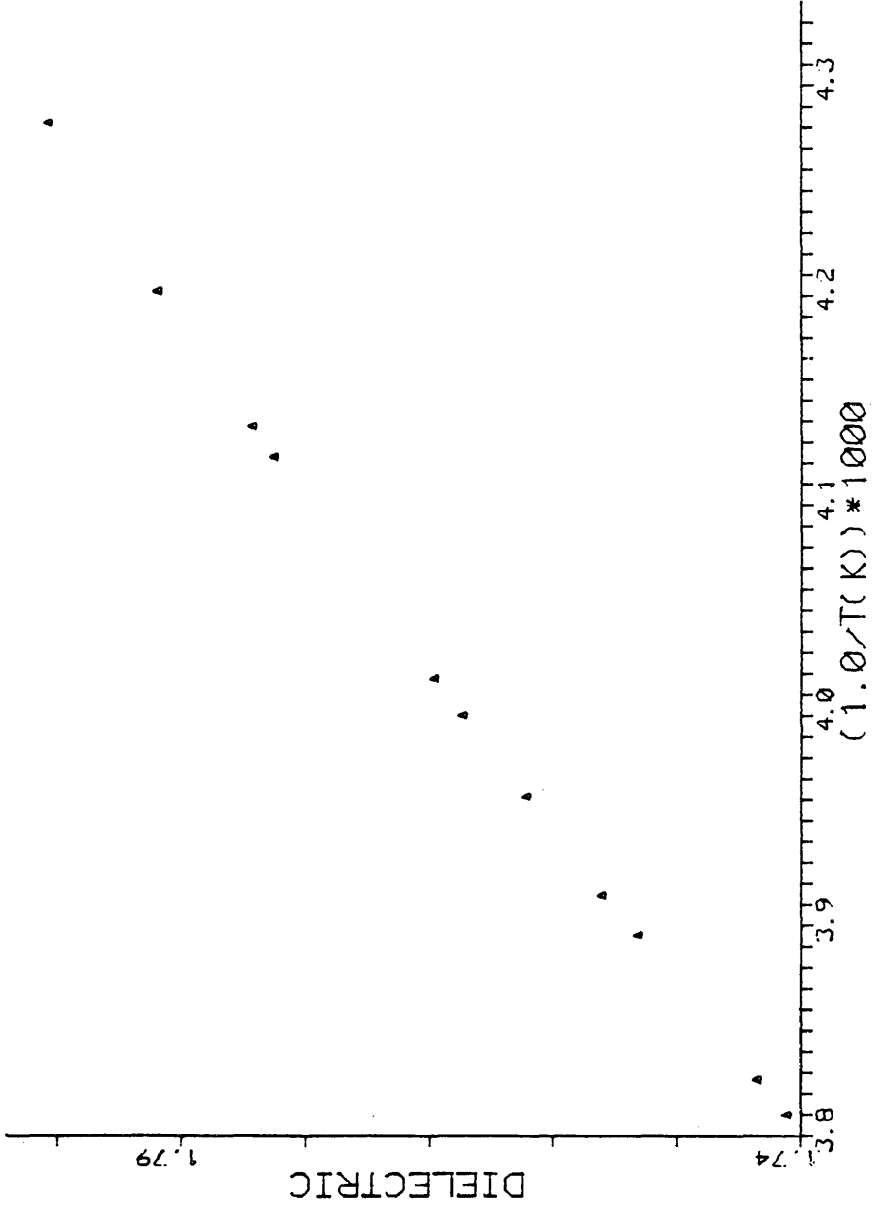
LIQUID PROPANE-WATER EXPERIMENTAL DATA

PROPANE - WATER (112 psia) Date: March 2, 1982
Water Loading System Temperature(°C) 39.48
Water Loading System Pressure(torr) 4.21

TEMPERATURE(K)	DIELECTRIC
262.48	1.74115
261.32	1.74353
256.73	1.75317
255.48	1.75607
252.44	1.76216
250.00	1.76733
248.91	1.76966
242.56	1.78261
241.71	1.78434
237.98	1.79197
233.54	1.80078

PROPANE - 16.92 PPM WATER

112 psia (3-2-82)



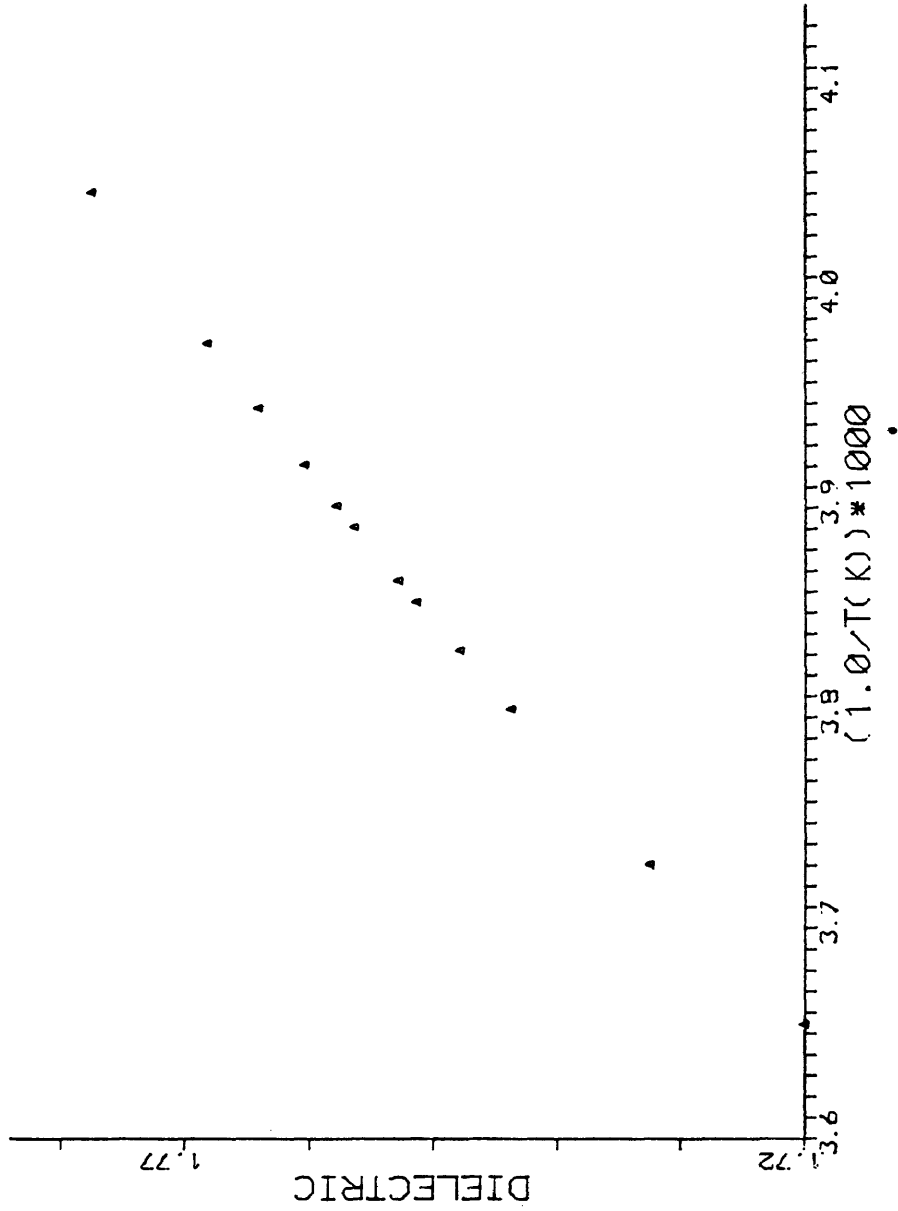
PROPANE - WATER (112 psia) Date: July 5, 1982
Water Loading System Temperature(°C) 35.80
Water Loading System Pressure(torr) 12.05

TEMPERATURE(K) DIELECTRIC

273.66	1.72003
268.09	1.73253
262.89	1.74380
260.96	1.74795
259.40	1.75143
258.71	1.75290
257.01	1.75789
256.35	1.76047
255.07	1.76416
253.33	1.76830
246.91	1.77761

PROPANE - 50.45 PPM WATER

112 psia (7-5-82)



PROPANE - WATER (112 psia) Date: August 2, 1982

Water Loading System Temperature(°C) 70.73

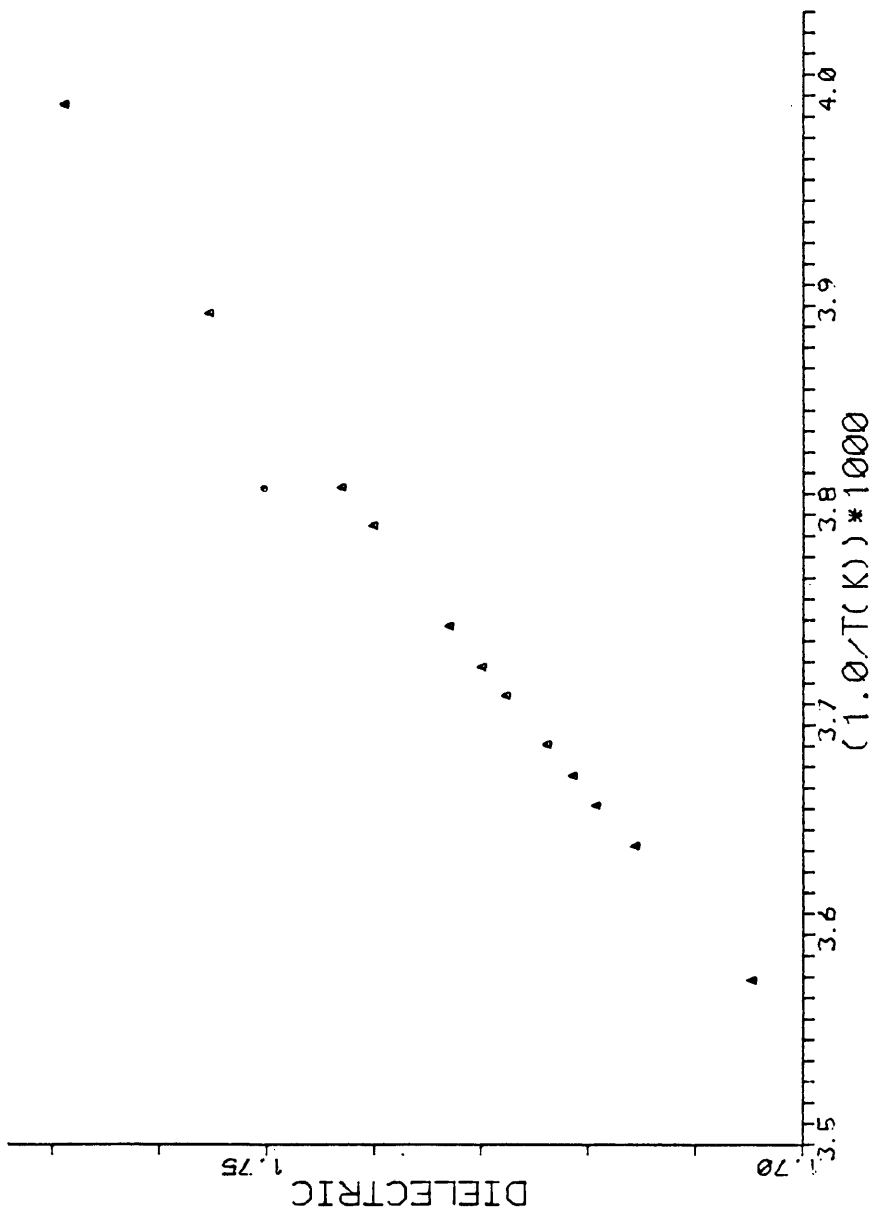
Water Loading System Pressure(torr) 22.95

TEMPERATURE(K) DIELECTRIC

279.46	1.70474
274.54	1.71562
273.10	1.71929
272.05	1.72147
270.95	1.72390
269.26	1.72774
268.27	1.73000
266.87	1.73310
263.52	1.74014
262.27	1.74311
256.66	1.75544
250.28	1.76893

PROPANE - 87.62 PPM WATER

112 psia (8-2-82)



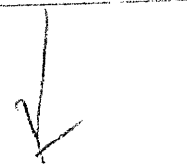
PROPANE - WATER (112 psia) Date: August 26, 1982

Water Loading System Temperature(°C) 71.18

Water Loading System Pressure(torr) 31.33

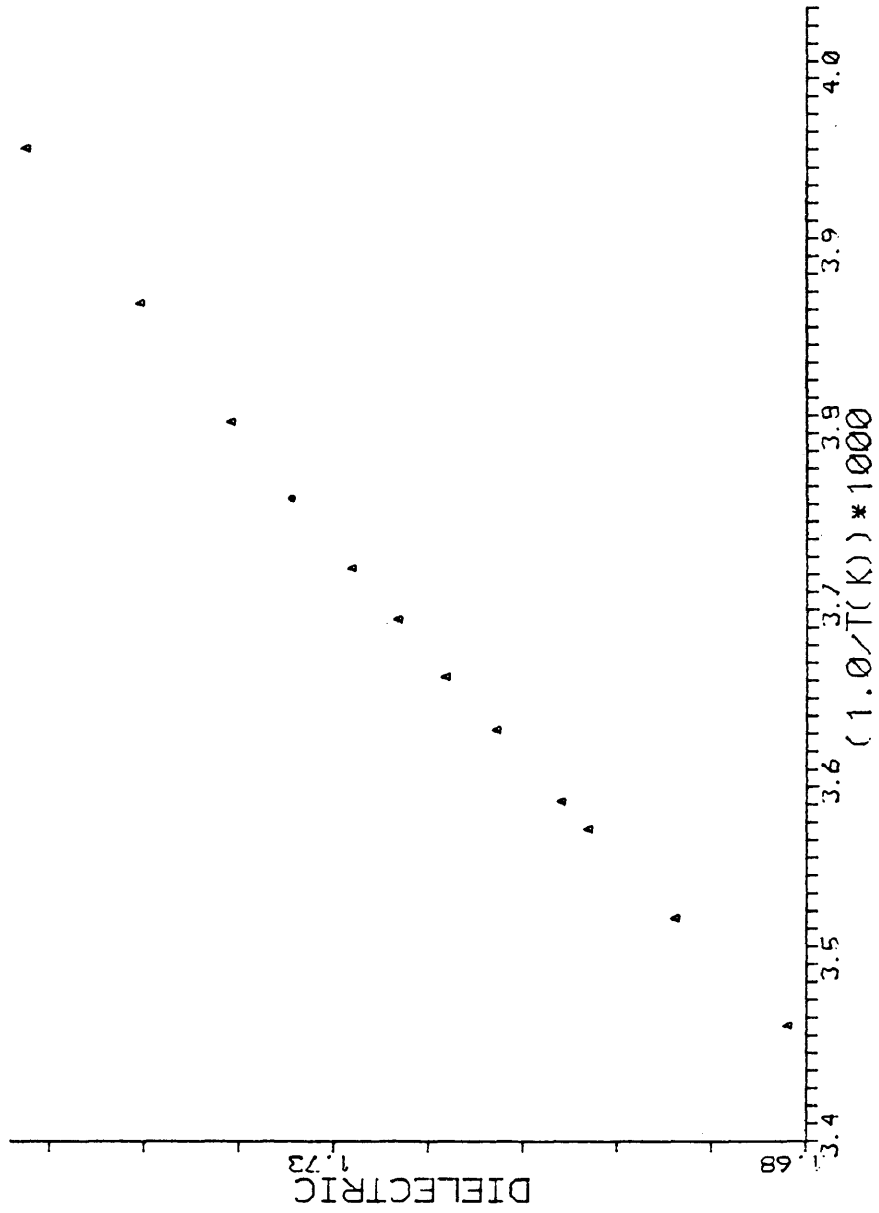
TEMPERATURE(K) DIELECTRIC

288.57	1.68196
283.63	1.69389
279.66	1.70306
278.43	1.70598
275.36	1.71291
273.09	1.71835
270.69	1.72342
268.58	1.72827
262.73	1.74102
258.23	1.75065
252.53	1.76273



PROPANE - 123.92 PPM WATER

112 psia (8-26-82)



PROPANE - WATER (112 psia) Date: September 8, 1982

Water Loading System Temperature(°C) 62.62

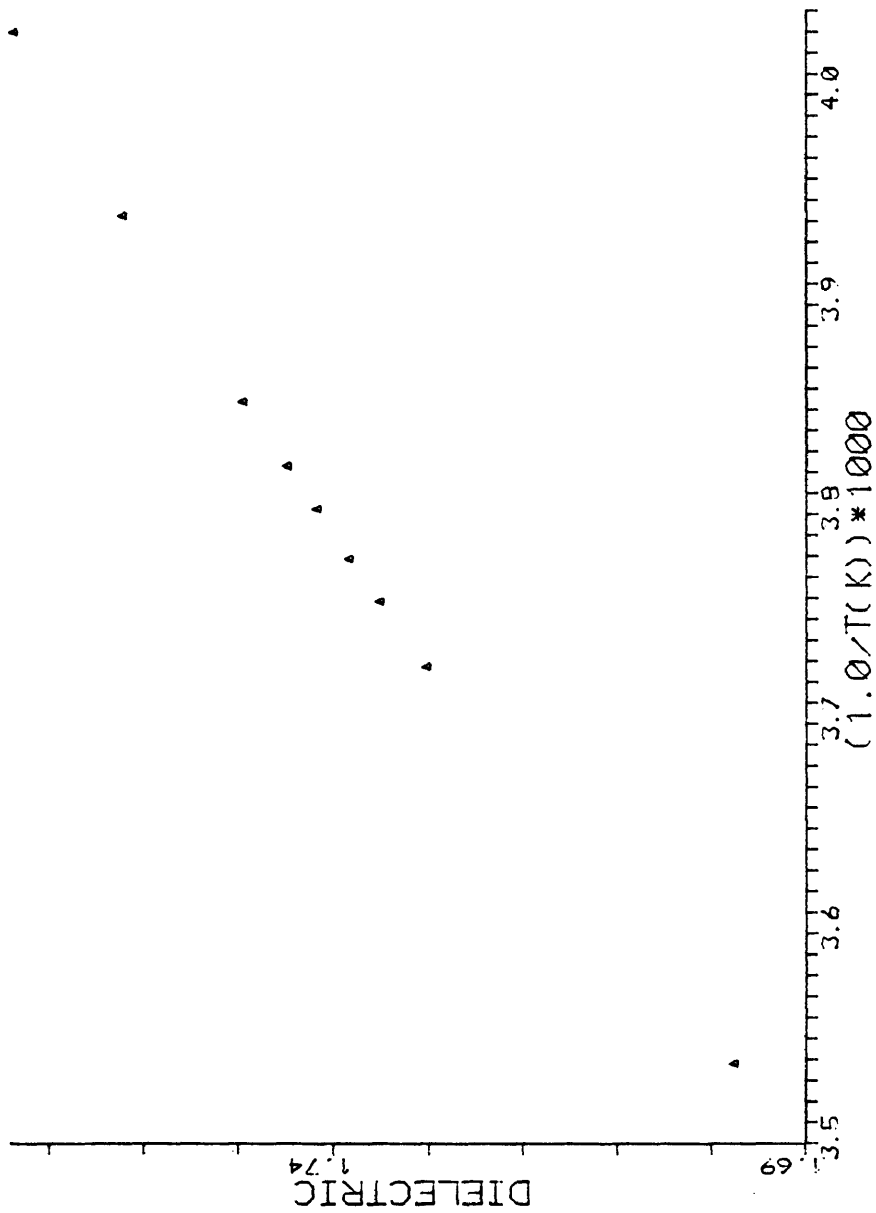
Water Loading System Pressure(torr) 16.87

TEMPERATURE(K) DIELECTRIC

282.64	1.69767
268.28	1.73029
266.07	1.73517
264.65	1.73844
263.00	1.74183
261.58	1.74497
259.49	1.74965
253.65	1.76238
248.14	1.77389

PROPANE - 65.68 PPM WATER

112 psia (9-8-82)



PROPANE - WATER (112 psia) Date: September 23, 1982

Water Loading System Temperature(°C) 69.50

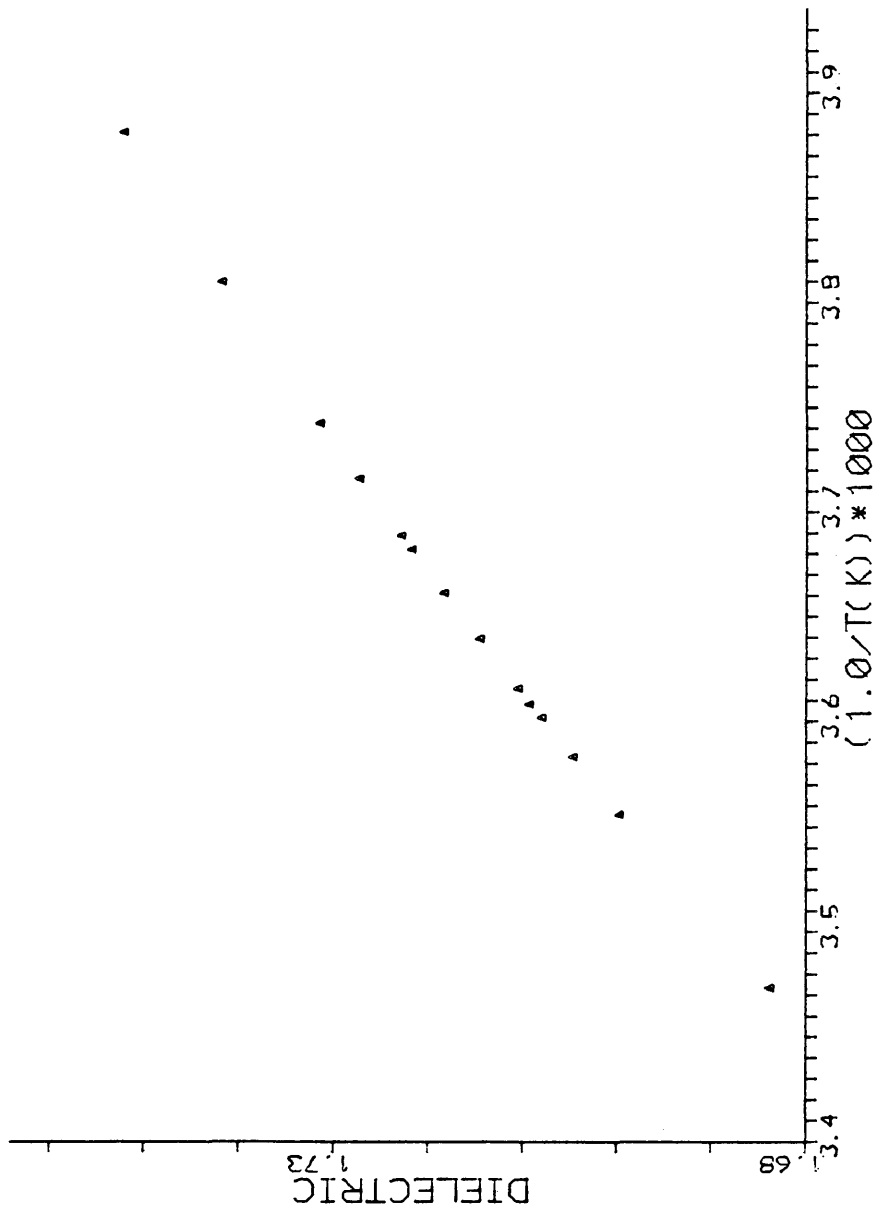
Water Loading System Pressure(torr) 35.02

TEMPERATURE(K) DIELECTRIC

287.91	1.68374
281.27	1.69972
279.09	1.70463
277.65	1.70801
277.15	1.70929
276.59	1.71049
274.78	1.71461
273.14	1.71837
271.61	1.72181
271.10	1.72295
269.13	1.72736
267.24	1.73155
262.51	1.74184
257.71	1.75226

PROPANE - 136.89 PPM WATER

112 psia (9-23-82)



PROPANE - WATER (112 psia) Date: October 12, 1982

Water Loading System Temperature(°C) 71.06

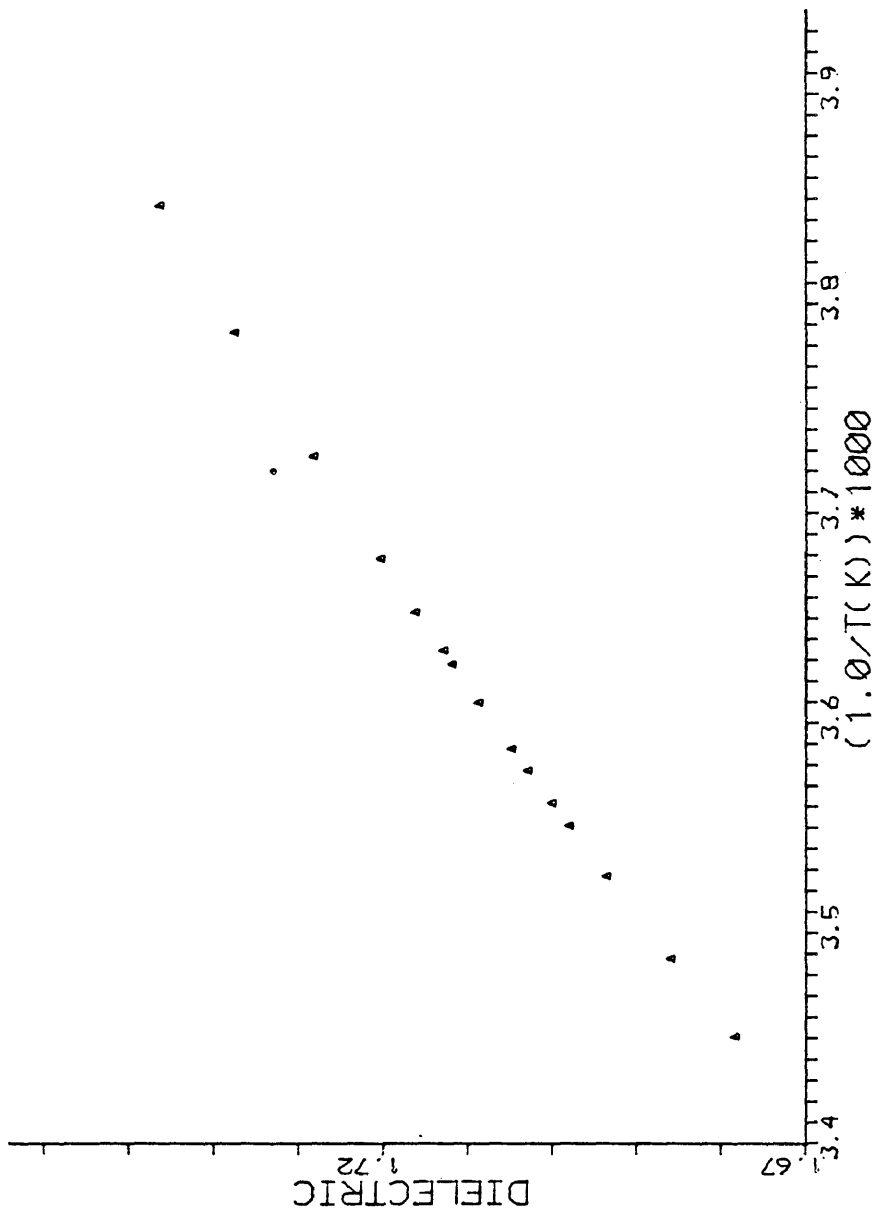
Water Loading System Pressure(torr) 44.96

TEMPERATURE(K) DIELECTRIC

289.80	1.67834
286.71	1.68596
283.53	1.69358
281.60	1.69798
280.74	1.70008
279.53	1.70291
278.71	1.70480
277.01	1.70880
275.63	1.71199
275.11	1.71298
273.75	1.71624
271.86	1.72041
268.30	1.72836
264.13	1.73765
259.95	1.74652
255.56	1.75602

PROPANE - 176.06 PPM WATER

112 psia (10-12-82)



PROPANE - WATER (112 psia) Date: November 5, 1982

Water Loading System Temperature(°C) 70.16

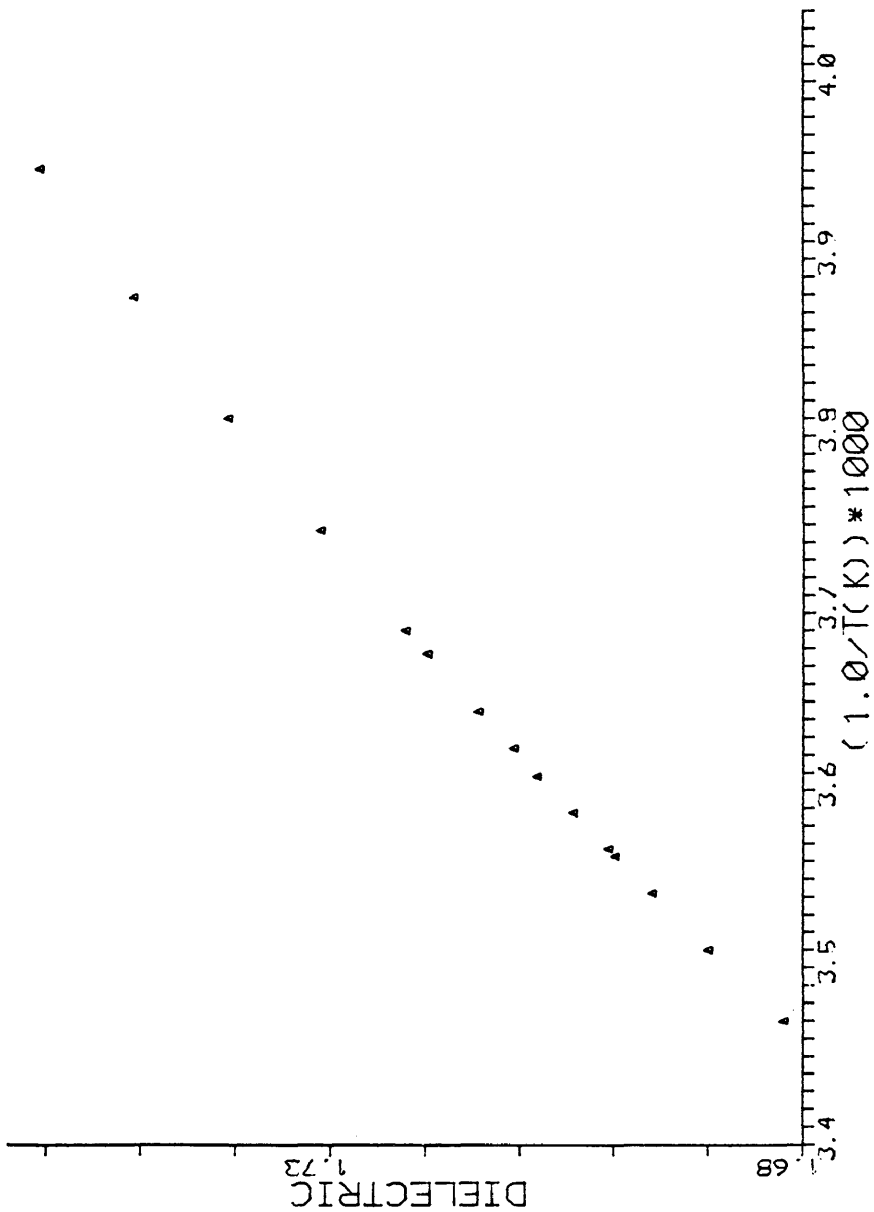
Water Loading System Pressure(torr) 32.22

TEMPERATURE(K) DIELECTRIC

288.22	1.68200
284.93	1.68996
282.34	1.69589
280.69	1.69984
280.37	1.70053
278.77	1.70426
277.19	1.70811
275.99	1.71060
274.42	1.71436
271.98	1.71977
271.01	1.72204
266.93	1.73108
262.48	1.74076
257.86	1.75070
253.15	1.76069

PROPANE - 125.78 PPM WATER

112 psia (11-5-82)



PROPANE - WATER (112 psia) Date: December 16, 1982

Water Loading System Temperature(°C) 77.45

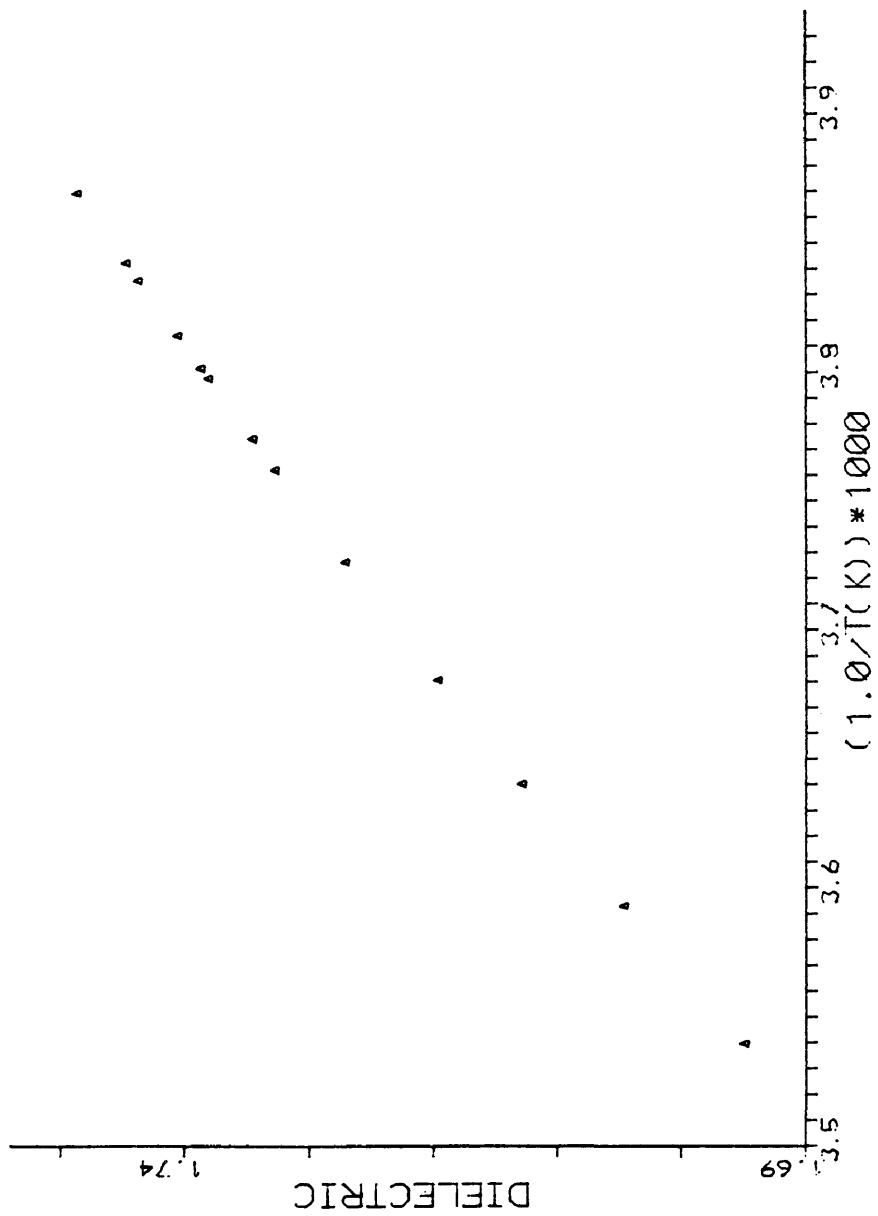
Water Loading System Pressure(torr) 27.11

TEMPERATURE(K) DIELECTRIC

282.52	1.69495
278.34	1.70464
274.71	1.71287
271.69	1.71968
268.36	1.72711
265.82	1.73274
264.98	1.73455
263.35	1.73812
263.08	1.73873
262.21	1.74058
260.75	1.74375
260.29	1.74469
258.46	1.74862

PROPANE - 102.50 PPM WATER

112 psia (12-16-82)



PROPANE - WATER (262 psia) Date: December 18, 1982

Water Loading System Temperature(°C) 77.45

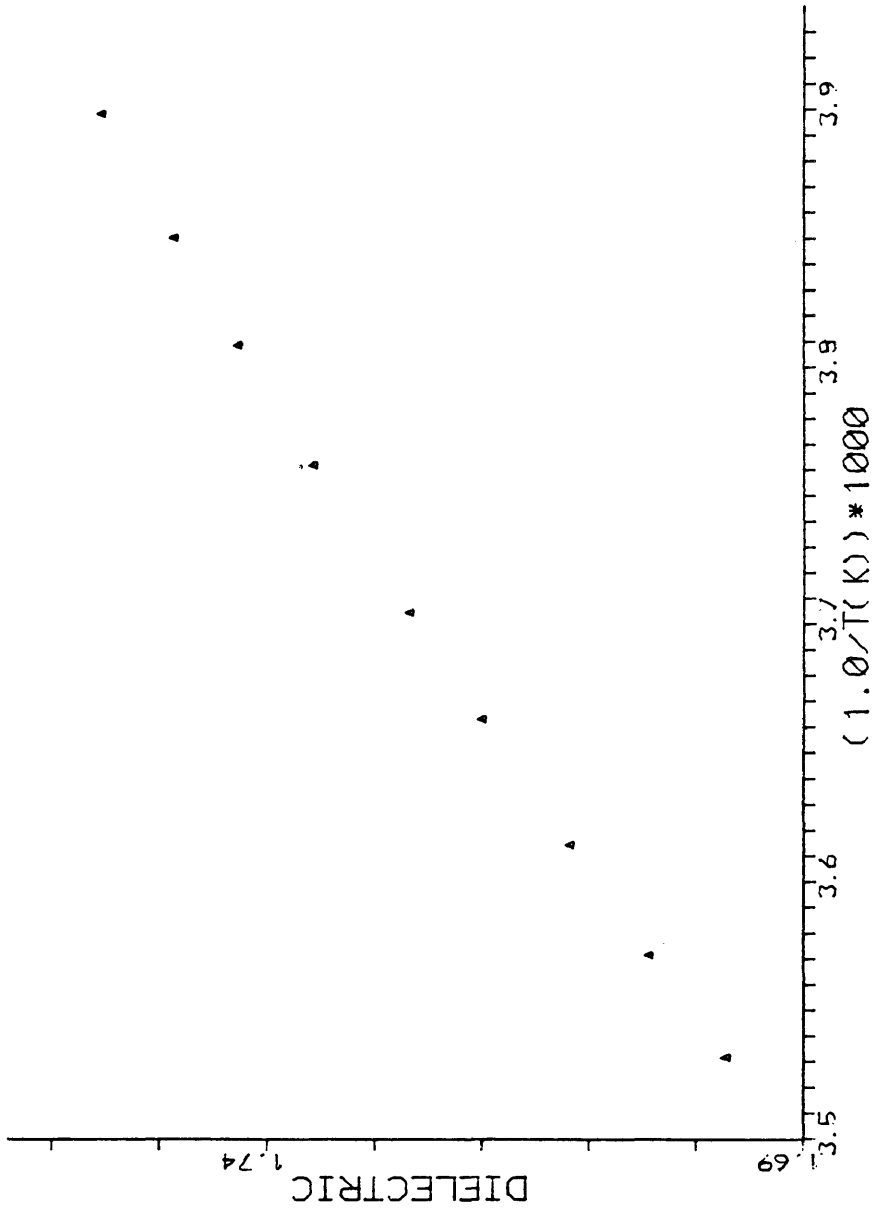
Water Loading System Pressure(torr) 27.11

TEMPERATURE(K)	DIELECTRIC
----------------	------------

283.14	1.69721
279.98	1.70438
276.67	1.71181
272.99	1.72003
269.94	1.72676
265.83	1.73571
262.56	1.74270
259.73	1.74870
256.54	1.75543

PROPANE - 101.78 PPM WATER

262 psia (12-18-82)



APPENDIX D

TWO-PHASE HYDRATE PREDICTION PROGRAM

LISTING AND OUTPUT

```

C *****
C
C THIS PROGRAM EVALUATES SYSTEM COMPOSITION
C BETWEEN A LIQUID HYDROCARBON(CONDENSED)
C PHASE AND HYDRATE IN EQUILIBRIUM.
C *****
C
C COMPONENT IDENTIFICATION
C
C 1 - WATER
C 2 - HYDROCARBON(PROPANE OR ETHANE)
C     (POSSIBLY CARBON DIOXIDE)
C
C DIMENSION X(2),CB(4),TTT(25),TK(25)
C INTEGER STRUCT,EOS
C
C INPUT PROGRAM INSTRUCTIONS
C
C WRITE(4,702)
C WRITE(4,705)
C WRITE(4,712)
C WRITE(4,711)
C READ(4,715)STRUCT
C
C WRITE(4,722)
C WRITE(4,725)
C WRITE(4,730)
C READ(4,715)EOS
C
C WRITE(4,735)
C WRITE(4,740)
C WRITE(4,745)
C READ(4,715)LC
C
C WRITE(4,785)
C WRITE(4,792)
C WRITE(4,795)
C READ(4,715)IFMT
C
C DETERMINE STRUCTURE AND CAVITYS OCCUPIED
C
C INPUT 2.0 FOR A FILLED HYDRATE CELL,0.0 FOR ALL OTHER
C POSSIBLE CELLS
C STRUCTURE I:  SMALL CELL - 1
C                LARGE CELL - 2
C STRUCTURE II: SMALL CELL - 3
C                LARGE CELL - 4
C
C IF(STRUCT.EQ.2)GOTO 100
C CB(1)=0.0

```

```

      CB(2)=2.0
      CB(3)=0.0
      CB(4)=0.0
      GOTO 105
100  CONTINUE
      CB(1)=0.0
      CB(2)=0.0
      CB(3)=0.0
      CB(4)=2.0
105  CONTINUE
C
C    ASSIGN THE APPROPRIATE VALUES FOR THE VARIOUS
C    THERMODYNAMIC PARAMETERS REQUIRED FOR PHASE
C    EQUILIBRIA CONDITIONS.
C
C    UNITS: DELMU - CAL/MOL
C           DELV  - CC/MOL
C           DELH  - CAL/MOL
C
C    .IF(STRUCT.EQ.2)GOTO 110
C    REF: P.B. DHARMAWARDHANA
C    DELMU=310.0
C    REF: VON STACKELBERG AND MULLER
C    DELV=3.0
C    REF: P.B. DHARMAWARDHANA
C    DELH=332.0
C    GOTO 115
110  CONTINUE
C    REF: P.B. DHARMAWARDHANA
C    DELMU=224.0
C    REF: VON STACKELBERG AND MULLER
C    DELV=3.4
C    REF: P.B. DHARMAWARDHANA
C    DELH=245.0
115  CONTINUE
C
C    INPUT TEMPERATURE AND PRESSURE OF INTEREST
C
C    WRITE(4,750)
C    READ(4,755)PPP
C    WRITE(4,800)
C    READ(4,715)NN
C    WRITE(4,805)
C    READ(4,810)(TTT(I),I=1,NN)
C
C
C    TEMPERATURE(K)
C    DO 5 J=1,NN
5    TK(J)=TTT(J)+273.15
C    PRESSURE(ATM)
C    P=PPP/14.696

```

```

C
  WRITE(4,815)PPP
  WRITE(4,825)
  WRITE(4,775)
C
C   INITIAL ESTIMATE FOR MOLE FRACTION
C   OF WATER IN THE CONDENSED LIQUID PHASE
C
  X(1)=137.4E-6
C
  DO 1000 I=1,NN
  T=TK(I)
C
C   CALCULATE LANGMUIR CONSTANT
C
  IF(LC.EQ.2)GO TO 201
  IDST=STRUCT
  IIID=EOS
  IF(STRUCT.EQ.3)GOTO 201
  GOTO 203
201  CONTINUE
     CALL LANG(T, IDST, CLSM)
     CONTINUE
     CALL LANG(T, 4, CLLG)
     GOTO 210
203  CONTINUE
C
     CALL LANG(T, IDST, CL)
C
     GO TO 212
205  CONTINUE
     IF(STRUCT.EQ.2)GO TO 205
     IF(STRUCT.EQ.3)GOTO 207
     CALL LCC2H6(T, CL)
     GOTO 210
205  CONTINUE
     CALL LCC3H8(T, CL)
     GOTO 210
207  CONTINUE
     CALL LCCO2S(T, CLSM)
     CONTINUE
     CALL LCCO2L(T, CLLG)
212  CONTINUE
C
C   INITIALIZE COUNTER
C
  ICOUNT=7
C   GAS CONSTANT(CC-ATM/GMOL-K)
  R=82.056
C
C

```

```

215  CONTINUE
      X1=X(1)
C
C
C    CALCULATE THE LIQUID PHASE FUGACITIES
C
      IF(FOS.EQ.2)GO TO 220
      CALL PRFUG(T,P,X1,STRUCT,EOS,FUG1,FUG2)
      GOTO 225
220  CONTINUE
      CALL SRKFUG(T,P,X1,STRUCT,EOS,FUG1,FUG2)
225  CONTINUE
C
C    CALCULATE THE FRACTION OF TYPE "M" CAVITIES
C    OCCUPIED BY THE GAS
C
      IF(STRUCT.EQ.3)GOTO 227
      THETA=CL*FUG2/(1.0+CL*FUG2)
      GOTO 228
227  CONTINUE
      THETAS=CLSM*FUG2/(1.0+CLSM*FUG2)
      THETAL=CLLG*FUG2/(1.0+CLLG*FUG2)
      TYPE *,THETAS,THETAL,CLSM,CLLG
228  CONTINUE
C
C    CALCULATE THE DIFFERENCE BETWEEN THE CHEMICAL
C    POTENTIAL OF WATER IN THE EMPTY HYDRATE LATTICE
C    AND THAT IN THE FILLED LATTICE.
C
      IF(STRUCT.EQ.2)GO TO 230
      IF(STRUCT.EQ.3)GOTO 233
      DMU=-R*T*(6.0/46.0)*ALOG(1.0-THETA)
      GO TO 235
230  CONTINUE
      DMU=-R*T*(8.0/136.0)*ALOG(1.0-THETA)
      GO TO 235
233  CONTINUE
      DMU=-R*T*((1.0/23.0)*ALOG(1.0-THETAS)+(3.0/23.0)*
1     ALOG(1.0-THETAL))
235  CONTINUE
C
C    CALCULATE THE FUGACITY OF THE WATER IN THE
C    EMPTY HYDRATE LATTICE
C
      IF(IFMT.EQ.2)GOTO 320
      CALL BENNET(T,P,DELV,STRUCT,FUGMT)
      GO TO 325
320  CONTINUE
      CALL NGROB(T,P,STRUCT,FUGMT)
325  CONTINUE
C

```

```

C      CALCULATE THE FUGACITY OF WATER IN THE FILLED
C      HYDRATE LATTICE
C
C      FUGHYD=FUGMT*EXP(-DMU/(R*T))
C
C      FUGACITY COEFFICIENT OF WATER IN THE CONDENSED PHASE
C
C      FUGC1=FUG1/(X1*P)
C
C      ITERATE UNTIL THE FUGACITY OF THE WATER IN THE LIQUID
C      PHASE EQUALS THE FUGACITY OF WATER IN THE HYDRATE PHASE
C
C      XCAL=FUGHYD/(P*FUGC1)
C
C      ERROR=1.E-8
C
C      XDIF=ABS((X1-XCAL))
C      IF(XDIF.LE.ERROR)GO TO 400
C      X(1)=XCAL
C      ICOUNT=ICOUNT+1
C      IF(ICOUNT.GT.1000)GO TO 605
C      GO TO 215
C
C
C      605  CONTINUE
C          WRITE(4,770)
C          GO TO 1000
C
C      PRINT RESULTS
C
C      400  CONTINUE
C          XPPM=X(1)*1.0E6
C
C          WRITE(4,780)TTT(I),XPPM
C      1000 CONTINUE
C
C          WRITE(4,1125)
C      1125 FORMAT(1X,///)
C
C      FORMAT STATEMENTS
C
C      700  FORMAT(1X,/, ' HYDRATE SYSTEM UNDER CONSIDERATION',/)
C      705  FORMAT(1X, 'ETHANE - WATER           --ENTER "1"')
C      710  FORMAT(1X, 'PROPANE - WATER           --ENTER "2"')
C      711  FORMAT(1X, 'CARBON DIOXIDE - WATER      --ENTER "3"')
C      715  FORMAT(I)
C      720  FORMAT(1X,/, ' EQUATION OF STATE FOR FUGACITY CALCULATION',/)
C      725  FORMAT(1X, 'PENG - ROBINSON EQUATION --ENTER "1"')
C      730  FORMAT(1X, 'SOAVE - RELICH KWONG EQ. --ENTER "2"')
C      735  FORMAT(1X,/, ' LANGMUIR CONSTANT EVALUATION',/)
C      740  FORMAT(1X, 'MCKOY AND SINANOGLU METHOD --ENTER "1"')

```

```
745  FORMAT(1X,"PARRISH & PRAUSNITZ METHOD --ENTER "2"")
750  FORMAT(1X,/, " INPUT SYSTEM PRESSURE(PSIA)")
755  FORMAT(2F)
770  FORMAT(1X,"SOLUTION DID NOT CONVERGE")
775  FORMAT(1X,/, " TEMPERATURE(C)",10X,"X(PPM)",/)
780  FORMAT(1X,F8.3,13X,F8.2)
785  FORMAT(1X,/, " EMPTY HYDRATE FUGACITY CALCULATION",/)
790  FORMAT(1X,"METHOD OF P.B. DHARMAWARDHANA --ENTER "1"")
795  FORMAT(1X,"METHOD OF NG & ROBINSON --ENTER "2"")
800  FORMAT(1X,"INPUT NUMBER OF SYSTEM TEMPERATURES")
805  FORMAT(1X,"INPUT TEMPERATURE(C) (5 PER LINE)")
810  FORMAT(5F)
815  FORMAT(1X,/,8X,"PRESSURE = ",F7.2," PSIA")
825  FORMAT(1X,/,19X,"WATER CONCENTRATION")
C
C
END
```

```

SUBROUTINE LANG(T, IDST, CCL)
C
C *****
C
C THIS PROGRAM CALCULATES THE LANGMUIR
C CONSTANT USING THE KIHARA POTENTIAL
C WITH A SPHERICAL CORE. THE PROGRAM
C EMPLOYS A FIFTEEN POINT FORMULA
C OF A GAUSS - LEGENDRE QUADRATURE
C INTEGRATION SCHEME.
C *****
C
C EXTERNAL FUNCTN
C
C BK=1.38060-23
C M=15
C PI=3.141592654
C VCONV=1.0-10**3
C
C ERROR=1.E-10
C INITIALIZE SUM
C SUM=0.0
C A=1.E-12
C B=0.025
C
C 200 CONTINUE
C
C AREA=GAUSS(A, B, M, IDST, T, FUNCTN)
C SUM1=SUM+AREA
C DIF=ABS((SUM-SUM1)/SUM1)
C IF(DIF.LE.ERROR)GO TO 605
C
C SUM=SUM1
C A=B
C B=B*0.025
C GO TO 200
C
C 605 CONTINUE
C LANGMUIR CONSTANT(4**2/N)
C C=4.0*PI*VCONV*SUM1/(T*BK)
C LANGMUIR CONSTANT(1/ATM)
C CCL=C*(1.05)*(1.0/.986923267)
C RETURN
C
C END

```

```

      FUNCTION FUNCTN(R, IDST, T)
C
C      ..... INTEGRAND FOR LANGMUIR CONSTANT CALCULATION .....
C
C      FUNCTION STATEMENTS
      DEL(R, N) = ((1.0 - R/CR - A/CR)**(-N) - (1.0 + R/CR - A/CR)**(-N))
1      /FLOAT(N)
C
      W(R) = 2. * Z * EPS * ((SIGMA**12 / (CR**11 * R)) * (DEL(R, 10)
1      + (A/CR) * DEL(R, 11)) - (SIGMA**6 / (CR**5 * R)) * (DEL(R, 4)
1      + (A/CR) * DEL(R, 5)))
C
C
C      BOLTZMANN'S CONSTANT
      BK = 1.3806D-16
C
C
      IF (IDST.EQ.2) GOTO 10
      IF (IDST.EQ.3) GOTO 15
      IF (IDST.EQ.4) GOTO 15
C      STRUCTURE I (LARGE CAVITY RADIUS(A))
      CR = 8.60 / 2.0
C      KIHARA POTENTIAL PARAMETERS (ETHANE - WATER)
C
C      CHARACTERISTIC ENERGY
      EPS = 177.01 * BK
C      CORE RADIUS(A)
      A = 0.5651
C      COLLISION DIAMETER (MINUS 2 * CORE RADIUS)
      SIGMA = 3.2444
C      COORDINATION NUMBER
      Z = 24.0
C
      GOTO 20
10     CONTINUE
C      STRUCTURE II (LARGE CAVITY RADIUS(A))
      CR = 9.46 / 2.0
C      KIHARA POTENTIAL PARAMETERS (PROPANE - WATER)
C
C      CHARACTERISTIC ENERGY
      EPS = 203.31 * BK
C      CORE RADIUS(A)
      A = 0.6502
C      COLLISION DIAMETER (MINUS 2 * CORE RADIUS)
      SIGMA = 3.30931
C      COORDINATION NUMBER
      Z = 28.0
      GOTO 20
C
15     CONTINUE

```

```
C      STRUCTURE I (SMALL CAVITY RADIUS(A))
C      CR=7.95/2.#
C      STRUCTURE I (LARGE CAVITY RADIUS(A))
C      IF(IDST.EQ.4)CR=8.6#/2.#
C      KIHARA POTENTIAL PARAMETERS(CO2-WATER)
C
C      CHARACTERISTIC ENERGY
C      EPS=163.27*BK
C      CORE RADIUS(A)
C      A=0.6825
C      COLLISION DIAMETER(MINUS 2*CORE RADIUS)
C      SIGMA=2.9718
C      COORDINATION NUMBER
C      Z=20.#
C      IF(IDST.EQ.4)Z=24.#
2#    CONTINUE
C
C      WW=W(R)
C      INTEGRAND FUNCTION
C      FUNCTN=EXP((-WW)/(BK*T))*R**2
C
C      RETURN
C
C      END
```

```

FUNCTION GAUSS(A,B,M,IDST,T,FUNCTN)
C
C THE FUNCTION GAUSS USES THE M-POINT GAUSS-LEGENDRE
C QUADRATURE FORMULA TO COMPUTE THE INTEGRAL OF
C FUNCTN(X)*DX BETWEEN INTEGRATION LIMITS A AND B.
C THE ROOTS OF SEVEN LEGENDRE POLYNOMIALS AND THE
C WEIGHT FACTORS FOR THE CORRESPONDING QUADRATURES
C ARE STORED IN THE Z AND WEIGHT ARRAYS RESPECTIVELY.
C M MAY ASSUME VALUES 2,3,4,5,6,10, AND 15 ONLY.
C THE APPROPRIATE VALUES FOR THE M-POINT FORMULA
C ARE LOCATED IN ELEMENTS Z(KEY(I))...Z(KEY(I+1)-1)
C AND WEIGHT (KEY(I))...WEIGHT(KEY(I+1)-1) WHERE THE
C PROPER VALUE OF I IS DETERMINED BY FINDING THE
C SUBSCRIPT OF THE ELEMENT OF THE ARRAY NPOINT
C WHICH HAS THE VALUE M. IF AN INVALID VALUE OF M
C IS USED, A TRUE ZERO IS RETURNED AS THE VALUE OF
C GAUSS.
C
C IMPLICIT REAL*8(A-H,O-Z)
C REAL*8 GAUSS,A,B,FUNCTN
C DIMENSION NPOINT(7),KEY(8),Z(24),WEIGHT(24)
C
C .....PRESET NPOINT, KEY, Z, AND WEIGHT ARRAYS.....
C DATA NPOINT / 2, 3, 4, 5, 6, 10, 15 /
C
C DATA KEY / 1, 2, 4, 6, 9, 12, 17, 25 /
C
C DATA Z
C 1 / 0.577350269,0.0 ,0.774596669,
C 2 0.339981744,0.861136312,0.0 ,0.538469310,
C 3 0.906179846,0.238619186,0.661209387,0.932469514,
C 4 0.148874339,0.433395394,0.679409568,0.865263367,
C 5 0.973906529,0.0 ,0.201194094,0.394151347,
C 6 0.570972173,0.724417731,0.848206583,0.937273392,
C 0.987992518 /
C
C DATA WEIGHT
C 1 / 1.0 ,0.888888889,0.555555556,
C 2 0.652145155,0.347854845,0.568888889,0.478628671,
C 3 0.236926885,0.467913935,0.360761573,0.171324493,
C 4 0.295524225,0.269266719,0.219086363,0.149451349,
C 5 0.066671344,0.202578242,0.198431485,0.186161000,
C 6 0.166269206,0.139570678,0.107159221,0.070366047,
C 0.030753242 /
C
C .....FIND SUBSCRIPT OF FIRST Z AND WEIGHT VALUE.....
C DO 1 I=1,7
C IF(M.EQ.NPOINT(I)) GO TO 2
C CONTINUE
C .....INVALID M USED.....
C GAUSS = 0.0
C RETURN
C

```

```
C      .....SET UP INITIAL PARAMETERS.....
2      JFIRST=KEY(I)
      JLAST=KEY(I+1)-1
      C=(B-A)/2.0
      D=(B+A)/2.0
C
C      .....ACCUMULATE THE SUM IN THE M-POINT FORMULA.....
      SUM=0.0
      DO 5 J=JFIRST,JLAST
      IF(Z(J).EQ.0.0)SUM=SUM+WEIGHT(J)*FUNCTN(D, IDST, T)
5      IF(Z(J).NE.0.0)SUM=SUM+WEIGHT(J)*(FUNCTN(Z(J)*C+D, IDST, T)
1      + FUNCTN(-Z(J)*C+D, IDST, T))
C
C      ..... MAKE INTERVAL CORRECTION AND RETURN .....
      GAUSS =C*SUM
      RETURN
C
      END
```



```
      SUBROUTINE LCC2H6(T,CM)
C
C      UNITS: TEMPERATURE(KELVIN)
C
C      STRUCTURE I CAVITIES (LARGE)
C
C      AM=0.4071E-2
C      BM=3820.7119
C
C      CM=(AM/T)*EXP(BM/T)
C
C      RETURN
C      END
C
C
```

```
      SUBROUTINE LCCO2S(T,CM)
C
C      UNITS: TEMPERATURE(KELVIN)
C
C      STRUCTURE I CAVITIES (SMALL)
C
      AM=1.5227E-3
      BM=2943.9948
C
      CM=(AM/T)*EXP(BM/T)
C
      RETURN
      END
C
```

```
      SUBROUTINE LCCO2L(T,CM)
C
C      UNITS: TEMPERATURE(KELVIN)
C
C      STRUCTURE I CAVITIES (LARGE)
C
C      AM=1.0242E-2
C      BM=3172.6655
C
C      CM=(AM/T)*EXP(BM/T)
C
C      RETURN
C      END
```

```

C      SUBROUTINE PRFUG(T,P,X1,ID1,ID2,FUG1,FUG2)
C
C      *****
C
C      THIS PROGRAM USES THE PENG-ROBINSON EQUATION
C      OF STATE TO DETERMINE THE FUGACITY OF TWO
C      COMPONENTS IN THE LIQUID PHASE.
C
C      *****
C
C      CALL PARPR(T, ID1, A1, A2, B1, B2)
C
C      CALL MIXX(X1, A1, A2, B1, B2, ID2, ID1, A12, A, B)
C
C      GAS CONSTANT(LITER-ATM/MOLE-DEG K)
C      R=82.056/1800.0
C
C      AAL=A*P/(R**2*T**2)
C      BBL=B*P/(R*T)
C
C      DL=-(1.0-BBL)
C      EL=AAL-3.0*BBL**2-2.0*BBL
C      FL=-(AAL*BBL-BBL**2-BBL**3)
C
C      CALL CUBIC(DL,EL,FL,Z1,Z2,Z3,Z,ZMAX,ZMIN, ID)
C      ZL=ZMIN
C      IF(ID.EQ.0)ZL=Z
C
C      CALCULATE LIQUID PHASE FUGACITY COEFFICIENTS
C
C      GL1=(B1/B)*(ZL-1.0)-ALOG(ZL-BBL)
C      GL2=(B2/B)*(ZL-1.0)-ALOG(ZL-BBL)
C      H=AAL/(2.0*SQRT(2.0)*BBL)
C      HH=ALOG((ZL+2.414*BBL)/(ZL-0.414*BBL))
C      H1=(2.0*((X1*A1)+((1.0-X1)*A12)))/A-B1/B
C      H2=(2.0*((X1*A12)+((1.0-X1)*A2)))/A-B2/B
C      P1L=EXP(GL1-H*H1*HH)
C      P2L=EXP(GL2-H*H2*HH)
C
C      CALCULATE FUGACITYS OF EACH COMPONENT
C
C      FUG1=X1*P1L*P
C      FUG2=(1.0-X1)*P2L*P
C
C      RETURN
C      END

```



```

SUBROUTINE PARPR(T, ID, A1, A2, B1, B2)
C
C   THIS SUBROUTINE EVALUATES THE PARAMETERS
C   A(T), AND B(T), FOR USE IN THE PENG-ROBINSON
C   EQUATION OF STATE.
C
REAL KAPPA1, KAPPA2
CALL WATER(T, TC1, PC1, OMEGA1, TR1)
C
IF(ID.EQ.2)GOTO 50
IF(ID.EQ.3)GOTO 55
CALL ETHANE(T, TC2, PC2, OMEGA2, TR2)
GOTO 100
50 CONTINUE
CALL PROPAN(T, TC2, PC2, OMEGA2, TR2)
GOTO 100
55 CONTINUE
CALL CO2(T, TC2, PC2, OMEGA2, TR2)
C
100 *CONTINUE
C
C   GAS CONSTANT (ATM-LITER/GMOLE-DEG K)
R=82.05*(1./1000.)
C
C   CALCULATE KAPPA
KAPPA1=7.37464+1.54226*OMEGA1-0.26992*OMEGA1**2
KAPPA2=0.37464+1.54226*OMEGA2-0.26992*OMEGA2**2
C
C   CALCULATE ALPHA
ALPHA1=(1.+KAPPA1*(1.-SQRT(TR1)))**2
ALPHA2=(1.+KAPPA2*(1.-SQRT(TR2)))**2
C
C   CALCULATE A(T)
A1=(0.45724*R**2*TC1**2/PC1)*ALPHA1
A2=(0.45724*R**2*TC2**2/PC2)*ALPHA2
C
C   CALCULATE B(T)
B1=0.07780*R*TC1/PC1
B2=0.07780*R*TC2/PC2
C
RETURN
END

```

```

SUBROUTINE PARSRK(T, ID, A1, A2, B1, B2)
C
C THIS SUBROUTINE EVALUATES THE PARAMETERS
C A(T), AND B(T), FOR USE IN THE MODIFIED SOAVE
C REDLICH - KWONG EQUATION OF STATE.
C
REAL KAPPA1, KAPPA2
CALL WATER(T, TC1, PC1, OMEGA1, TR1)
C
IF(ID.EQ.2)GOTO 50
IF(ID.EQ.3)GOTO 55
CALL ETHANE(T, TC2, PC2, OMEGA2, TR2)
GOTO 100
50 CONTINUE
CALL PROPAN(T, TC2, PC2, OMEGA2, TR2)
GOTO 100
55 CONTINUE
CALL CO2(T, TC2, PC2, OMEGA2, TR2)
C
100 CONTINUE
C
C GAS CONSTANT (ATM-LITER/GMOLE-DEG K)
R=82.056*(1./1000.)
C
C CALCULATE KAPPA
KAPPA1=.480+1.574*OMEGA1-.176*OMEGA1**2
KAPPA2=.480+1.574*OMEGA2-.176*OMEGA2**2
C
C CALCULATE ALPHA
ALPHA1=(1.+KAPPA1*(1.-SQRT(TR1)))**2
ALPHA2=(1.+KAPPA2*(1.-SQRT(TR2)))**2
C
C CALCULATE A(T)
A1=(.42747*R**2*TC1**2/PC1)*ALPHA1
A2=(.42747*R**2*TC2**2/PC2)*ALPHA2
C
C CALCULATE B(T)
B1=.08664*R*TC1/PC1
B2=.08664*R*TC2/PC2
C
RETURN
END

```

```

SUBROUTINE MIXX(X1,A1,A2,B1,B2, ID1, ID2, A12, A, B)
C
C THIS SUBROUTINE CALCULATES THE MIXTURE
C PARAMETERS FOR THE PENG-ROBINSON EQUATION
C OF STATE AND THE SRK EQUATION OF STATE,
C SPECIFICALLY FOR A BINARY SYSTEM.
C
  X2=1.-X1
  EQUATION OF STATE
  IF(ID1.EQ.1)GOTO 250
C
C INTERACTION PARAMETERS FOR SRK EQUATION
C OF STATE
  IF(ID2.EQ.2)GOTO 300
  IF(ID2.EQ.3)GOTO 365
C ETHANE - WATER INTERACTION PARAMETER
  DELTA=0.516
  GOTO 305
300 CONTINUE
C PROPANE - WATER INTERACTION PARAMETER
  DELTA=0.496
  GOTO 305
365 CONTINUE
C CARBON DIOXIDE - WATER INTERACTION PARAMETER
  DELTA=-0.03
  GOTO 305
C
250 CONTINUE
C INTERACTION PARAMETERS FOR PENG - ROBINSON
C EQUATION OF STATE
  IF(ID2.EQ.2)GOTO 310
  IF(ID2.EQ.3)GOTO 375
C ETHANE - WATER INTERACTION PARAMETER
  DELTA=0.500
  GOTO 305
310 CONTINUE
C PROPANE - WATER INTERACTION PARAMETER
  DELTA=0.48
  GOTO 305
375 CONTINUE
C CARBON DIOXIDE - WATER INTERACTION PARAMETER
  DELTA=0.13
  GOTO 305
305 CONTINUE
C
C CROSS COEFFICIENT
  A12=(1.-DELTA)*SQRT(A1*A2)
C
  A=X1**2*A1+2.*X1*X2*A12+X2**2*A2
C
  B=X1*B1+X2*B2

```

C

RETURN
END

```
      SUBROUTINE WATER(T,TC,PC,OMEGA,TR)
C     THIS SUBROUTINE CONTAINS THE CRITICAL
C     PROPERTIES FOR WATER. IT ALSO CALCULATES
C     THE REDUCED TEMPERATURE GIVEN T.
C
C     CRITICAL TEMPERATURE(K)
C     TC=647.1
C     CRITICAL PRESSURE(ATM)
C     PC=217.6
C     ACENTRIC FACTOR
C     OMEGA=0.348
C     REDUCED TEMPERATURE
C     TR=T/TC
C
C     RETURN
C     END
```

```
      SUBROUTINE ETHANE(T,TC,PC,OMEGA,TR)
C
C   THIS SUBROUTINE CONTAINS THE CRITICAL
C   PROPERTIES FOR ETHANE. IT ALSO CALCULATES
C   THE REDUCED TEMPERATURE GIVEN T.
C
C   CRITICAL TEMPERATURE(K)
C   TC=305.4
C   CRITICAL PRESSURE(ATM)
C   PC=48.2
C   ACENTRIC FACTOR
C   OMEGA=0.291
C   REDUCED TEMPERATURE
C   TR=T/TC
C
      RETURN
      END
```

```
      SUBROUTINE PROPAN(T,TC,PC,OMEGA,TR)
C
C      THIS SUBROUTINE CONTAINS THE CRITICAL
C      PROPERTIES FOR PROPANE.  IT ALSO CALCULATES
C      THE REDUCED TEMPERATURE GIVEN T.
C
C      CRITICAL TEMPERATURE(K)
C      TC=369.8
C      CRITICAL PRESSURE (ATM)
C      PC=41.9
C      ACENTRIC FACTOR
C      OMEGA=0.145
C      REDUCED TEMPERATURE
C      TR=T/TC
C
      RETURN
      END
```

```
      SUBROUTINE CO2(T,TC,PC,OMEGA,TR)
C
C      THIS SUBROUTINE CONTAINS THE CRITICAL
C      PROPERTIES FOR CARBON DIOXIDE. IT ALSO
C      CALCULATES THE REDUCED TEMPERATURE GIVEN T.
C
C      CRITICAL TEMPERATURE(K)
C      TC=304.2
C      CRITICAL PRESSURE(ATM)
C      PC=72.8
C      ACENTRIC FACTOR
C      OMEGA=0.225
C      REDUCED TEMPERATURE
C      TR=T/TC
C
      RETURN
      END
```

```

C      SUBROUTINE CUBIC(B,C,D,Z1,Z2,Z3,Z,ZMAX,ZMIN,ICHECK)
C
C      THIS SUBROUTINE SOLVES A CUBIC
C      EQUATION ANALYTICALLY.
C      THE METHOD FOLLOWS THE ONE GIVEN
C      IN THE CHEMICAL ENGINEERS HANDBOOK,
C      FIFTH EDITION.
C
C      QC=1.
C      P=(1./3.)*(3.*C-B**2)
C      Q=(1./27.)*(27.*D-9.*B*C+2.*B**3)
C      R=(P/3.)**3+(Q/2.)**2
C
C      IF(R.LE.0.)GOTO 10
C      A3=(-Q/2.)+SQRT(R)
C      B3=(-Q/2.)-SQRT(R)
C      IF(A3)20,30,30
C      A1=-((-A3)**(1./3.))
C      GOTO 40
C      A1=A3**(1./3.)
C      IF(B3)50,60,60
C      B1=-((-B3)**(1./3.))
C      GOTO 70
C      B1=B3**(1./3.)
C
C      THERE IS ONE REAL ROOT
C
C      Z=A1+B1-B/3.
C      GOTO 90
C
C      THERE ARE THREE REAL ROOTS
C
C      IF(Q.GT.0.)QC=-1.
C      XX=SQRT((Q**2/4.)/(-P**3/27.))
C      THETA=ACOS(XX)
C      Z1=QC*2.*SQRT(-P/3.)*COS(THETA/3.)-B/3.
C      Z2=QC*2.*SQRT(-P/3.)*COS(THETA/3.+2.0944)-B/3.
C      Z3=QC*2.*SQRT(-P/3.)*COS(THETA/3.+4.188)-B/3.
C
C      TAKE LARGEST Z
C
C      ZMAX=AMAX1(Z1,Z2,Z3)
C
C      TAKE SMALLEST Z
C
C      ZMIN=AMIN1(Z1,Z2,Z3)
C
C      ICHECK=1
C      GOTO 100
C
C      ICHECK=2
C
C      90

```

103 CONTINUE
RETURN
END

```

SUBROUTINE BENNET(T,P,DELV, ID1,FUGMT)
C
C *****
C
C THIS PROGRAM USES METHODS DEVELOPED BY
C P.B. DHARMAWARDHANA TO EVALUATE THE FUGACITY
C OF WATER IN THE EMPTY HYDRATE LATTICE.
C *****
C
C PRESSURE(PASCAL)
C PA=P*101325.0
C
C VOLUME OF ICE AT 1 ATM AS A FUNCTION OF TEMPERATURE
C UNITS(FT3/LBMOLE)
C
C VT=1.069989-0.249933E-4*T+0.371606E-6*T**2
C
C VOLUME OF ICE AS A FUNCTION OF TEMPERATURE AND
C PRESSURE
C
C VPT=VT*(1.0-(8.875+0.2165*T)*(PA-101325.0)*1.E-11)
C
C VICE=0.208589006*VPT
C
C VOLUME OF ICE(CC/MOL)
C VICECC=VICE*(1.0E6/35.3147)*(1.0/453.5929)
C
C GAS CONSTANT(CM3-ATM/G-MOLE-K)
C R=82.056
C
C CALCULATE THE VOLUME OF HYDRATE(CC/MOL)
C
C VHVD=VICECC+DELV
C
C CALCULATE THE VAPOR PRESSURE OF THE EMPTY HYDRATE
C LATTICE
C
C IF(ID1.EQ.2)GO TO 50
C CALL VPMT1(T,VP)
C GO TO 60
50 CONTINUE
C CALL VPMT2(T,VP)
60 CONTINUE
C
C CALCULATE THE POYNTING CORRECTION FACTOR
C
C PCF=EXP(VHVD*(P-VP)/(R*T))
C
C FUGACITY COEFFICIENT FOR WATER IN THE EMPTY

```

```
C      HYDRATE LATTICE
C
C      PHI=1.0
C      CALCULATE THE FUGACITY OF WATER IN THE EMPTY
C      HYDRATE LATTICE
C      FUGMT=VP*PHI*PCF
C
C      RETURN
C      END
```

```
      SUBROUTINE VPMT1(T,VPMT1)
C
C *****
C
C THIS PROGRAM USES THE FORMULATION DESCRIBED
C BY P.B. DHARMAWARDHANA TO CALCULATE THE
C EMPTY HYDRATE VAPOR PRESSURES FOR STRUCTURE
C I AND STRUCTURE II.
C *****
C
C UNITS: TEMPERATURE(KELVIN)
C          PRESSURE(ATM)
C
C EMPTY HYDRATE(STRUCTURE I) VAPOR PRESSURE
C
C A=17.448
C B=6703.925
C
C VPMT1=EXP(A-B/T)
C
C RETURN
C END
C
C
C
```



```

SUBROUTINE NGROB(T,P,ID,FUGMT)
C
C *****
C
C THIS PROGRAM USES A METHOD FORMULATED BY
C NG & ROBINSON TO CALCULATE THE FUGACITY
C OF THE WATER IN THE EMPTY HYDRATE LATTICE.
C
C REF:A METHOD FOR PREDICTING THE EQUILIBRIUM
C GAS PHASE WATER CONTENT IN GAS-HYDRATE
C EQUILIBRIUM, NG & ROBINSON, IND. ENG. CHEM.
C FUNDAM. 1980, 19, 33-36
C *****
C
C DETERMINE STRUCTURE
C
C IF(ID.EQ.2)GO TO 50
C STRUCTURE I EMPTY HYDRATE FUGACITY
C
C A=14.269-5393.0/T
C B=0.00036*T-0.1025
C
C FUGMT=EXP(A+B*P)
C GO TO 63
50 CONTINUE
C STRUCTURE II EMPTY HYDRATE FUGACITY
C
C A=18.062-6512.0/T
C B=0.0021109*T-0.03192
C
C FUGMT=EXP(A+B*P)
60 CONTINUE
C
C RETURN
C END

```

EX
 [11:29:55]
 LINK:Loadins
 [LNKXCTHYDRAT execution]

HYDRATE SYSTEM UNDER CONSIDERATION

ETHANE - WATER --ENTER '1'
 PROPANE - WATER --ENTER '2'
 CARBON DIOXIDE - WATER --ENTER '3'
 1

EQUATION OF STATE FOR FUGACITY CALCULATION

PENG - ROBINSON EQUATION --ENTER '1'
 SOAVE - RELICH KWONG EQ. --ENTER '2'
 1

LANGMUIR CONSTANT EVALUATION

MCKOY AND SINANOGLU METHOD --ENTER '1'
 PARRISH & PRAUSNITZ METHOD --ENTER '2'
 1

EMPTY HYDRATE FUGACITY CALCULATION

METHOD OF F.B. DHARMAWARDHANA --ENTER '1'
 METHOD OF NG & ROBINSON --ENTER '2'
 1

INPUT SYSTEM PRESSURE(Psia)

500

INPUT NUMBER OF SYSTEM TEMPERATURES

5

INPUT TEMPERATURE(C) (5 PER LINE)

-30,-20,-10,0,10

PRESSURE = 500.00 PSIA

WATER CONCENTRATION

TEMPERATURE(C)	X(PPM)
-30.000	8.89
-20.000	20.98
-10.000	46.98
0.000	100.76
10.000	209.36


```

EX
[11:33:34]
LINK:Loading
[LNKXCTHYDRAT execution]

HYDRATE SYSTEM UNDER CONSIDERATION

ETHANE - WATER          --ENTER '1'
PROPANE - WATER         --ENTER '2'
CARBON DIOXIDE - WATER --ENTER '3'
1

EQUATION OF STATE FOR FUGACITY CALCULATION

PENG - ROBINSON EQUATION --ENTER '1'
SOAVE - RELICH KWONG EQ. --ENTER '2'
1

LANGMUIR CONSTANT EVALUATION

MCKOY AND SINANOGLU METHOD --ENTER '1'
PARRISH & PRAUSNITZ METHOD --ENTER '2'
2

EMPTY HYDRATE FUGACITY CALCULATION

METHOD OF P.B. DHARMAWARDHANA --ENTER '1'
METHOD OF NG & ROBINSON       --ENTER '2'
1

INPUT SYSTEM PRESSURE(PSIA)
500
INPUT NUMBER OF SYSTEM TEMPERATURES
5
INPUT TEMPERATURE(C) (5 PER LINE)
-30,-20,-10,0,10

      PRESSURE = 500.00 PSIA

      WATER CONCENTRATION

TEMPERATURE(C)          X(PPM)

-30.000                 8.90
-20.000                 20.99
-10.000                 46.98
  0.000                 100.75
 10.000                 209.32

```

```

EX
[11:34:47]
LINK:Loading
[LNKXCTHYDRAT execution]

HYDRATE SYSTEM UNDER CONSIDERATION

ETHANE - WATER          --ENTER '1'
PROPANE - WATER         --ENTER '2'
CARBON DIOXIDE - WATER  --ENTER '3'
1

EQUATION OF STATE FOR FUGACITY CALCULATION

PENG - ROBINSON EQUATION --ENTER '1'
SOAVE - RELICH KWONG EQ. --ENTER '2'
1

LANGMUIR CONSTANT EVALUATION

MCKOY AND SINANOGLU METHOD --ENTER '1'
PARRISH & FRAUSNITZ METHOD --ENTER '2'
1

EMPTY HYDRATE FUGACITY CALCULATION

METHOD OF P.B. DHARMAWARDHANA --ENTER '1'
METHOD OF NG & ROBINSON       --ENTER '2'
2

INPUT SYSTEM PRESSURE(PSIA)
500
INPUT NUMBER OF SYSTEM TEMPERATURES
5
INPUT TEMPERATURE(C) (5 PER LINE)
-30,-20,-10,0,10

      PRESSURE = 500.00 PSIA

      WATER CONCENTRATION

TEMPERATURE(C)          X(PPM)
-30.000                 2.66
-20.000                 6.44
-10.000                 14.89
  0.000                 33.17
 10.000                 72.05

```

```

EX
[11:36:58]
LINK:Loading
[LNKXCTHYDRAT execution]

HYDRATE SYSTEM UNDER CONSIDERATION

ETHANE - WATER           --ENTER '1'
PROPANE - WATER          --ENTER '2'
CARBON DIOXIDE - WATER  --ENTER '3'
2

EQUATION OF STATE FOR FUGACITY CALCULATION

PENG - ROBINSON EQUATION --ENTER '1'
SOAVE - RELICH KWONG EQ. --ENTER '2'
1

LANGMUIR CONSTANT EVALUATION

MCKOY AND SINANOGLU METHOD --ENTER '1'
PARRISH & PRAUSNITZ METHOD --ENTER '2'
1

EMPTY HYDRATE FUGACITY CALCULATION

METHOD OF P.B. DHARMAWARDHANA --ENTER '1'
METHOD OF NG & ROBINSON       --ENTER '2'
1

INPUT SYSTEM PRESSURE(Psia)
112
INPUT NUMBER OF SYSTEM TEMPERATURES
5
INPUT TEMPERATURE(C) (5 PER LINE)
-30,-20,-10,0,10

      PRESSURE = 112.00 PSIA

      WATER CONCENTRATION

TEMPERATURE(C)           X(PPM)

-30.000                  14.03
-20.000                  31.38
-10.000                  66.59
  0.000                  134.78
 10.000                  261.80

```

```

EX
[11:39:04]
LINK:Loadins
[LNKXCTHYDRAT execution]

HYDRATE SYSTEM UNDER CONSIDERATION

ETHANE - WATER           --ENTER '1'
PROPANE - WATER          --ENTER '2'
CARBON DIOXIDE - WATER   --ENTER '3'
2

EQUATION OF STATE FOR FUGACITY CALCULATION

PENG - ROBINSON EQUATION --ENTER '1'
SOAVE - RELICH KWONG EQ. --ENTER '2'
2

LANGMUIR CONSTANT EVALUATION

MCKOY AND SINANOGLU METHOD --ENTER '1'
PARRISH & FRAUSNITZ METHOD --ENTER '2'
1

EMPTY HYDRATE FUGACITY CALCULATION

METHOD OF P.B. DHARMAWARDHANA --ENTER '1'
METHOD OF NG & ROBINSON       --ENTER '2'
1

INPUT SYSTEM PRESSURE(PSIA)
112
INPUT NUMBER OF SYSTEM TEMPERATURES
5
INPUT TEMPERATURE(C) (5 PER LINE)
-30,-20,-10,0,10

PRESSURE = 112.00 PSIA

WATER CONCENTRATION

TEMPERATURE(C)           X(PPM)
-30.000                  13.96
-20.000                  31.35
-10.000                  66.78
 0.000                   135.64
10.000                   264.36

```

```

EX
[11:40:04]
LINK:Loading
[LNKXCTHYDRAT execution]

HYDRATE SYSTEM UNDER CONSIDERATION

ETHANE - WATER          --ENTER '1'
PROPANE - WATER         --ENTER '2'
CARBON DIOXIDE - WATER --ENTER '3'
2

EQUATION OF STATE FOR FUGACITY CALCULATION

PENG - ROBINSON EQUATION --ENTER '1'
SOAVE - RELICH KWONG EQ. --ENTER '2'
1

LANGMUIR CONSTANT EVALUATION

MCKOY AND SINANOGLU METHOD --ENTER '1'
FARRISH & FRAUSNITZ METHOD --ENTER '2'
2

EMPTY HYDRATE FUGACITY CALCULATION

METHOD OF P.B. DHARMAWARDHANA --ENTER '1'
METHOD OF NG & ROBINSON       --ENTER '2'
1

INPUT SYSTEM PRESSURE(PSIA)
112
INPUT NUMBER OF SYSTEM TEMPERATURES
5
INPUT TEMPERATURE(C) (5 PER LINE)
-30,-20,-10,0,10

        PRESSURE = 112.00 PSIA

                WATER CONCENTRATION

TEMPERATURE(C)          X(PPM)
-30.000                 13.64
-20.000                 30.55
-10.000                 64.88
  0.000                 131.45
 10.000                 255.56

```

```

EX
[16:35:35]
LINK: Loading
[LNKXCT HYDRAT execution]

HYDRATE SYSTEM UNDER CONSIDERATION

ETHANE - WATER           --ENTER '1'
PROPANE - WATER          --ENTER '2'
CARBON DIOXIDE - WATER  --ENTER '3'
2

EQUATION OF STATE FOR FUGACITY CALCULATION

PENG - ROBINSON EQUATION --ENTER '1'
SOAVE - RELICH KWONG EQ. --ENTER '2'
1

LANGMUIR CONSTANT EVALUATION

MCKOY AND SINANOGLU METHOD --ENTER '1'
PARRISH & FRAUSNITZ METHOD --ENTER '2'
1

EMPTY HYDRATE FUGACITY CALCULATION

METHOD OF P.B. DHARMAWARDHANA --ENTER '1'
METHOD OF NG & ROBINSON       --ENTER '2'
2

INPUT SYSTEM PRESSURE(Psia)
112
INPUT NUMBER OF SYSTEM TEMPERATURES
5
INPUT TEMPERATURE(C) (5 PER LINE)
-30,-20,-10,0,10

PRESSURE = 112.00 PSIA

WATER CONCENTRATION

TEMPERATURE(C)          X(PPM)
-30.000                 3.64
-20.000                 8.90
-10.000                 20.50
  0.000                 44.83
 10.000                 93.62

```

EX
 [11:38:04]
 LINK:Loading
 [LNKXCTHYDRAT execution]

HYDRATE SYSTEM UNDER CONSIDERATION

ETHANE - WATER --ENTER '1'
 PROPANE - WATER --ENTER '2'
 CARBON DIOXIDE - WATER --ENTER '3'
 2

EQUATION OF STATE FOR FUGACITY CALCULATION

PENG - ROBINSON EQUATION --ENTER '1'
 SOAVE - RELICH KWONG EQ. --ENTER '2'
 1

LANGMUIR CONSTANT EVALUATION

MCKOY AND SINANOGLU METHOD --ENTER '1'
 PARRISH & FRAUSNITZ METHOD --ENTER '2'
 1

EMPTY HYDRATE FUGACITY CALCULATION

METHOD OF P.B. DHARMAWARDHANA --ENTER '1'
 METHOD OF NG & ROBINSON --ENTER '2'
 1

INPUT SYSTEM PRESSURE(PSIA)

262

INPUT NUMBER OF SYSTEM TEMPERATURES

5

INPUT TEMPERATURE(C) (5 PER LINE)

-30,-20,-10,0,10

PRESSURE = 262.00 PSIA

WATER CONCENTRATION

TEMPERATURE(C)	X(PPM)
-30.000	13.91
-20.000	31.10
-10.000	65.92
0.000	133.28
10.000	258.48

APPENDIX E

DIELECTRIC-TEMPERATURE DATA REDUCTION ROUTINE

PROGRAM LISTING AND OUTPUT

```

C      *****
C
C      THIS PROGRAM IS USED IN THE DETERMINATION OF THE
C      "BREAK" POINT OF THE EXPERIMENTAL DIELECTRIC DATA.
C      THE SOLUTION IS OBTAINED BY LOOKING AT EVERY
C      POSSIBLE DIVISION OF EXPERIMENTAL POINTS ASSIGNED
C      TO TWO STRAIGHT LINES. THE PARAMETERS OF THE TWO
C      LINES ARE ESTIMATED BY LINEAR LEAST SQUARES AND THE
C      RESIDUAL SUM OF SQUARES IS ALSO EVALUATED FOR EACH
C      DIVISION. THE DIVISION AND SET OF PARAMETERS THAT
C      GIVE RISE TO THE SMALLEST OF ALL THE RESIDUAL SUM OF
C      SQUARES SHOULD BE CHOSEN AS THE APPROPRIATE MODEL
C      DESCRIPTION OF THE EXPERIMENTAL DATA.
C
C      *****
C
C      IMPLICIT DOUBLE PRECISION (A-H,O-Z)
C      DIMENSION X(30),Y(30)
C      DOUBLE PRECISION FILIN
C      TYPE 10
10    FORMAT(1X,'ENTER INPUT FILE NAME')
C      ACCEPT 20, FILIN
20    FORMAT(A10)
C      OPEN(UNIT=1,FILE=FILIN)
C
C      READ(1,30)N
30    FORMAT(I)
C      DO 40 J=1,N
C      READ(1,50)X(J),Y(J)
50    FORMAT(15X,F15.8,15X,F15.8)
C      Y(J)=(Y(J)-1.0)/(Y(J)+2.0)
40    CONTINUE
C
C      PRINT HEADING
C      WRITE(15,900)FILIN
900   FORMAT(1X,'FILE = ',A10/)
C      WRITE(15,600)N
600   FORMAT(1X,'N = ',I2,/)
C      WRITE(15,650)
650   FORMAT(1X,5X,'M',8X,'R21',12X,'R22',12X,'T(C)',10X,/)
C      WRITE(16,655)
655   FORMAT(1X,8X,'A1',12X,'A2',12X,'B1',12X,'B2',12X,'T(C)',/)
C      WRITE(17,660)
660   FORMAT(1X,5X,'T(C)',12X,'S1',12X,'S2',12X,'SSE',12X,/)
C
C      DO 100 M=2,N-2
C
C      INITIALIZE SUMMATIONS
C      SUMX1=0.0
C      SUMX2=0.0

```

```

SUMY1=0.0
SUMY2=0.0
SUMXY1=0.0
SUMXY2=0.0
SUMXX1=0.0
SUMXX2=0.0
SUMYY1=0.0
SUMYY2=0.0
C
C
C
DO 200 I=1,M
SUMX1=SUMX1+X(I)
SUMY1=SUMY1+Y(I)
SUMXY1=SUMXY1+X(I)*Y(I)
SUMXX1=SUMXX1+X(I)**2
SUMYY1=SUMYY1+Y(I)**2
C
200 CONTINUE
C
C
C
SUM OF THE SQUARES
SXX1=SUMXX1-FLOAT(M)*(SUMX1/FLOAT(M))**2
SYY1=SUMYY1-FLOAT(M)*(SUMY1/FLOAT(M))**2
SXY1=SUMXY1-FLOAT(M)*(SUMX1/FLOAT(M))*(SUMY1/FLOAT(M))
B1=SXY1/SXX1
A1=SUMY1/FLOAT(M)-B1*SUMX1/FLOAT(M)
C
C
C
COEFFICIENT OF DETERMINATION
R21=(A1*SUMY1+B1*SUMXY1-1./FLOAT(M)*SUMY1**2)
1 /((SUMYY1-1./FLOAT(M)*SUMY1**2)
C
SSE1=SYY1-B1*SXY1
IF(M.EQ.2)SS1=J.0
IF(M.EQ.2)GOTO 905
SS1=SSE1/(FLOAT(M)-2.0)
S1=SQRT(SS1)
905 CONTINUE
C
C
C
DO 300 II=M+1,N
SUMX2=SUMX2+X(II)
SUMY2=SUMY2+Y(II)
SUMXY2=SUMXY2+Y(II)*X(II)
SUMXX2=SUMXX2+X(II)**2
SUMYY2=SUMYY2+Y(II)**2
C
300 CONTINUE
C
C
C

```

```

C
C
C
SUM OF THE SQUARES
SXX2=SUMXX2-FLOAT(N-M)*(SUMX2/FLOAT(N-M))**2
SYY2=SUMYY2-FLOAT(N-M)*(SUMY2/FLOAT(N-M))**2
SXY2=SUMXY2-FLOAT(N-M)*(SUMX2/FLOAT(N-M))*(SUMY2/FLOAT(N-M))
B2=SXY2/SXX2
A2=SUMY2/FLOAT(N-M)-B2*SUMX2/FLOAT(N-M)
C
C
COEFFICIENT OF DETERMINATION
C
R22=(A2*SUMY2+B2*SUMXY2-1./FLOAT(N-M)*SUMY2**2)
1 /((SUMYY2-1./FLOAT(N-M)*SUMY2**2)
C
SSE2=SYY2-B2*SXY2
IF(N-M.EQ.2)SS2=.0
IF(N-M.EQ.2)GOTO 925
SS2=SSE2/(FLOAT(N-M)-2.0)

S2=SQRT(SS2)
925 CONTINUE
C
C
C
SOLUTION OF SIMULTANEOUS EQUATIONS
XX=(A1-A2)/(B2-B1)
T=1000./XX-273.15
ERROR=(ABS(1.-R21)+ABS(1.-R22))
SSE=SSE1+SSE2
C
C
C
PRINT RESULTS
WRITE(15,800)M,R21,R22,T
800 FORMAT(1X,4X,I2,2X,3F15.8)
WRITE(16,815)A1,A2,B1,B2,T
815 FORMAT(5F15.8)
WRITE(17,820)T,S1,S2,SSE
820 FORMAT(4G15.8)
C
C
C
100 CONTINUE
C
END

```

```

EX LEAST.FOR
[11:55:43]
LINK: Loading
[LNKXCT LEAST execution]
ENTER INPUT FILE NAME
110582.DAT

```

CPU time 0.55 Elapsed time 10.57

EXIT

```

.TYPE FOR15.DAT
[11:56:07]
FILE = 110582.DAT

```

N = 15

M	R21	R22	T(C)
2	1.00000000	0.99730483	7.23133632
3	0.99951054	0.99760734	5.48881269
4	0.99966733	0.99772983	4.70325753
5	0.99967533	0.99808853	3.83076862
6	0.99961530	0.99839911	2.87715701
7	0.99966791	0.99845359	2.17642610
8	0.99937110	0.99877605	0.94800437
9	0.99929830	0.99895687	-0.16384313
10	0.99891506	0.99902928	-1.57164761
11	0.99887112	0.99941992	-3.31960209
12	0.99825103	0.99974826	-5.67536400
13	0.99735764	1.00000000	-8.53762296

TYPE FOR16.DAT
[11:56:44]

A1	A2	B1	B2	T(C)
0.03290566	0.06670405	0.04390072	0.03442428	7.23133632
0.03783419	0.06783163	0.04248527	0.03412682	5.48881269
0.03898430	0.06874011	0.04215586	0.03388811	4.70325753
0.03972018	0.07007005	0.04194524	0.03353891	3.83076862
0.04086999	0.07135348	0.04161738	0.03320311	2.87715701
0.04160153	0.07236382	0.04140936	0.03293969	2.17642610
0.04328683	0.07388869	0.04093108	0.03254317	0.94800437
0.04459157	0.07539891	0.04056169	0.03215171	-0.16384313
0.04683203	0.07682704	0.03992931	0.03178332	-1.57164761
0.04817868	0.07976492	0.03954968	0.03102675	-3.31960209
0.05116570	0.08283802	0.03871115	0.03023960	-5.67536400
0.05508168	0.08598727	0.03761559	0.02943759	-8.53762296

.TYPE FOR17.DAT
[11:57:28]

T(C)	S1	S2	SSE
7.2313363	0.00000000	0.23981467E-03	0.63262183E-06
5.4888127	0.48089837E-04	0.22161300E-03	0.49343586E-06
4.7032575	0.38191229E-04	0.21325639E-03	0.41222174E-06
3.8307686	0.35489744E-04	0.19060968E-03	0.29443497E-06
2.8771570	0.39430462E-04	0.17036545E-03	0.20938976E-06
2.1764261	0.38916900E-04	0.16425543E-03	0.16945171E-06
0.94800437	0.56364807E-04	0.14165299E-03	0.11938979E-06
-0.16384313	0.63689147E-04	0.12574234E-03	0.91638695E-07
-1.5716476	0.87291856E-04	0.11818128E-03	0.10285939E-06
-3.3196021	0.95452555E-04	0.80427306E-04	0.94937816E-07
-5.6753640	0.13465923E-03	0.47679338E-04	0.18360441E-06
-8.5376230	0.19260917E-03	0.47679338E-04	0.40808123E-06

APPENDIX F

MONTE CARLO ERROR ANALYSIS OF "BREAK" TEMPERATURE
REGRESSION ROUTINE
PROGRAM LISTING AND OUTPUT

```

C *****
C
C THIS PROGRAM UTILIZES MONTE CARLO SIMULATION TO
C ESTIMATE THE VARIANCE OF THE HYDRATE EQUILIBRIUM
C TEMPERATURE FOUND FROM LINEAR REGRESSION OF THE
C EXPERIMENTAL DATA.
C *****
C
C IMPLICIT DOUBLE PRECISION (A-H,O-Z)
C DIMENSION T1(10),T2(10),DIE1(10),DIE2(10),Y1(10),Y2(10)
C DIMENSION IP(13),IM(13),ICP(13),ICM(13)
C
C INPUT PARAMETER FOR MEAN VALUES
C
C WRITE(4,100)
100 FORMAT(1X,"INPUT INTERCEPTS(A1 & A2)")
C READ(4,105)A1,A2
C WRITE(4,107)
107 FORMAT(1X,"INPUT SLOPES(B1 & B2)")
C READ(4,105)B1,B2
105 FORMAT(2F)
C
C TINV=(A1-A2)/(B2-B1)/1000.0
C TKMEAN=1.0/TINV
C
C DO 50 J=1,10
C T1(J)=TKMEAN+FLOAT(J)
C T2(J)=TKMEAN-FLOAT(J)
50 CONTINUE
C
C DO 60 I=1,10
C DIE1(I)=A1+B1*(1000.0/T1(I))
C DIE2(I)=A2+B2*(1000.0/T2(I))
60 CONTINUE
C
C INPUT ESTIMATED STANDARD DEVIATION(FROM REGRESSION)
C WRITE(4,110)
110 FORMAT(1X,"INPUT ESTIMATED STANDARD DEVIATION(S1 & S2)")
C READ(4,115)S1,S2
115 FORMAT(2F)
C VAR1=S1**2
C VAR2=S2**2
C
C 450 CONTINUE
C
C INPUT NUMBER OF EXPERIMENTAL SIMULATIONS
C WRITE(4,120)
120 FORMAT(1X,"INPUT NUMBER OF EXPERIMENTAL SIMULATIONS")
C READ(4,125)N
125 FORMAT(I)

```

```

C
C   INITIALIZE SUMMATION
SUM1=0.0
SUM2=0.0
C   INITIALIZE HISTOGRAM COUNTERS
DO 235 J=1,13
  IP(J)=0
  IM(J)=0
235 CONTINUE
C
C   OPEN(UNIT=8,FILE='HISTO')
C
C
C
C   DO 1000 K=1,N
C
C   INITIALIZE SUMMATIONS REQUIRED FOR REGRESSION
SUMX1=0.0
SUMX2=0.0
SUMY1=0.0
SUMY2=0.0
SUMXY1=0.0
SUMXY2=0.0
SUMXX1=0.0
SUMXX2=0.0
SUMYY1=0.0
SUMYY2=0.0
C   INITIALIZE HISTOGRAM COUNTERS
DO 245 I=1,13
  ICP(I)=0
  ICM(I)=0
245 CONTINUE
C
C
C
C   DO 500 JJ=1,10
  Y1(JJ)=RNORM(DIE1(JJ),VAR1)
  Y2(JJ)=RNORM(DIE2(JJ),VAR2)
500 CONTINUE
C
C   DO 600 I=1,10
SUMX1=SUMX1+1000.0/T1(I)
SUMX2=SUMX2+1000.0/T2(I)
SUMY1=SUMY1+Y1(I)
SUMY2=SUMY2+Y2(I)
SUMXY1=SUMXY1+1000.0/T1(I)*Y1(I)
SUMXY2=SUMXY2+1000.0/T2(I)*Y2(I)
SUMXX1=SUMXX1+(1000.0/T1(I))**2
SUMXX2=SUMXX2+(1000.0/T2(I))**2
SUMYY1=SUMYY1+Y1(I)**2
SUMYY2=SUMYY2+Y2(I)**2

```

```

673 CONTINUE
C
X1BAR=SUMX1/10.0
X2BAR=SUMX2/10.0
Y1BAR=SUMY1/10.0
Y2BAR=SUMY2/10.0
C
SXY1=SUMXY1-10.0*X1BAR*Y1BAR
SXY2=SUMXY2-10.0*X2BAR*Y2BAR
SXX1=SUMXX1-10.0*X1BAR**2
SXX2=SUMXX2-10.0*X2BAR**2
C
B1=SXY1/SXX1
B2=SXY2/SXX2
A1=Y1BAR-B1*X1BAR
A2=Y2BAR-B2*X2BAR
C
C
SOLUTION OF SIMULTANEOUS EQUATIONS
XX=(A1-A2)/(B2-B1)
TTK=1000.0/XX
SUM1=SUM1+TTK
SUM2=SUM2+TTK**2
DIF=TTK-TKMEAN
IF(DIF.GE.0.0.AND.DIF.LE.0.25)ICP(1)=1
IF(DIF.GE.0.25.AND.DIF.LE.0.5)ICP(2)=1
IF(DIF.GE.0.5.AND.DIF.LE.0.75)ICP(3)=1
IF(DIF.GE.0.75.AND.DIF.LE.1.0)ICP(4)=1
IF(DIF.GE.1.0.AND.DIF.LE.1.25)ICP(5)=1
IF(DIF.GE.1.25.AND.DIF.LE.1.5)ICP(6)=1
IF(DIF.GE.1.5.AND.DIF.LE.1.75)ICP(7)=1
IF(DIF.GE.1.75.AND.DIF.LE.2.0)ICP(8)=1
IF(DIF.GE.2.0.AND.DIF.LE.2.25)ICP(9)=1
IF(DIF.GE.2.25.AND.DIF.LE.2.5)ICP(10)=1
IF(DIF.GE.2.5.AND.DIF.LE.2.75)ICP(11)=1
IF(DIF.GE.2.75.AND.DIF.LE.3.0)ICP(12)=1
IF(DIF.GE.3.0)ICP(13)=1
IF(DIF.LE.0.0.AND.DIF.GE.-.25)ICM(1)=1
IF(DIF.LE.-.25.AND.DIF.GE.-.5)ICM(2)=1
IF(DIF.LE.-.5.AND.DIF.GE.-.75)ICM(3)=1
IF(DIF.LE.-.75.AND.DIF.GE.-1.0)ICM(4)=1
IF(DIF.LE.-1.0.AND.DIF.GE.-1.25)ICM(5)=1
IF(DIF.LE.-1.25.AND.DIF.GE.-1.5)ICM(6)=1
IF(DIF.LE.-1.5.AND.DIF.GE.-1.75)ICM(7)=1
IF(DIF.LE.-1.75.AND.DIF.GE.-2.0)ICM(8)=1
IF(DIF.LE.-2.0.AND.DIF.GE.-2.25)ICM(9)=1
IF(DIF.LE.-2.25.AND.DIF.GE.-2.5)ICM(10)=1
IF(DIF.LE.-2.5.AND.DIF.GE.-2.75)ICM(11)=1
IF(DIF.LE.-2.75.AND.DIF.GE.-3.0)ICM(12)=1
IF(DIF.LE.-3.0)ICM(13)=1
C
C

```

```

DO 285 J=1,13
IP(J)=IP(J)+ICP(J)
IM(J)=IM(J)+ICM(J)
285 CONTINUE
C
1#0# CONTINUE
C
C
C AVERAGE TEMPERATURE
TAVE=SUM1/FLOAT(N)
C VARIANCE OF RANDOM SAMPLE
VARIAN=(FLOAT(N)*SUM2-SUM1**2)/(FLOAT(N)*FLOAT(N-1))
C STANDARD DEVIATION
SDEV=SQRT(VARIAN)
C
C PRINT RESULTS
C
WRITE(4,200)TKMEAN
200 FORMAT(1X,/,/, ' REGRESSION TEMP(K) = ',F8.3)
WRITE(4,205)TAVE
205 FORMAT(1X, ' SIMULATION TEMP(K) = ',F8.3)
WRITE(4,210)SDEV
210 FORMAT(1X, ' STANDARD DEVIATION(K) = ',F10.6)
WRITE(4,215)N
215 FORMAT(1X, ' NUMBER OF SIMULATIONS = ',I10,/)
C
DO 415 I=1,13
J=I-1
XXY=FLOAT(J)*.25+.125
FRAC=FLOAT(IP(I))/FLOAT(N)
WRITE(8,420)XXY,FRAC
415 CONTINUE
DO 435 I=1,13
J=I-1
XXY=FLOAT(J)*(-.25)-.125
FRAC=FLOAT(IM(I))/FLOAT(N)
WRITE(8,420)XXY,FRAC
435 CONTINUE
C
CLOSE(UNIT=8,FILE='HISTO')
C
420 FORMAT(2F)
C
C
WRITE(4,305)
305 FORMAT(1X, ' DO YOU WISH TO CHANGE THE NUMBER OF ITERATIONS')
WRITE(4,310)
310 FORMAT(1X, ' YES --ENTER "1"')
WRITE(4,315)
315 FORMAT(1X, ' NO --ENTER "2"')
READ(4,320)ID

```

```
320  FORMAT(I)
      IF(ID.EQ.1)GOTO 450
C
      END
```

```
EX MCREG.FOR,NAC:NAC/SEARCH
[12:23:59]
LINK: Loading
[LNKXCT MCREG execution]
INPUT INTERCEPTS(A1 & A2)
1.04071501,1.16919420
INPUT SLOPES(B1 & B2)
.18494606,.14987751
INPUT ESTIMATED STANDARD DEVIATION(S1 & S2)
.26190093E-3,.53159412E-3
INPUT NUMBER OF EXPERIMENTAL SIMULATIONS
1000
```

```
REGRESSION TEMP(K) = 272.951
SIMULATION TEMP(K) = 273.029
STANDARD DEVIATION(K) = 0.883290
NUMBER OF SIMULATIONS = 1000
```

```
DO YOU WISH TO CHANGE THE NUMBER OF ITERATIONS
YES --ENTER '1'
NO --ENTER '2'
1
INPUT NUMBER OF EXPERIMENTAL SIMULATIONS
10000
```

```
REGRESSION TEMP(K) = 272.951
SIMULATION TEMP(K) = 273.014
STANDARD DEVIATION(K) = 0.876564
NUMBER OF SIMULATIONS = 10000
```

```
DO YOU WISH TO CHANGE THE NUMBER OF ITERATIONS
YES --ENTER '1'
NO --ENTER '2'
2
```

```
CPU time 59.05 Elapsed time 4:24.45
```

```
EXIT
```

APPENDIX G

CALCULATION OF WATER CONCENTRATION AND CORRESPONDING
MONTE CARLO ANALYSIS FOR THE DETERMINATION OF THE
VARIANCE OF THE WATER CONCENTRATION

PROGRAM LISTING AND OUTPUT

```

C *****
C
C THIS PROGRAM CALCULATES THE WATER CONCENTRATION
C IN EITHER LIQUID PROPANE OR LIQUID ETHANE. IT
C ALSO IS CAPABLE OF UTILIZING MONTE CARLO
C SIMULATION TO ESTIMATE THE VARIANCE OF THE
C AMOUNT OF WATER LOADED INTO THE EQUILIBRIA CELL.
C *****
C
C IMPLICIT DOUBLE PRECISION(A-H,O-Z)
C DIMENSION IHM(0:50),IHP(0:50),IHMM(0:50),IHPP(0:50)
C
C SELECT SYSTEM FOR CONSIDERATION
C WRITE(4,50)
50 FORMAT(1X,/, ' SYSTEM UNDER CONSIDERATION',/)
C WRITE(4,55)
55 FORMAT(1X, 'CONDENSED ETHANE.- WATER MIXTURE <ENTER "1">')
C WRITE(4,60)
60 FORMAT(1X, 'CONDENSED PROPANE - WATER MIXTURE -ENTER "2">')
C READ(4,65)ID1
65 FORMAT(I)
C
C SELECT EQUATION OF STATE
C WRITE(4,1030)
1030 FORMAT(1X,/, ' EQUATION OF STATE EMPLOYED',/)
C WRITE(4,1035)
1035 FORMAT(1X, 'CORRESPONDING STATES -ENTER "1">')
C WRITE(4,1040)
1040 FORMAT(1X, 'GOODWIN EQUATION -ENTER "2">')
C READ(4,65)IDD
C
C INPUT LOADING TEMPERATURE AND PRESSURE
C
C WRITE(4,70)
70 FORMAT(1X,/, ' INPUT LOADING SYSTEM TEMPERATURE(DORIC(C))')
C READ(4,90)TM
C WRITE(4,75)
75 FORMAT(1X, 'INPUT LOADING SYSTEM PRESSURE(BAROCEL(TORR))')
C READ(4,90)PM
C
C INPUT SYSTEM TEMPERATURE AND PRESSURE
C
C WRITE(4,80)
80 FORMAT(1X, 'INPUT SYSTEM TEMPERATURE(C)')
C READ(4,90)TTT
C WRITE(4,85)
85 FORMAT(1X, 'INPUT SYSTEM PRESSURE(PSIA)')
C READ(4,90)PPP
90 FORMAT(F)

```

```

C
C   SELECT OPERATION MODE
C
C   WRITE(4,95)
95  FORMAT(1X,/' MODE OF ANALYSIS',/)
C   WRITE(4,100)
100 FORMAT(1X,'WATER CONCENTRATION      -ENTER "1"'')
C   WRITE(4,105)
105 FORMAT(1X,'MONTE CARLO SIMULATION  -ENTER "2"'')
C   READ(4,65)ID2
C
C
C   CELL VOLUME(CM3)
C   CV=15.12
C
C   IF(ID2.EQ.1)GOTO 200
C   WRITE(4,135)
135 FORMAT(1X,/' INPUT REGRESSION STANDARD DEVIATION')
C   READ(4,90)SDREG
C
C
C   VARIANCE OF VARIABLES
C
C   VARIANCE OF "BREAK" TEMPERATURE
C   VAR1=SDREG**2
C   VARIANCE OF SYSTEM PRESSURE
C   VAR2=((0.1/100.0)*PPP/3.29)**2
C   VARIANCE OF BAROCEL PRESSURE MEASUREMENT
C   VAR3=((5.0/100.0)*PM/3.29)**2
C   VARIANCE OF LOADING TEMPERATURE
C   VAR4=((0.023/100.0)*TM/3.29)**2
C   VARIANCE OF CELL VOLUME
C   VAR5=0.1**2
C
C
C   CALCULATED CONCENTRATION
200 CONTINUE
C   IF(ID1.EQ.1)GOTO 250
C   CALL GOODC3(IDD,TTT,PPP,TM,PM,CV,CV,D,XPPM)
C   GOTO 275
250 CONTINUE
C   CALL GOODC2(IDD,TTT,PPP,TM,PM,CV,CV,D,XPPM)
275 CONTINUE
C
C   IF(ID2.EQ.1)GOTO 300
C
C   CONTINUE
500 WRITE(4,110)
110 FORMAT(1X,/' INPUT NUMBER OF SIMULATIONS')
C   READ(4,65)N
C   INITIALIZE SUMMATIONS

```

```

SUM1=0.0
SUM2=0.0
C   INITIALIZE COUNTERS
DO 635 I=1,51
    J=I-1
    IHM(J)=0
    IHP(J)=0
635 CONTINUE
C
C   OPEN DATA FILE
OPEN(UNIT=25,FILE='DIST')
C
C
C   DO 1000 K=1,N
C
C   GENERATE RANDOM VARIABLES
T1=RNORM(TTT,VAR1)
P1=RNORM(PPP,VAR2)
P2=RNORM(PM,VAR3)
T2=RNORM(TM,VAR4)
CV1=RNORM(CV,VAR5)
CV2=RNORM(CV,VAR5)
C
IF(ID1.EQ.1)GOTO 335
CALL GOODC3(IDD,T1,P1,T2,P2,CV1,CV2,D,XXX)
GOTO 340
335 CONTINUE
CALL GOODC2(IDD,T1,P1,T2,P2,CV1,CV2,D,XXX)
340 CONTINUE
C
SUM1=SUM1+XXX
SUM2=SUM2+XXX**2
C
C   DETERMINE HISTOGRAM INTERVAL
DEL=XXX-XPPM
C
DO 665 J=1,51
    I=J-1
    ZP1=FLOAT(I)*0.2
    ZP2=FLOAT(J)*0.2
    ZM1=FLOAT(-I)*0.2
    ZM2=FLOAT(-J)*0.2
    IHPP(I)=0
    IHMM(I)=0
    IF(I.EQ.50)GOTO 1055
    GOTO 1060
1055 CONTINUE
    ZP2=1.E6
    ZM2=-1.E6
1060 CONTINUE
C

```

```

IF(DEL.GE.ZP1.AND.DEL.LE.ZP2)IHPP(I)=1
IF(DEL.LE.ZM1.AND.DEL.GE.ZM2)IHMM(I)=1
IHP(I)=IHP(I)+IHPP(I)
IHM(I)=IHM(I)+IHMM(I)
C
665 CONTINUE
C
C
C
1000 CONTINUE
C
XAVE=SUM1/FLOAT(N)
C
SS=(FLOAT(N)*SUM2-SUM1**2)/(FLOAT(N)*FLOAT(N-1))
C
SDEV=SQRT(SS)
C
C OUTPUT DISTRIBUTION
DO 735 I=1,51
J=I-1
X11=FLOAT(J)*0.2+0.1
X22=FLOAT(-J)*0.2-0.1
Y11=FLOAT(IHP(J))/FLOAT(N)
Y22=FLOAT(IHM(J))/FLOAT(N)
WRITE(25,745)X11,Y11
WRITE(25,745)X22,Y22
735 CONTINUE
745 FORMAT(2F15.5)
C
C CLOSE DATA FILE
CLOSE(UNIT=25,FILE='DIST')
C
C
C
300 CONTINUE
C OUTPUT RESULTS
WRITE(4,805)
805 FORMAT(1X,/, ' RESULTS OF ANALYSIS',/)
WRITE(4,810)TTT
810 FORMAT(1X, 'SYSTEM TEMPERATURE(C) = ',F14.2)
WRITE(4,815)PPP
815 FORMAT(1X, 'SYSTEM PRESSURE(PSIA) = ',F14.2)
WRITE(4,820)XPPM
820 FORMAT(1X, 'WATER CONCENTRATION(PPM) = ',F11.4)
IF(ID2.EQ.1)GOTO 890
WRITE(4,825)XAVE
825 FORMAT(1X, 'AVERAGE CONCENTRATION(PPM) = ',F8.4)
WRITE(4,830)SDEV
830 FORMAT(1X, 'STANDARD DEVIATION(PPM) = ',F18.8)
WRITE(4,880)N
880 FORMAT(1X, 'NUMBER OF SIMULATIONS = ',I11,/)

```

```
      WRITE(4,835)
835  FORMAT(1X,"CHANGE NUMBER OF SIMULATIONS")
      WRITE(4,840)
840  FORMAT(1X," YES  -ENTER "1"")
      WRITE(4,845)
845  FORMAT(1X," NO   -ENTER "2"")
      READ(4,65)ID3
C
      IF(ID3.EQ.1)GOTO 500
C
890  CONTINUE
      WRITE(4,865)
865  FORMAT(1X,/)
      END
```

```

SUBROUTINE GOODC2(IDD,TTT,PPP,TM,PM,CV1,CV2,D,XPPM)
C
C *****
C
C THIS PROGRAM CALCULATES THE DENSITY OF LIQUID ETHANE
C GIVEN TEMPERATURE AND PRESSURE.
C THE EQUATION OF STATE EMPLOYED IS OUTLINED IN THE NBS
C TECHNICAL NOTE 684 - THERMOPHYSICAL PROPERTIES OF
C ETHANE, FROM 90 TO 600 K AT PRESSURES TO 700 BAR
C
C NOTE: A MORE DETAILED DESCRIPTION OF THE EQUATION OF
C STATE IS GIVEN IN AN ARTICLE BY ROBERT D. GOODWIN.
C THE ARTICLE IS ENTITLED: EQUATION OF STATE FOR
C THERMODYNAMIC PROPERTIES OF FLUIDS
C REFERENCE: JOURNAL OF RESEARCH OF THE NATIONAL BUREAU
C OF STANDARDS - A. PHYSICS AND CHEMISTRY VOL. 79A, NO. 1,
C JANUARY - FEBRUARY 1975
C *****
C
C
C
C IMPLICIT DOUBLE PRECISION (A-H,O-Z)
C
C LIST CRITICAL AND TRIPLE POINT CONSTANTS
C TT=90.348
C TC=305.33
C TDIF=TC-TT
C TRAT=TT/TC
C DC=6.74
C DT=21.680
C DDIF=DT-DC
C DRAT=DT/DC
C
C LIST COEXISTANCE TEMPERATURE CONSTANTS
C EPS=1.0/3.0
C A=0.719684501
C B=0.201866182
C C=-0.289937306
C
C LIST COEXISTANCE PRESSURE CONSTANTS
C EPSEPS=1.3
C AA=-11.3899624306
C BB=18.8452282876
C CC=-7.6354151345
C DD=5.4284431006
C EE=-1.3623270362
C FF=0.7692492586
C
C LIST EQUATION OF STATE CONSTANTS FOR
C DERIVED PARAMETERS

```

```

ALPHA=1.
SIGMA=2.0/3.0
C
B1=.48752227313
B2=.33198750982
B3=.06854249828
C0=2.0
C1=-.43113918548
C2=.0
C3=.03779460468
C
C
LIST CONSTANTS FOR PROGRAM CALCULATIONS
R=.0831434*DC
CONV=10.**(-12)
CON=10.**(-9)
DHIGH=18.0
SEQ=.0
SEQU=.0
SEQUE=.0
C
C
INPUT SYSTEM TEMPERATURE AND PRESSURE AND ESTIMATE DENSITY
C
C
OF LIQUID ETHANE.
C
CALL C2H6(TTT,PPP,TM,PM,CV2,DLOW,H2OMOL)
C
TEMP=TTT+273.15
PRESS=PPP/14.696*1.01325
D=DLOW
IF(IDD.EQ.1)GOTO 935
C
C
CALCULATE THE COEXISTANCE TEMPERATURE GIVEN DENSITY
C
C
USING THE ORTHOBARIC LIQUID DENSITY EQUATION
200 Y=(D-DC)/DDIF
X=(TC-TEMP)/TDIF
250 CONTINUE
YY=(Y-X)/(X**EPS-X)
YYNEW=A+B*X**(1.0-EPS)+C*X
DELTA=(YYNEW-YY)/YY
IF(ABS(DELTA).LE.CONV)GOTO 300
C
C
USE NEWTON'S METHOD CONVERGENCE TO DETERMINE NEW X
DFDX=(1.0-EPS)*B**(-EPS)+C-1.0/(X**3-X)-(Y-X)*(3.0*X**2-1.0)
1 / (X**3-X)
X=X-(YYNEW-YY)/DFDX
GOTO 250
C
C
BACK OUT THE COEXISTANCE TEMPERATURE AFTER X AT
C
C
COEXISTANCE HAS BEEN FOUND
300 T=TC-X*TDIF
C
C
CALCULATE THE COEXISTANCE PRESSURE GIVEN DENSITY

```

```

C      USING THE VAPOR PRESSURE EQUATION
      XX=(1.0-TT/T)/(1.0-TT/TC)
      UU=(T-TT)/(TC-TT)
      P=EXP(AA+BB*XX+CC*UU+DD*UU**2+EE*UU**3+FF*UU*(1.0-UU)**EPSEPS)
C
C      CALCULATE FUNCTION RED OF THE EQUATION OF STATE
      RED1=TEMP/TC
      RED2=ALOG(TEMP/T)
      RED=(RED1**.5)*RED2
C
C      CALCULATE FUNCTION BLUE OF THE EQUATION OF STATE
      DENS=D/DC
      BLUE1=(ABS(DENS-1.))**3/((DRAT-1.))**3)
      BLUE2=T*EXP(-ALPHA*BLUE1)
      BLUE3=1.-(BLUE2/TEMP)
      BLUE4=1.-BLUE3+BLUE3*ALOG(BLUE3)
      BLUE=SIGMA/RED1+(1.-SIGMA)*BLUE4
C
C      CALCULATE FUNCTION GREEN, THE COEXISTANCE EQUIVALENT
      OF FUNCTION BLUE AND RED1
      GREEN1=T/TC
      GREEN3=1.-(BLUE2/T)
      GREEN4=1.-GREEN3+GREEN3*ALOG(GREEN3)
      GREEN=SIGMA/GREEN1+(1.-SIGMA)*GREEN4
C
C      CALCULATE FUNCTION GRAY OF THE EQUATION OF STATE
      GRAY=BLUE-GREEN
C
C      CALCULATE FUNCTIONS CAPB, CAPC, AND CAPF OF THE
      EQUATION OF STATE
      CAPB=B1+B2*DENS+B3*DENS**2
      CAPC=(DENS-1.0)*(DENS-C0)*(C1+C2*DENS+C3*DENS**2)
      CAPF=CAPB*RED+CAPC*GRAY
C
C      CALCULATE THE PRESSURE GIVEN ESTIMATED DENSITY AND
      THE KNOWN TEMPERATURE USING THE EQUATION OF STATE
      PCALC1=P+DENS*R*(TEMP-T)
      PCALC2=DENS**2*R*TC*CAPF
      PCALC=PCALC1+PCALC2
C
C      CALCULATE THE CONVERGENCE OF PRESSURE TO
      KNOWN PRESSURE
      DIFF=ABS((PRESS-PCALC)/PRESS)
      IF(DIFF.LE.CON) GO TO 550
C
C      CALCULATE A NEW DENSITY USING REGULA-FALSI CONVERGENCE
      ON PRESSURE
      IF(SEQ.LT.1.) GOTO 350
325  DNEW1=(PCALC-PRESS)/(PCALC-PPOLE)
      DNEW2=D-DPOLE
      D=D-DNEW1*DNEW2

```

```

      GOTO 200
C
C   CALCULATE THE HIGH PRESSURE BOUNDARY IN THE
C   REGULA-FALSI CONVERGENCE
350  IF(SEQU.GT.1.) GOTO 400
      PLGW=PCALC
      D=DHIGH
      SEQU=2.
      GOTO 200
C
C   CALCULATE THE FIRST NEW DENSITY USING THE ESTABLISHED
C   REGULA-FALSI LIMITS
400  IF(SEQU.GT.1.) GOTO 450
      PHIGH=PCALC
      PPOLE=PLOW
      DPOLE=DLOW
      SEQU=2.
      GOTO 325
C
C   CALCULATE WHICH POLE TO USE FOR SUBSEQUENT ITERATIONS
450  SEQU=2.
      IF ((PCALC-PRESS).GT.0.) GOTO 500
      PPOLE=PHIGH
      DPOLE=DHIGH
      GOTO 325
500  PPOLE=PLOW
      DPOLE=DLOW
      GOTO 325
C
C
550  CONTINUE
C
935  CONTINUE
C   *****
C
C   CALCULATE CONCENTRATION OF WATER IN EQUILIBRIA CELL.
C
C
      XPPM=H2OMOL/(H2OMOL+(CV1/1000.0)*D)*1.256
C   *****
C
C   RETURN
C
      END

```

```

C      SUBROUTINE GOODC3(IDD,TTT,PPP,TM,PM,CV1,CV2,D,XPPM)
C
C      *****
C
C      THIS PROGRAM CALCULATES THE DENSITY OF LIQUID PROPANE
C      GIVEN TEMPERATURE AND PRESSURE.
C      THE EQUATION OF STATE EMPLOYED IS OUTLINED IN THE NBSIR
C      77-860, PROVISIONAL THERMODYNAMIC FUNCTIONS OF PROPANE,
C      FROM 85 TO 700 K AT PRESSURES TO 700 BAR, BY ROBERT
C      D. GOODWIN.
C
C      *****
C
C      IMPLICIT DOUBLE PRECISION (A-H,O-Z)
C
C      LIST CRITICAL AND TRIPLE POINT CONSTANTS
C      TT=85.47
C      TC=369.83
C      TDIF=TC-TT
C      TRAT=TT/TC
C      DC=4.96
C      DT=16.62
C      DDIF=DT-DC
C      DRAT=DT/DC
C      PT=3.*10.**(-9)
C
C      LIST COEXISTENCE TEMPERATURE CONSTANTS
C      EPS=.35
C      A=.7753967
C      B=-.1679136
C      C=.0811668
C
C      LIST COEXISTENCE PRESSURE CONSTANTS
C      EPSEPS=1.3
C      AA=23.3722838
C      BB=5.7166879
C      CC=-8.5117071
C      DD=3.9758738
C
C      LIST EQUATION OF STATE CONSTANTS FOR
C      DERIVED PARAMETERS
C      ALPHA=1.
C      GAMMA=.76
C      SIGMA=.75
C
C      B1=.22566372605
C      B2=1.04646227554
C      B3=-.44491000068
C      B4=.12708270211

```

```

C      CN=2.
C      C1=-.59883339489
C
C      LIST CONSTANTS FOR PROGRAM CALCULATIONS
C      R=.0831434*DC
C      CONV=10.**(-12)
C      CON=10.**(-9)
C      SEQ=3.
C      SEQU=0.
C      SEQUE=0.
C
C      INPUT SYSTEM TEMPERATURE AND PRESSURE AND ESTIMATE DENSITY
C      OF LIQUID PROPANE.
C
C      CALL C3H8(TTT,PPP,TM,PM,CV2,DLOW,H2OMOL)
C
C      TEMP=TTT+273.15
C      PRESS=PPP/14.696*1.01325
C      DHIGH=1.2*DLOW
C      D=DLOW
C      IF(IDD.EQ.1)GOTO 935
C
C      CALCULATE THE COEXISTANCE TEMPERATURE GIVEN DENSITY
C      USING THE ORTHOBARIC LIQUID DENSITY EQUATION
200  Y=(D-DC)/DDIF
C      X=(TC-TEMP)/TDIF
250  Y1=X**EPS-X
C      Y2=A+B*X**2+C*X**3
C      YNEW=X+Y1*Y2
C      DELTA=ABS((Y-YNEW)/Y)
C      IF(DELTA.LE.CONV) GOTO300
C
C      USE NEWTON-RAPHSON CONVERGENCE TO DETERMINE NEW X
C      X1=1.+EPS*A*X**(EPS-1.)
C      X2=A+(2.+EPS)*B*X**(EPS+1.)
C      X3=3.*B*X**2
C      X4=(3.+EPS)*C*X**(EPS+2.)
C      X5=4.*C*X**3
C      DYDX=X1-X2-X3+X4-X5
C      X=X-(YNEW-Y)/DYDX
C      GOTO 250
C
C      BACK OUT THE COEXISTANCE TEMPERATURE AFTER X AT
C      COEXISTANCE HAS BEEN FOUND
300  T=TC-X*TDIF
C
C      CALCULATE THE COEXISTANCE PRESSURE GIVEN DENSITY
C      USING THE VAPOR PRESSURE EQUATION
C      XX=(T-TT)/TDIF
C      U=(1.-TT/T)/(1.-TRAT)

```

```

P1=AA*U
P2=BB+CC*XX+DD*XX**2
P3=XX*(1.-XX)**EPSEPS
P=PT*EXP(P1+P2*P3)
C
C
CALCULATE FUNCTION RED OF THE EQUATION OF STATE
RED1=TEMP/TC
RED2=ALOG(TEMP/T)
RED=(RED1**.5)*RED2
C
C
CALCULATE FUNCTION BLUE OF THE EQUATION OF STATE
DENS=D/DC
BLUE1=(ABS(DENS-1.))**3/((DRAT-1.))**3)
BLUE2=T*EXP(-ALPHA*BLUE1)
BLUE3=1.-(BLUE2/TEMP)
BLUE4=1.-BLUE3+BLUE3*ALOG(BLUE3)
BLUE=SIGMA/RED1+(1.-SIGMA)*BLUE4
C
C
CALCULATE FUNCTION GREEN, THE COEXISTANCE EQUIVALENT
OF FUNCTION BLUE AND RED1
GREEN1=T/TC
GREEN3=1.-(BLUE2/T)
GREEN4=1.-GREEN3+GREEN3*ALOG(GREEN3)
GREEN=SIGMA/GREEN1+(1.-SIGMA)*GREEN4
C
C
CALCULATE FUNCTION GRAY OF THE EQUATION OF STATE
GRAY=BLUE-GREEN
C
C
CALCULATE FUNCTIONS CAPB, CAPC, AND CAPF OF THE
EQUATION OF STATE
CAPB=B1+B2*DENS+B3*DENS**2+B4*DENS**3
CAPC=C1*(DENS-1.)*(DENS-C0)*EXP(-GAMMA*DENS**4)
CAPF=CAPB*RED+CAPC*GRAY
C
C
CALCULATE THE PRESSURE GIVEN ESTIMATED DENSITY AND
THE KNOWN TEMPERATURE USING THE EQUATION OF STATE
PCALC1=P+DENS*R*(TEMP-T)
PCALC2=DENS**2*R*TC*CAPF
PCALC=PCALC1+PCALC2
C
C
CALCULATE THE CONVERGENCE OF PRESSURE TO
KNOWN PRESSURE
DIFF=ABS((PRESS-PCALC)/PRESS)
IF(DIFF.LE.CON) GO TO 550
C
C
CALCULATE A NEW DENSITY USING REGULA-FALSI CONVERGENCE
ON PRESSURE
IF(SEQ.LT.1.) GOTO 350
325 DNEW1=(PCALC-PRESS)/(PCALC-PPOLE)
DNEW2=D-DPOLE
D=D-DNEW1*DNEW2

```

```

      GOTO 200
C
C   CALCULATE THE HIGH PRESSURE BOUNDARY IN THE
C   REGULA-FALSI CONVERGENCE
350  IF(SEQU.GT.1.) GOTO 400
      PLOW=PCALC
      D=DHIGH
      SEQU=2.
      GOTO 200
C
C   CALCULATE THE FIRST NEW DENSITY USING THE ESTABLISHED
C   REGULA-FALSI LIMITS
400  IF(SEQU.GT.1.) GOTO 450
      PHIGH=PCALC
      PPOLE=PLOW
      DPOLE=DLOW
      SEQUE=2.
      GOTO 325
C
C   CALCULATE WHICH POLE TO USE FOR SUBSEQUENT ITERATIONS
450  SEQ=2.
      IF ((PCALC-PRESS).GT.0.) GOTO 500
      PPOLE=PHIGH
      DPOLE=DHIGH
      GOTO 325
500  PPOLE=PLOW
      DPOLE=DLOW
      GOTO 325
C
C   550  CONTINUE
C
C   935  CONTINUE
C   *****
C
C   CALCULATE CONCENTRATION OF WATER IN EQUILIBRIA CELL.
C
C
C   XPPM=H2OMOL/(H2OMOL+(CV1/1000.0)*D)*1.0E6
C
C   *****
C
C   RETURN
C
C   END

```

```

C      SUBROUTINE LOAD(TM,PM,CV,H2OMOL)
C      *****
C      THIS PROGRAM CALCULATES THE NUMBER OF
C      MOLES OF WATER LOADED INTO THE EQUILIBRIA
C      CELL.
C      *****
C      IMPLICIT DOUBLE PRECISION (A-H,O-Z)
C
C      PARAMETERS
C
C      CORRECT TEMPERATURE
C      TACT=TM+0.994377E-2+0.29582E-2*TM-0.6603E-4*TM**2
1      -0.17229E-5*TM**3+0.27143E-7*TM**4
C      CORRECT PRESSURE
C      IF(PM.LE.30.)GOTO 100
C      IF(PM.LE.60.)GOTO 120
C      IF(PM.LE.100.)GOTO 140
C      IF(PM.GT.100.)GOTO 160
C
100    PACT=PM*0.985978+0.207593
      GOTO 180
120    PACT=PM*0.964443+1.459493
      GOTO 180
140    PACT=PM*0.990453+0.344983
      GOTO 180
160    PACT=PM*0.993366-0.036471
180    CONTINUE
C
C      GAS CONSTANT
C      R=82.057
C      TEMPERATURE(K)
C      TK=TACT+273.15
C      PRESSURE(ATM)
C      PATM=PACT/760.
C
C      MOLES OF WATER(ASSUMING IDEAL GAS)
C      H2OMOL=PATM*CV/(R*TK)
C
C      RETURN
C      END

```



```

C      MW=30.070
C      CRITICAL COMPRESSIBILITY
C      ZC=0.285
C      REFERENCE LIQUID DENSITY (GMOL/LITER)
C      NBS TECHNICAL NOTE 684
C      DENREF=11.279
C      TEMPERATURE AT REFERENCE POINT (K)
C      TREF=293.631
C
C      CALCULATE NUMBER OF MOLES OF WATER LOADED INTO THE CELL
C
C      CALL LOAD(TM,PM,CV,H2OMOL)
C
C
C      SYSTEM TEMPERATURE (K)
C      T=TTT+273.15
C      SYSTEM PRESSURE (ATM)
C      P=PPP/14.696
C      SYSTEM REDUCED TEMPERATURE
C      TR=T/TC
C      REFERENCE REDUCED TEMPERATURE
C      TRREF=TREF/TC
C
C      DO 10 I=1,3
C      J=I-1
C      VR(J)=A(J)+B(J)*TR+C(J)*TR**2+D(J)*TR**3+E(J)/TR
C      1 +F(J)*ALOG(1.-TR)
C      VRREF(J)=A(J)+B(J)*TRREF+C(J)*TRREF**2+D(J)*TRREF**3+E(J)/TRREF
C      1 +F(J)*ALOG(1.-TRREF)
C      10 CONTINUE
C      RATIO=VR(0)+OMEGA*VR(1)+OMEGA**2*VR(2)
C      RREF=VRREF(0)+OMEGA*VRREF(1)+OMEGA**2*VRREF(2)
C
C      DD=DENREF
C      DENSAT=DD*RREF/RATIO
C
C      VAPOR PRESSURE (NBS TECHNICAL NOTE 684)
C      UNITS: BAR
C
C      AA=-11.3899624306
C      BB=18.8452282876
C      CC=-7.6354151345
C      DD=5.4284431706
C      EE=-1.3623270362
C      FF=0.7692492586
C
C      EPS=1.30
C      TRIPLE POINT TEMPERATURE(K)
C      TTRIP=90.348

```

```
C      XT=(1.0-TTRIP/T)/(1.0-TTRIP/TC)
C      UT=(T-TTRIP)/(TC-TTRIP)
C      PV=EXP(AA+BB*XT+CC*UT+DD*UT**2+EE*UT**3+FF*UT*(1.-UT)**EPS)
C      VAPOR PRESSURE(ATM)
C      PVAP=PV/1.01325
C
C      N=(1.-.89*OMEGA)*(EXP(6.9547-76.2854*TR+191.326*
1     TR**2-203.5472*TR**3+82.7631*TR**4))
C      DEN=DENSAT*(1.+(9.*ZC*N*(P-PVAP)/PC))**(1./9.)
C      DCSP=DEN
C
C      RETURN
C      END
```

```

SUBROUTINE C3H8(TTT,PPP,TM,PM,CV,DCSP,H2OMOL)
C
C *****
C
C THIS SUBROUTINE USES THE METHOD OF CHUEH AND PRAUSNITZ, A
C TECHNIQUE BASED ON CORRESPONDING STATES TO ESTIMATE THE
C DENSITY OF LIQUID PROPANE.
C *****
C
C IMPLICIT DOUBLE PRECISION (A-H,O-Z)
C
C DIMENSION VARIABLES
C DIMENSION A(2:3),B(2:3),C(2:3),D(2:3),E(2:3),F(2:3),VR(2:3)
C DIMENSION VRREF(2:3)
C
C REAL*8 MW,N
C CALCULATE NUMBER OF MOLES OF WATER LOADED INTO THE CELL
C
C CALL LOAD(TM,PM,CV,H2OMOL)
C
C PARAMETERS
C
C A(2)=0.11917
C A(1)=2.98465
C A(2)=-2.55314
C B(2)=0.009513
C B(1)=-1.60378
C B(2)=-0.15793
C C(2)=0.21091
C C(1)=1.82484
C C(2)=-1.01601
C D(2)=-0.06922
C D(1)=-0.61432
C D(2)=0.34095
C E(2)=0.07487
C E(1)=-0.34546
C E(2)=0.46795
C F(2)=-2.084476
C F(1)=0.087037
C F(2)=-0.239938
C
C PROPANE PARAMETERS
C (REID SHERWOOD AND PRAUSNITZ)
C
C CRITICAL TEMPERATURE (K)
C TC=369.8
C CRITICAL PRESSURE (ATM)

```

```

C      PC=41.9
C      ACENTRIC FACTOR
C      OMEGA=0.152
C      MOLECULAR WEIGHT
C      MW=44.097
C      CRITICAL COMPRESSIBILITY
C      ZC=0.281
C      REFERENCE LIQUID DENSITY (G/CM3)
C      DENREF=0.582
C      TEMPERATURE AT REFERENCE POINT (K)
C      TREF=231.0
C
C      SYSTEM TEMPERATURE (K)
C      T=TTT+273.15
C      SYSTEM PRESSURE (ATM)
C      P=PPP/14.696
C      SYSTEM REDUCED TEMPERATURE
C      TR=T/TC
C      REFERENCE REDUCED TEMPERATURE
C      TRREF=TREF/TC
C
C
C      DO 10 I=1,3
C      J=I-1
C      VR(J)=A(J)+B(J)*TR+C(J)*TR**2+D(J)*TR**3+E(J)/TR
1      +F(J)*ALOG(1.-TR)
C      VRREF(J)=A(J)+B(J)*TRREF+C(J)*TRREF**2+D(J)*TRREF**3+E(J)/TRREF
1      +F(J)*ALOG(1.-TRREF)
10     CONTINUE
C      RATIO=VR(0)+OMEGA*VR(1)+OMEGA**2*VR(2)
C      RREF=VRREF(0)+OMEGA*VRREF(1)+OMEGA**2*VRREF(2)
C
C
C      DD=DENREF*1000./MW
C      DENSAT=DD*RREF/RATIO
C
C      VAPOR PRESSURE (ANTOINE EQUATION)
C      UNITS: ATM
C      PVAP=EXP(15.726-1872.46/(T-25.16))/760.0
C      N=(1.-.89*OMEGA)*(EXP(6.9547-76.2854*TR+191.306*
1      TR**2-263.5472*TR**3+82.7631*TR**4))
C
C      DEN=DENSAT*(1.+(9.*ZC*N*(P-PVAP)/PC)**(1./9.))
C
C
C      DCSP=DEN
C      RETURN
C      END

```

```
EX
[11:59:47]
LINK: Loadins
[LNKXCT XPPM execution]

SYSTEM UNDER CONSIDERATION

CONDENSED ETHANE - WATER MIXTURE -ENTER '1'
CONDENSED PROPANE - WATER MIXTURE -ENTER '2'
2

EQUATION OF STATE EMPLOYED

CORRESPONDING STATES -ENTER '1'
GOODWIN EQUATION -ENTER '2'
2

INPUT LOADING SYSTEM TEMPERATURE(DORIC(C))
70
INPUT LOADING SYSTEM PRESSURE(BAROCEL(TORR))
25
INPUT SYSTEM TEMPERATURE(C)
0
INPUT SYSTEM PRESSURE(PSIA)
112

MODE OF ANALYSIS

WATER CONCENTRATION -ENTER '1'
MONTE CARLO SIMULATION -ENTER '2'
1

RESULTS OF ANALYSIS

SYSTEM TEMPERATURE(C) = 0.00
SYSTEM PRESSURE(PSIA) = 112.00
WATER CONCENTRATION(PPM) = 96.8303

CPU time 1.13 Elapsed time 28.53

EXIT
.
```

```
EX
[11:58:46]
LINK:  Loading
[LNKXCT XPPM execution]

SYSTEM UNDER CONSIDERATION

CONDENSED ETHANE - WATER MIXTURE -ENTER '1'
CONDENSED PROPANE - WATER MIXTURE -ENTER '2'
1

EQUATION OF STATE EMPLOYED

CORRESPONDING STATES -ENTER '1'
GOODWIN EQUATION -ENTER '2'
2

INPUT LOADING SYSTEM TEMPERATURE(DORIC(C))
70
INPUT LOADING SYSTEM PRESSURE(BAROCEL(TORR))
25
INPUT SYSTEM TEMPERATURE(C)
0
INPUT SYSTEM PRESSURE(PZIA)
500

MODE OF ANALYSIS

WATER CONCENTRATION -ENTER '1'
MONTE CARLO SIMULATION -ENTER '2'
1

RESULTS OF ANALYSIS

SYSTEM TEMPERATURE(C) = 0.00
SYSTEM PRESSURE(PZIA) = 500.00
WATER CONCENTRATION(PFM) = 86.0919
```

CPU time 2.35 Elapsed time 45.28

EXIT

.

EX
[12:17:56]
LINK: Loading
[LNKXCT XPPM execution]

SYSTEM UNDER CONSIDERATION

CONDENSED ETHANE - WATER MIXTURE -ENTER '1'
CONDENSED PROPANE - WATER MIXTURE -ENTER '2'
2

EQUATION OF STATE EMPLOYED

CORRESPONDING STATES -ENTER '1'
GOODWIN EQUATION -ENTER '2'
1

INPUT LOADING SYSTEM TEMPERATURE(DORIC(C))
70.205
INPUT LOADING SYSTEM PRESSURE(BAROCEL(TORR))
31.89
INPUT SYSTEM TEMPERATURE(C)
-0.2
INPUT SYSTEM PRESSURE(PSIA)
112

MODE OF ANALYSIS

WATER CONCENTRATION -ENTER '1'
MONTE CARLO SIMULATION -ENTER '2'
2

INPUT REGRESSION STANDARD DEVIATION
.904418

INPUT NUMBER OF SIMULATIONS
10000

RESULTS OF ANALYSIS

SYSTEM TEMPERATURE(C) = -0.20
SYSTEM PRESSURE(Psia) = 112.00
WATER CONCENTRATION(PPM) = 125.7775
AVERAGE CONCENTRATION(PPM) = 125.7814
STANDARD DEVIATION(PPM) = 2.19177236
NUMBER OF SIMULATIONS = 10000

CHANGE NUMBER OF SIMULATIONS

YES -ENTER '1'
NO -ENTER '2'

11

CPU time 1:01.89 Elapsed time 2:31.93

EXIT

.